

# JOURNAL OF THE CHEMICAL SOCIETY.

## ABSTRACTS OF PAPERS ON ORGANIC CHEMISTRY.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
BRITISH AND FOREIGN JOURNALS.

## PART I.

### Organic Chemistry.

**New Dodecane.** MAURICE DELACRE (*Bull. Soc. chim.*, 1911, [iv], 9, 1023—1024).—Crude  $\gamma\gamma$ -dimethyl- $\Delta^2$ -butylene,  $\text{CMe}_3\cdot\text{CH}:\text{CH}_2$  (Abstr., 1906, i, 476), furnishes with hydrogen bromide the compound  $\text{CMe}_3\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$  (*loc. cit.*), and this on treatment with sodium yields, in addition to the products described already (*loc. cit.*), the dodecane [ $\beta\beta\eta\eta$ -tetramethyloctane],  $\text{CMe}_3\cdot[\text{CH}_2]_4\cdot\text{CMe}_3$ , b. p. 185—190°, which crystallises in needles and melts at the temperature of the hand to a colourless liquid, possessing a faintly aromatic odour.

T. A. H.

**Very Sensitive New Colour Reaction for Ethylenic Linkings and for Tautomeric Modifications.** IWAN OSTROMISLENSKY (*J. pr. Chem.*, 1911, [ii], 84, 489—495).—Tetranitromethane dissolved in petroleum (or other paraffin hydrocarbon) produces intense colorations with substances containing ethylenic linkings. The test is responded to by unsaturated hydrocarbons, alcohols, ketones, ethers, esters, and aromatic substances, but not by aromatic nitro-compounds or by many unsaturated carboxylic acids.

The view is generally accepted that a tautomeric substance exists in one definite form in the solid phase, but acquires, in the liquid or gaseous phase, a state of equilibrium between two (or more) modifications, determined by external conditions. This view is substantiated by experiments with tetranitromethane. In aqueous, alcoholic, or ethereal solution, phloroglucinol and ethyl acetoacetate develop

respectively a brownish-red and a golden-yellow coloration. The enolic form of ethyl benzylidenebisacetoacetate, in the solid state or in solution, instantly develops a citron-yellow coloration, whilst the ketonic form remains colourless under similar conditions, although its sodium derivative produces an intense yellow coloration.

Tetranitromethane acts as a mild oxidising agent. It converts quinol into quinhydrone (nitric oxide, nitrous and nitric acids, but not nitroform, have been detected among the products of the reaction), and dimethylaniline into crystal-violet. C. S.

**Chemistry of Amyl Compounds.** ARTHUR MICHAËL and FRITZ ZEIDLER (*Annalen*, 1911, 385, 227—292).—The structural theory based on a purely mechanical conception of valency does not suffice to explain many organic reactions, in particular, that of substitution. Many facts are known which show that, for example, the conversion of an alcohol into an alkyl halide by an acid is not merely the substitution of the halogen atom for a hydroxyl group, but must be due to an elimination of water from the alcohol followed by the addition of hydrogen halide to the olefine thus produced. It has been commonly accepted that the elimination of water from the alcohol is due to the dehydrating action of the hydrogen halide. The authors show, however, that in the series of *iso*amyl alcohols the production of an amylene can be effected at 100° by 4·5*N*-dichloroacetic acid or by *N*/50-hydrochloric acid, although not by water alone; they regard the action of an acid in causing an elimination of water from an alcohol as being due to catalysis, the rate of formation of amylene being faster the more concentrated the acid. This being so, with the necessary consequence that the formation of abnormal substitution products must be conditioned by the molecular structure of the alcohol, the two following problems require solution: (1) which of the several isomerides that could be formed from a given substance in a reaction is actually produced; (2) which of two isomerides that can be converted into the same unsaturated substance is the more easily decomposed. The law of entropy, the "law of addition and elimination," and the thermochemical structure law (*Abstr.*, 1906, i, 550; 1909, i, 494) are applied in answering these questions. The application of these laws leads to the expectations that (1)  $\beta$ -methyl- $\Delta^{\beta}$ -butylene, not  $\beta$ -methyl- $\Delta^{\alpha}$ -butylene, will be formed by the dehydration of  $\beta$ -methylbutane- $\beta$ -ol; (2)  $\beta$ -methylbutane- $\gamma$ -ol will yield  $\beta$ -methyl- $\Delta^{\beta}$ -butylene almost exclusively; (3) the elimination of water from  $\beta$ -methylbutane- $\delta$ -ol will be more difficult than from  $\beta$ -methylbutane- $\gamma$ -ol, and from  $\beta$ -methylbutane- $\alpha$ -ol more easy than from  $\beta$ -methylbutane- $\delta$ -ol; (4) by the action of hydrobromic acid,  $\beta$ -methylbutane- $\beta$ -ol will yield only the tertiary bromide,  $\beta$ -methylbutane- $\gamma$ -ol mainly the tertiary bromide,  $\beta$ -methylbutane- $\delta$ -ol only the primary bromide, and  $\beta$ -methylbutane- $\alpha$ -ol the primary bromide, together with a little of the tertiary bromide. The experimental results show that these expectations are fulfilled completely in practice. The ease with which the preceding primary, secondary, and tertiary *iso*amyl alcohols yield amylenes varies so much that the authors have based on this property

a method for the detection of each of these alcohols in mixtures of all of them.

The remainder of the paper is mainly an extension of Michael and Leupold's work on the intramolecular transformations of alkyl bromides (Abstr., 1911, i, 250) to the *isoamyl* bromides. C. S.

**Metallic Alkylloxides.** E. CHABLAY (*Compt. rend.*, 1911, 153, 953—955. Compare Abstr., 1911, i, 939).—Further experimental details are given for the preparation of metallic alkylloxides according to the methods outlined in an earlier communication. Calcium methoxide, ethoxide, *isobutyl*oxide, and *isoamyl*oxide have thus been obtained. *Barium methoxide* is particularly easy to prepare by the interaction of sodium methoxide and barium nitrate in liquid ammonia solution. It crystallises in slender needles. *Barium ethoxide* and *strontium methoxide* and *ethoxide* have also been prepared. *Lead methoxide*, *ethoxide*, *isobutyl*oxide, and *isoamyl*oxide were obtained by the action of the sodium alkylxide on lead iodide or nitrate dissolved in liquid ammonia; they are exceedingly sensitive to the action of heat or of moisture.

W. O. W.

**The Action of Certain Acid Chlorides on Potassium Nitrate and the Formation of Acid Anhydrides.** OTTO DIELS and HARUKICHI OKADA (*Ber.*, 1911, 44, 3333—3336).—The authors have investigated the action of acetyl chloride, chloroacetyl chloride, and benzoyl chloride on potassium nitrate, whereby they have obtained good yields of acetic anhydride, chloroacetic anhydride, and benzoic anhydride respectively. They consider that a mixed anhydride is first formed, which subsequently reacts with the excess of acid chloride to form the acid anhydride. This is supported by the fact that acetic anhydride is obtained in 93% yield by the action of acetyl chloride on acetyl nitrate.

H. W.

**The Photochemical Transformations of Solutions of Ferric Trichloroacetate.** FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 342—356).—On exposure to light a concentrated (32—33% by weight) solution of ferric trichloroacetate is decomposed, carbon dioxide being evolved and hexachloroethane deposited as a heavy, white precipitate. A dilute solution, owing to hydrolysis, is orange-yellow in colour, and is not sensitive to light; it becomes sensitive, however, if it is rendered colourless by the addition of an excess of trichloroacetic acid. No reaction takes place in the dark.

In the presence of free oxygen, the separation of hexachloroethane may be prevented (in all cases it is diminished) by another reaction, which gives rise to chlorine, hydrogen chloride, and, in the absence of excess of free acid, ferric oxide; a little chloroform is also produced. Trichloroacetic acid acts as an oxygen carrier, the free acid itself being oxidised with liberation of chlorine.

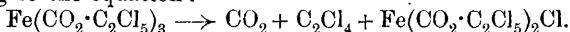
The photochemical reaction takes place in blue light, less rapidly in green light, and not at all in red or yellow light. The light obtained from uviol lamps is convenient to use for the reaction. Rise in temperature first increases the hydrolysis of a solution, and then causes

the liberation of carbon dioxide; at the same time, deposition of ferric oxide takes place and some chloroform is formed. Similarly, thallous tribromoacetate and ferric tribromoacetate both give carbon dioxide and bromoform.

When a 0.68*N*-solution of trichloroacetic acid is electrolysed between platinum electrodes, hydrogen is, at first, evolved continuously at the cathode, whereas a discontinuous evolution of gas occurs at the anode. After a time an oily drop forms at the surface of the liquid above the anode, finally becoming of such a size that it breaks away from the liquid surface and falls to the bottom of the solution. The evolution of hydrogen ceases after a time. The electrolyte finally contains carbonyl chloride, chlorine, and hydrochloric acid; the oil formed was trichloromethyl trichloroacetate (compare Kaufer and Herzog, *Abstr.*, 1909, i, 870); it generally solidified at 22°, and the solid had m. p. 32–34°. The presence of carbonyl chloride, etc., in the electrolyte was probably due to the decomposition of this ester by water, according to the equation:  $\text{CCl}_3 \cdot \text{CO}_2 \cdot \text{CCl}_3 + \text{H}_2\text{O} = \text{CCl}_3 \cdot \text{CO}_2\text{H} + \text{HCl} + \text{COCl}_2$ .

The author confirms the results of Anschütz and Emery (*Abstr.*, 1893, i, 188) that trichloromethyl trichloroacetate is a different substance from pentachloroethyl chloroformate,  $\text{Cl} \cdot \text{CO}_2 \cdot \text{C}_2\text{Cl}_5$ .

Solutions of ferric pentachloropropionate are very sensitive to light, carbon dioxide being evolved and tetrachloroethylene formed, probably according to the equation:



The formation of hexachloroethane in the photochemical decomposition of ferric trichloroacetate is possibly due to the decomposition of the anion, thus:  $2\text{CCl}_3 \cdot \text{CO} \cdot \text{O} \longrightarrow 2\text{CO}_2 + \text{C}_2\text{Cl}_6$ . T. S. P.

**Action of Acid Chlorides on Ethyl Diethoxyacetate.** BRUNO MYLO (*Ber.*, 1911, 44, 3211–3215).—By the action of phosphorus pentachloride on ethyl diethoxyacetate, *ethyl chloroethoxyacetate*,  $\text{OEt} \cdot \text{CHCl} \cdot \text{CO}_2\text{Et}$ , is formed; it has b. p. 79°/12 mm. On heating with copper powder, it is converted into ethyl  $\alpha\beta$ -diethoxysuccinate,  $\text{C}_2\text{H}_5(\text{OEt})_2(\text{CO}_2\text{Et})_2$ , b. p. 140–143°/12.5 mm. In the above reaction phosphorus pentachloride may be replaced by thionyl chloride, acetyl bromide or chloride. Ethyl diethoxyacetate and acetyl bromide give rise to *ethyl ethoxybromoacetate*, b. p. 90–91.5°/11 mm. When acetyl chloride is used, a little copper bronze is required as a catalyst. Benzoyl chloride reacts with the acetal in presence of zinc chloride, but the reaction is obscured by secondary changes. E. F. A.

**The Optically Active Dibromosuccinic Acid.** BROR HOLMBERG (*Svensk Kem. Tidskr.*, No. 5, 1911, Reprint, 5 pp. Compare *Abstr.*, 1911, i, 767).—The author has shown that *r*- $\alpha\beta$ -dibromosuccinic acid is obtained by addition of bromine to maleic acid or maleic anhydride, whilst *meso*- $\alpha\beta$ -dibromosuccinic acid is formed by direct bromination of succinic acid or by addition of bromine to fumaric acid.

*r*- $\alpha\beta$ -Dibromosuccinic acid was resolved by means of cinchonine. A crystalline salt,  $2\text{C}_{19}\text{H}_{22}\text{ON}_2 \cdot \text{C}_4\text{H}_2\text{O}_4\text{Br}_2 \cdot 6\text{H}_2\text{O}$ , separates when aqueous solutions of cinchonine nitrate and sodium  $\alpha\beta$ -dibromosuccinate are mixed. From this salt, *l*- $\alpha\beta$ -dibromosuccinic acid m. p.

152—154° (decomp.), was isolated. In ethyl acetate it has  $[\alpha]_D^{20} - 101.4^\circ$ , which remained unchanged during two days. In ether it has  $[\alpha]_D^{20} - 105.4^\circ$ ; in water,  $[\alpha]_D^{24} - 48.3^\circ$ . After nine days this value had decreased to  $[\alpha]_D^{20} - 20.15^\circ$ . Further purification was effected by dissolving this acid in a mixture of ethyl acetate and carbon tetrachloride. After removal of a crop of less active acid, the filtrate, on evaporation, left a residue of *l*-acid, m. p. 152—153°, which had  $[\alpha]_D^{20} - 137.6^\circ$  in ethyl acetate. This was the most highly active acid obtained by the author.

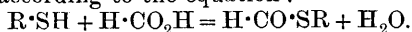
Impure *d*- $\alpha$ - $\beta$ -dibromosuccinic acid was obtained from the filtrate from the original *cinchonine* salt. The crude acid had  $[\alpha]_D^{23} + 84.9^\circ$  in ethyl acetate. When purified in the manner adopted for the *l*-acid, it had m. p. 151—153°, and  $[\alpha]_D^{24} + 126.3^\circ$  in ethyl acetate.

Attempts to resolve *r*- $\alpha$ - $\beta$ -dibromosuccinic acid by means of quinine were less successful.

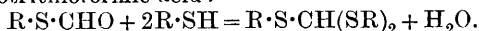
*meso*-Dibromosuccinic acid could not be resolved by means of morphine or brucine.

H. W.

**Preparation of Esters of Orthotrithioformic Acid.** JOSEF HOUBEN and KARL M. L. SCHULTZE (*Ber.*, 1911, 44, 3235—3241).—Esters of thiolformic acid should be formed by direct formylation of the mercaptans, according to the equation :



Owing probably to the fact that the ester produced contains the aldehyde group, the reaction proceeds further, with the formation of esters of orthotrithioformic acid :



The reaction is readily carried out by heating the mercaptan with anhydrous formic acid under reflux for some time; in the case of methyl mercaptan, the reaction mixture is kept in a sealed tube for forty-eight hours at the ordinary temperature.

*Methyl orthotrithioformate*,  $CH(SMe)_3$ , is a colourless oil, b. p.  $96^\circ/9$  mm.,  $220^\circ/760$  mm. (decomp.), which becomes yellow on warming; it solidifies at  $16^\circ$ . The odour is characteristic, but by no means disagreeable. The solution in chloroform decolorises bromine at first, but further addition of bromine leads to the evolution of hydrogen bromide and the formation of a brownish-red coloration, which is not due to bromine. Ethyl orthotrithioformate has b. p.  $124$ — $125^\circ/11$  mm.,  $235^\circ/760$  mm. (decomp.); the odour is only slight, the ester being purer than that prepared by Holmberg (*Abstr.*, 1907, i, 474). Benzyl orthotrithioformate has m. p.  $102.5^\circ$ . It can be prepared by using oxalic acid in place of formic acid, carbon dioxide being first evolved. *p*-Tolyl orthotrithioformate,  $HC(S \cdot C_6H_4Me)_3$ , forms snow-white crystals, m. p.  $109^\circ$ .  *$\alpha$* -Naphthyl orthotrithioformate,  $HC(S \cdot C_{10}H_{17})_3$ , has m. p.  $134^\circ$ . On exposure to light, it gradually becomes pale green in colour. Allyl orthotrithioformate could not be obtained pure.

T. S. P.

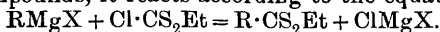
**Carbithionic Acids. V. Preparation of New Esters of Carbithionic Acid and of Ethyl Chlorocarbithionate.** JOSEF HOUBEN and KARL M. L. SCHULTZE (*Ber.*, 1911, 44, 3226—3234).—The ethyl esters of the carbithionic acids are readily obtained by the

action of ethyl sulphate on aqueous solutions of the acids prepared by the action of carbon disulphide on the organo-magnesium compounds (compare Abstr., 1906, i, 847; 1907, i, 382, 474). The method of preparation is similar to that described for the methyl esters, but the esterification with ethyl sulphate does not take place so readily as with methyl sulphate, it being necessary to warm for some time on the water-bath. Moreover, excess of ethyl sulphate does not produce decomposition to the same extent as methyl sulphate, so that in the treatment of the reaction mixture it is not usually necessary to decompose the excess of ethyl sulphate with steam. The yields obtained are generally small, except in the case of  $\alpha$ -naphthylcarbithionic esters, where they amount to 40—43%.

*Ethyl methylcarbithionate (ethyl dithioacetate)*,  $\text{CH}_3 \cdot \text{CS}_2 \text{Et}$ , is an intense yellow liquid, possessing an odour somewhat similar to that of ethyl acetate. It has b. p. 42—43°/11 mm.,  $D_4^{16}$  1.036, and is rapidly oxidised by the air or oxidising agents. With mineral acids or aqueous-alcoholic sodium hydroxide, it gives acetic acid and mercaptan.

*Ethyl ethylcarbithionate (ethyl dithiopropionate)*,  $\text{C}_2\text{H}_5 \cdot \text{CS}_2 \text{Et}$ , has b. p. 60—61°/10 mm. It is a yellow liquid with a pronounced, characteristic odour. Methyl phenylcarbithionate (methyl dithiobenzoate),  $\text{C}_6\text{H}_5 \cdot \text{CS}_2 \text{Me}$ , was obtained in a slightly purer condition than the specimen prepared by Höhn and Bloch (Abstr., 1910, i, 256), and had b. p. 141—142°/12 mm. At the temperature of liquid air it forms a flesh-coloured, solid mass. *Methyl  $\alpha$ -naphthylcarbithionate (methyl dithio- $\alpha$ -naphthoate)*,  $\text{C}_{10}\text{H}_7 \cdot \text{CS}_2 \text{Me}$ , forms orange-yellow needles, which melt to a dark red oil at 54°, b. p. 210°/15 mm. It is quite stable in the air, as also is *ethyl  $\alpha$ -naphthylcarbithionate (ethyl dithio- $\alpha$ -naphthoate)*,  $\text{C}_{10}\text{H}_7 \cdot \text{CS}_2 \text{Et}$ , which forms orange-yellow crystals, melting to a dark red oil at 39—40°. Both these esters are stable towards dilute and concentrated hydrochloric acid, but are decomposed in the usual way by aqueous-alcoholic sodium hydroxide.

*Ethyl chlorocarbithionate (ethyl chlorodithioformate)*,  $\text{Cl} \cdot \text{CS}_2 \text{Et}$ , is obtained by the gradual addition (lasting twenty-four hours) of thiocarbonyl chloride (25 grams) to a solution of ethyl mercaptan (13.5 grams) in carbon disulphide (75 c.c.), and fractionation of the reaction mixture, after further keeping for two days, under diminished pressure. It forms an intense reddish-yellow oil, which excites to tears and has a penetrating odour, b. p. 80—81°/19 mm. and 74—75°/15 mm. It is stable when kept away from air and moisture. It reacts with amino-acids; for example, on shaking with an aqueous solution of potassium anthranilate, a red oil is formed, which rapidly crystallises, and is probably  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CS}_2 \text{Et}$ . With organo-magnesium compounds, it reacts according to the equation:



With a solution of sodium iodide in acetone, it gives the corresponding iodo-compound. When reduced with potassium arsenite in alkaline solution, a brown oil is obtained, which, on fractional distillation, gives a light yellow oil with b. p. 131—132°/19 mm. and 115°/11 mm. The composition corresponds with that of ethyl thioformate

( $\text{H}\cdot\text{CS}_2\text{Et}$ ), but the high boiling point indicates that it is probably a polymeride of that substance.

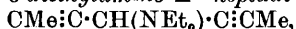
In the preparation of ethyl chlorocarbithionate, a by-product, b. p. 115—125°/19 mm., is obtained, especially if the reaction mixture is not too strongly diluted with carbon disulphide, which is probably ethyl trithiocarbonate. T. S. P.

**$\alpha$ -Bromoacraldehyde.** ROBERT LESPIEAU (*Compt. rend.*, 1911, 153, 951—953).—Pyrazole is produced when  $\alpha$ -bromoacraldehyde is added to a solution of hydrazine hydrate. The aldehyde does not unite with hydrogen cyanide unless a trace of potassium cyanide is present, when the action becomes violent. Hydrolysis of the resulting nitrile leads to formation of  $\beta$ -bromo- $\alpha$ -hydroxy- $\Delta^{\beta}$ -butenoic acid,  $\text{CH}_2\cdot\text{CBr}\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , m. p. 119—120°; the potassium salt is very deliquescent; the ethyl ester has b. p. 216—217°/750 mm.

$\beta\gamma$ -Tribromo- $\alpha$ -hydroxybutyric acid,  $\text{CH}_2\text{Br}\cdot\text{CBr}_2\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ , obtained by the action of bromine on the foregoing unsaturated acid, has m. p. 140—141°. The high boiling residue from the distillation of  $\alpha$ -bromoacraldehyde yields a nitrile under the above-mentioned conditions. On hydrolysis a mixture of acids is obtained, from which crystals, m. p. 104—105°, have been isolated; they probably consist of  $\beta\gamma\gamma$ -tribromo- $\alpha$ -hydroxybutyric acid, which arises from the presence of  $\beta\gamma\gamma$ -tribromopropionaldehyde in the original aldehyde.

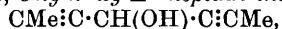
W. O. W.

**Attempt at the Direct Preparation of Tetrolaldehyde.** PAUL L. VIGUIER (*Compt. rend.*, 1911, 153, 955—957).—In the expectation of obtaining tetrolaldehyde, diethylformamide (1 mol.) was treated with the magnesium derivative of bromopropinene (1 mol.). After the usual treatment, the product was found to consist of unaltered amide with  $\delta$ -diethylamino- $\Delta^{\beta\epsilon}$ -heptadi-inene,



an oily liquid, b. p. 99—99.5°/14—15 mm.,  $D_0^{18}$  0.871,  $n_D^{18}$  1.477. The picrate occurs in slender needles, m. p. 169°; the platinumchloride crystallises with  $2\text{H}_2\text{O}$ , and decomposes at 120°; the ethiodide decomposes at 148—150°.

When the magnesium derivative of bromopropinene is treated with excess of ethyl formate,  $\delta$ -hydroxy- $\Delta^{\beta\epsilon}$ -heptadi-inene,



results instead of the expected aldehyde. This substance resembles boric acid in appearance, and has m. p. 105—106°. The required aldehyde appears to be produced when the sodium derivative of propinene is treated with ethyl formate, but the reaction is so slow that decomposition occurs and no definite product can be isolated. W. O. W.

**Catalytic Reactions at High Pressures and Temperatures.** XXIII. Hydrogenation of Acetone in the Presence of Copper Oxide and Zinc Dust. WLADIMIR IPATIEFF and G. BALATSCHINSKY (*Ber.*, 1911, 44, 3459—3461).—The action of zinc dust and of copper oxide as catalysts on the hydrogenation of acetone under pressure has

been investigated (compare Abstr., 1907, i, 828). An iron tube was used, the temperature being 280—300°, it having been proved that iron has no catalytic effect at 300°. The initial pressure of the hydrogen was 100—130 atmospheres.

With copper oxide as catalyst the resulting product contains 65% of *isopropyl* alcohol, whilst the percentage when zinc is used is about 50%.

It was also shown that with initial hydrogen pressures of 40 atmospheres, *isopropyl* alcohol gives acetone and hydrogen at 300°, with zinc dust as catalyst. Also, with acetone and copper oxide, condensation products of an unsaturated character are formed. Thus the reaction:  $\text{CHMe}_2\cdot\text{OH} \rightleftharpoons \text{H}_2 + \text{COMe}_2$  is reversible in the presence of zinc dust or copper oxide. T. S. P.

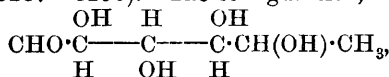
**The Electrolytic Reduction of Ketones.** JULIUS TAFEL [with WILHELM SCHEPSS] (*Zeitsch. Elektrochem.*, 1911, 17, 972—976. Compare Abstr., 1911, i, 784).—Acetone and methyl ethyl ketone are readily reduced electrolytically to the corresponding saturated hydrocarbons at a cadmium cathode in sulphuric acid solution. With the higher aliphatic ketones, for example, methyl *iscamyl* ketone, similar results can only be obtained with very high current densities (compare Abstr., 1909, i, 766).

Similar results are obtained with mercury and lead cathodes in the case of acetone, but the yield of propane is not so great, owing to side reactions, such as, in the case of lead cathodes, the formation of *isopropyl* alcohol, pinacone, and lead alkyls.

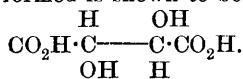
*isoPropyl* alcohol does not undergo reduction under conditions which lead to the formation of propane from acetone. T. S. P.

**The Action of Chlorine on Hexonic Acids (Hexonsäuren)** [Maltol]. PAUL DREYERHOFF (*Chem. Zeit.*, 1911, 35, 1323).—The substance (maltol; compare Abstr., 1910, i, 225, 544) which is formed when moist malt, etc., is heated, is decomposed by chlorine, 2 molecules of the substance yielding first salicylic acid and then phenol. Traces of maltol are present in certain dark-coloured beers, and may be detected by adding a very small quantity of chlorine to the beer, an odour of phenol being produced immediately. W. P. S.

**Degradation of *isoRhodeose*.** EMIL VOTOCÉK and CYRILL KRAUZ (*Ber.*, 1911, 44, 3287—3290).—The configuration,



previously assigned to *isorhodeose* (Abstr., 1911, i, 354) has now been confirmed by oxidation of the sugar with bromine to *isorhodeonic* acid, treatment of the calcium salt of this with hydrogen peroxide and iron, and oxidation of the methyltetrose formed with nitric acid to tartaric acid. The modification formed is shown to be *l*-tartaric acid,



E. F. A.

**Behaviour of Sucrose and its Decomposition Products on Heating.** IV. Reducing Substances in the Refinery Products. J. E. DUSCHSKY (*Zeitsch. ver. deut. Zuckerind.*, 1911, 989—1005. Compare Abstr., 1911, i, 769).—In the refinery, sugar solutions are only exposed to a high temperature for a relatively short time, but undergo protracted treatment at lower temperatures. The formation of reducing substances has been followed quantitatively in great detail throughout every stage of the process.

In the melting department there is an increase of reducing substance which is greatest when the crude sugar is dissolved in waste water, and least when dissolution is effected in pure water.

There is a considerable increase of reducing substance in a relatively short time when the syrup is left at a high temperature in the boilers of the melter. The filtration of the syrup through bone charcoal does not cause any increase in the reducing substances. During the boiling of the raffinade syrup there is no noticeable increase in the reducing substances; the same applies to the interval during crystallisation and subsequent drying of the crystals. E. F. A.

**Sugar Solutions and Lime.** P. J. H. VON GINNEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 442—461. Compare Claasen, Abstr., 1911, i, 606).—From the point of view of the phase rule the author first gives a theoretical discussion of the phenomena which are likely to be observed in systems containing the three components: lime, sugar, and water. Details are then given of experiments on the decomposition of the trisucrate, and on the position of the eutectic line at 80°. The solubility of calcium hydroxide in sugar solutions of varying concentrations at 80° was also determined.

The results obtained are applied to the explanation of various well-known facts. T. S. P.

**Methylethylammonium Chlorides.** JOHN E. MACKENZIE (*J. pr. Chem.*, 1911, [ii], 84, 549—554).—For the purpose of a comparative study of their toxic actions, the methylethylammonium chlorides intermediate between tetramethyl- and tetraethyl-ammonium chloride have been prepared by the direct interaction of an amine and an alkyl chloride in alcoholic solution at 40—60°. C. S.

**The Behaviour of Certain Hydroxides towards Solutions of Alkylenediamines.** WILHELM TRAUBE (*Ber.*, 1911, 44, 3319—3324).—Whilst copper hydroxide is only slightly soluble in aqueous solutions of primary aliphatic amines and insoluble in solutions of secondary aliphatic amines, it dissolves readily in aqueous solutions of aliphatic diamines. Whether in concentrated or dilute solution, two molecules of ethylenediamine were found to dissolve one molecule of copper hydroxide. The formula,  $[\text{Cu}(\text{C}_2\text{H}_8\text{N}_2)_2](\text{OH})_2$ , is ascribed to the compound so formed, which could not, however, be obtained in the solid state. The solutions have a deep bluish-violet colour, absorb oxygen from the air, and readily dissolve cellulose.

A similar reaction occurs with propylenediamine and copper hydroxide.

The hydroxides of nickel, cobalt, zinc, and cadmium, and the oxides of silver and mercury are also soluble in solutions of alkylenediamines. The respective formulæ,  $[\text{Ni}(\text{C}_2\text{H}_5\text{N}_2)_3](\text{OH})_2$ ,  $[\text{Zn}(\text{C}_2\text{H}_5\text{N}_2)_6](\text{OH})_2$ , and  $[\text{Ag}(\text{C}_2\text{H}_5\text{N}_2)_3]\text{OH}$ , have been assigned to the nickel, zinc, and silver complexes.

The solutions were prepared by shaking the metallic hydroxide, or oxide in the case of silver, with aqueous solutions of ethylenediamine. The solutions containing zinc and nickel were found to be more readily obtained by shaking the metal with aqueous ethylenediamine in the presence of oxygen.

H. W.

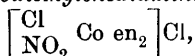
**The Asymmetric Cobalt Atom. III. and IV.** ALFRED WERNER (*Ber.*, 1911, 44, 3272—3278, 3279—3284).—III.—The present paper deals with the resolution of 1:2-chloronitrodiethylenediaminecobaltic salts,  $[\text{Cl} \text{ Co en}_2 \text{ NO}_2]\text{X}$ , into their optical isomerides. Theoretically, the optical isomerism of these salts is of the same type as that of 1:2-chloroamminediethylenediaminecobaltic salts,  $[\text{Cl} \text{ Co en}_2 \text{ NH}_3]\text{Cl}_2$ , dealt with in the first paper of this series (*Abstr.*, 1911, i, 613), except that two acid groups are now in direct combination with the cobalt atom, so that the complex is univalent.

Although the 1:2-chloronitrodiethylenediaminecobaltic salts show a great tendency to form aquo-salts in aqueous solution, it was found possible to resolve them by means of the silver camphorsulphonates. The least soluble isomerides are *l*-chloronitrodiethylenediaminecobaltic *d*-camphorsulphonate and *d*-chloronitrodiethylenediaminecobaltic *l*-bromocamphorsulphonate and from these the iodides could be obtained by means of sodium iodide. Owing to the formation of aquo-salts, however, it was difficult to obtain the active isomerides in quantity by this method. Much better results were obtained by a method similar to that used in the resolution of chromium compounds (*Abstr.*, 1911, i, 960). When *d*-ammonium camphorsulphonate or *d*-ammonium bromocamphorsulphonate is added to a freshly prepared, saturated solution of 1:2-chloronitrodiethylenediaminecobaltic chloride, crystals of *l*-chloronitrodiethylenediaminecobaltic *d*-camphorsulphonate or of *d*-chloronitrodiethylenediaminecobaltic *d*-bromocamphorsulphonate are deposited in a pure condition after a short time. From these the corresponding chlorides can be obtained by solution in concentrated hydrochloric acid and precipitation with alcohol.

The active chloronitrodiethylenediaminecobaltic salts show the phenomenon of mutarotation. The initial rotation gradually increases, the colour of the solution at the same time changing from red to yellow, owing to the formation of *cis*-nitroaquo-salts, in accordance with the equation:  $[\text{Cl} \text{ Co en}_2 \text{ NO}_2]\text{Cl} + \text{H}_2\text{O} = [\text{H}_2\text{O} \text{ Co en}_2 \text{ NO}_2]\text{Cl}_2$ . Also, by interaction with sodium nitrite they can be transformed without loss into the dinitro-salts, and the dinitro-perchlorates so obtained have  $[\alpha]_D + 39^\circ$  and  $-40^\circ$  in a 1% solution, which is the

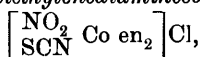
same as that obtained with the active dinitro-salts obtained by direct resolution (Abstr., 1911, i, 838).

d- and l-1:2-*Chloronitrodiethylenediaminecobaltic chlorides*,



have  $[\alpha]_D + 20^\circ$  and  $-21.5^\circ$  respectively. In 50% (by volume) hydrochloric acid solution they have  $[\alpha]_c + 16^\circ$  and  $-16.5^\circ$ , and  $[\alpha]_D \pm 25^\circ$ ; the hydrochloric acid solution is more stable than the aqueous solution. In aqueous solution the rotation gradually increases to  $[\alpha]_c + 31^\circ$  and  $-35^\circ$ ,  $[\alpha]_D + 52^\circ$  and  $-48^\circ$ , owing to the formation of the d- and l-*nitroaquadithylenediaminecobaltic chlorides*,  $\left[ \begin{array}{c} \text{H}_2\text{O} \\ \text{NO}_2 \end{array} \text{Co en}_2 \right] \text{Cl}$ . From these solutions potassium iodide precipitates a periodide, from which the active iodide can be isolated. After keeping for weeks, the solutions become inactive.

l-1:2-*Nitrothiocyanatodithylenediaminecobaltic chloride*,



is obtained from the chloronitro-salt by interaction with potassium thiocyanate. It has  $[\alpha]_c - 50^\circ$ ,  $[\alpha]_D - 84^\circ$ . l-*Chloronitrodiethylenediaminecobaltic nitrate*,  $\left[ \begin{array}{c} \text{Cl} \\ \text{NO}_2 \end{array} \text{Co en}_2 \right] \text{NO}_3$ , is prepared from the chloride by interaction with nitric acid. It has  $[\alpha]_c - 10^\circ$ ,  $[\alpha]_D - 36.5^\circ$ .

IV.—The 1:2-dichlorodiethylenediaminecobaltic salts,  $[\text{Cl}_2 \text{Co en}_2] \text{X}$ , are of the same type as the corresponding dinitro-salts (Abstr., 1911, i, 838), and can be resolved into the optical isomerides. Owing to the ready formation of the chloroaquo- and diaquo-salts in aqueous solution, the resolution is best accomplished by means of d- and l-ammonium bromocamphorsulphonates, the method used being similar to that just described. The least soluble salts are l-*dichlorodiethylenediaminecobaltic d-bromocamphorsulphonate* and d-*dichlorodiethylenediaminecobaltic l-bromocamphorsulphonate*. From these salts the *chloride*, *bromide*, and *nitrate* are readily obtained by treatment with the appropriate acids. The *sulphate* and *dithionate* are prepared from the chloride by reaction with ammonium sulphate and sodium dithionate, respectively. The optical rotations (for white light) of these salts are as follows:

	$[\alpha]$ .	$[M]$ .		$[\alpha]$ .	$[M]$ .
Chloride	$\left\{ \begin{array}{l} +184^\circ \\ -200 \end{array} \right.$	$\left\{ \begin{array}{l} +558^\circ \\ -607 \end{array} \right.$	Sulphate	$\left\{ \begin{array}{l} +180^\circ \\ -182 \end{array} \right.$	$\left\{ \begin{array}{l} +536^\circ \\ -540.5 \end{array} \right.$
Bromide	$\left\{ \begin{array}{l} +168^\circ \\ -176 \end{array} \right.$	$\left\{ \begin{array}{l} +554^\circ \\ -581 \end{array} \right.$	Dithionate	$\left\{ \begin{array}{l} +160^\circ \\ -164 \end{array} \right.$	$\left\{ \begin{array}{l} +542^\circ \\ -556 \end{array} \right.$
Nitrate	$\left\{ \begin{array}{l} +164^\circ \\ -164 \end{array} \right.$	$\left\{ \begin{array}{l} +511^\circ \\ -511 \end{array} \right.$			

The above values are not very accurate, owing to the fact that the rotations of the aqueous solutions diminish very rapidly, generally becoming zero after about three hours. The solid salts preserve their activity unchanged, so that the racemisation in solution must be referred to the action of the solvent, which forms chloroaquo- and

diaquo-salts. The exact process of racemisation cannot be given as yet. In some cases the chlorine atoms in the complex can be replaced by other acid radicles without loss of activity; for example, with potassium carbonate, an active carbonatodiethylenediaminecobaltic salt is formed, which is readily isolated from some inactive salt produced at the same time; the salt rotates in a direction opposite to that of the dichloro-salt from which it was made. In other cases the replacement of the chlorine atoms in the complex gives inactive salts, for example, inactive 1:2-hydroxyaquo- and 1:2-dinitro-diethylenediaminecobaltic salts.

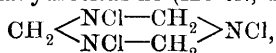
Racemic 1:2-dichlorodiethylenediaminecobaltic chloride is best prepared as follows: Finely powdered carbonatodiethylenediaminecobaltic chloride is heated on the water-bath with a saturated solution of hydrogen chloride in absolute alcohol until the red colour of the salt changes to violet. The violet salt is collected and digested at the ordinary temperature with successive portions of aqueous alcohol (1:1) until the filtrate is no longer coloured green, but violet. The salt is then washed with absolute alcohol and ether.

1 - *Dichlorodiethylenediaminecobaltic d - bromocamphorsulphonate*,  $[\text{Cl}_2 \text{ Co en}_2] \text{O}_3\text{S} \cdot \text{C}_{10}\text{H}_{14}\text{OBr}$ , forms violet crystals, and has  $[\text{M}] - 414^\circ$ . The corresponding d-l-salt has  $[\text{M}] + 381^\circ$ . Active l-dichlorodiethylenediaminecobaltic chlorides,  $\text{YCl} \cdot \text{H}_2\text{O}$ , where  $\text{Y} = [\text{Cl}_2 \text{ Co en}_2]$ , crystallise in violet-coloured leaflets. The active bromides,  $\text{YBr}$ , form crystals, which are coloured almost indigo-blue. The active nitrates,  $\text{YNO}_3$ , give small, violet crystals; those of the sulphates,  $\text{Y}_2\text{SO}_4$ , are coloured dark violet, whilst those of the dithionates,  $\text{Y}_2\text{S}_2\text{O}_6 \cdot \text{H}_2\text{O}$ , are light violet in colour.  
T. S. P.

**Action of Sodium Hypochlorite on Hexamethylenetetramine.** MARCEL DELÉPINE (*Bull. Soc. chim.*, 1911, [iv], 9, 1025—1029).—Sodium hypochlorite reacts with aqueous solutions of hexamethylenetetramine to form *N*-dichloropentamethylenetetramine, but in presence of acetic acid gives *N*-trichlorotrimethylenetriamine (1:3:5-trichlorohexahydrotriazine), which is isomeric with Cross, Bevan, and Bacon's methylenechloroamine (*Trans.*, 1910, 97, 2404).

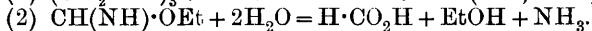
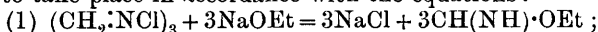
*N*-Dichloropentamethylenetetramine,  $\text{C}_5\text{H}_{10}\text{N}_4\text{Cl}_2$ , crystallises in brilliant lamellæ from water, or in octahedra from ether, possesses the odour peculiar to compounds containing chlorine and nitrogen, is sparingly soluble in water, and moderately so in ether or benzene, and deflagrates at  $78-82^\circ$ , giving an odour of carbylamines. It can be kept for long periods in sealed tubes, but decomposes in the course of a few days on exposure to air, forming ammonium chloride and hexamethylenetetramine hydrochloride. With sodium hydroxide in alcohol, ammonia is produced, and the chlorine is removed as alkali chloride.

1:3:5-Trichlorohexahydrotriazine (*Abstr.*, 1899, i, 326),



crystallises in brilliant needles, has a slight odour of chlorine, is nearly insoluble in water, but soluble in alcohol or chloroform, and deflagrates at  $78^\circ$ , evolving fumes having the odour of hydrogen cyanide and carbylamines, and leaving a residue of ammonium chloride. It decomposes in

air, or when kept in solution in organic solvents. With sodium hydroxide in alcohol, it yields ammonia and sodium chloride, and the residue on distillation with a dilute acid gives formic acid: this decomposition appears to take place in accordance with the equations:



T. A. H.

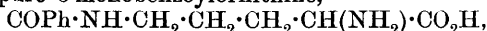
**Condensation of Amino-acids in Presence of Glycerol: *cyclo*-Glycylglycines and Polypeptides.** LOUIS C. MAILLARD (*Compt. rend.*, 1911, 153, 1078—1080).—Attempts to prepare glycerides of amino-acids have proved unsuccessful. Glycine is converted into diketopiperazine by heating with four or five times its weight of glycerol for some hours. The yield of the pure anhydride is 80%. Other condensation products are also formed under these conditions; triglycylglycine occurs as an intermediate product, but this in turn loses water, forming the anhydride, together with pentaglycylglycine and a brown oxidation product. The yield of polypeptides is greatly increased by employing a smaller proportion of glycerol. By the same method sarcosine and alanine have been transformed into their cyclic anhydrides, and leucine into leucinimide. The reaction appears to be general, and can be applied to the preparation of mixed anhydrides. It probably involves formation of an unstable glyceride, which decomposes, losing glycerol and water. The suggestion is made that the synthetic reactions effected by enzymes are of this type.

The author proposes to use the prefix *cyclo* for the anhydrides of amino-acids; thus diketopiperazine is termed *cycloglycylglycine*, and the condensation product of tyrosine and leucine becomes *cyclo*-tyrosyl-leucine.

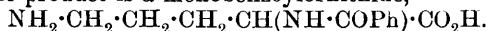
W. O. W.

**Synthesis of Amino-acids. IX. Racemic Arginine ( $\alpha$ -Amino- $\delta$ -guanidino-*n*-valeric Acid) and the Isomeric  $\delta$ -Amino- $\alpha$ -guanidino-*n*-valeric Acid.** SÖREN P. L. SÖRENSEN, MARGRETHE HÖYRUP, and A. C. ANDERSEN (*Zeitsch. physiol. Chem.*, 1911, 76, 44—94. Compare Abstr., 1910, i, 227).—In part already published.

When ornithuric acid is treated with warm concentrated hydrochloric acid, pure  $\delta$ -monobenzoylornithine,

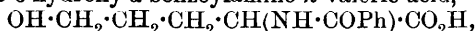


is obtained. On boiling ornithuric acid, however, with *N*/5-barium hydroxide, the product is  $\alpha$ -monobenzoylornithine,



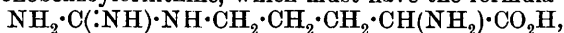
Under suitable experimental conditions the yield of both these compounds is satisfactory.

When the amino-group is eliminated,  $\alpha$ -monobenzoylornithine is converted into  $\delta$ -hydroxy- $\alpha$ -benzoylamino-*n*-valeric acid,



whilst  $\delta$ -monobenzoylornithine yields  $\alpha$ -hydroxy- $\delta$ -benzoylamino-*n*-valeric acid. When the benzoyl group is eliminated, the  $\delta$ -amino- $\alpha$ -hydroxy-*n*-valeric acid described by Fischer and Zemplén (Abstr., 1910, i, 100) is obtained.

From both the isomeric monobenzoylornithines the corresponding guanidinomonobenzoylamino-*n*-valeric acids are obtained on the addition of cyanamide, and these after removal of the benzoyl group are converted into the isomeric aminoguanidino-*n*-valeric acids. That from  $\alpha$ -monobenzoylornithine, which must have the formula



proved to be in every way identical with *racemic* arginine. The isomeric  $\delta$ -amino- $\alpha$ -guanidino-*n*-valeric acid had entirely different properties, and readily lost water, forming an anhydride.

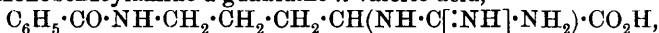
The yield in each of these operations amounted to 60% or more of the possible, and a rearrangement at any stage is considered impossible. It is also proved that the cyanamide addition takes place at the free primary amino-group and not at the secondary amino-group, since the monobenzoylguanidinovaleric acids cannot be titrated in presence of formaldehyde.

$\alpha$ -Monobenzoylornithine, m. p. 264—267° (Maquenne block), forms long crystals, some rectangular, others flat needles. On treatment with barium nitrite,  $\alpha$ -benzoylamino- $\delta$ -hydroxy-*n*-valeric acid is obtained.

$\alpha$ -Monobenzoylamino- $\delta$ -guanidino-*n*-valeric acid is obtained by the addition of cyanamide to  $\alpha$ -monobenzoylornithine dissolved in barium hydroxide; it has m. p. 315°, shows no alteration in acidity on the addition of formaldehyde, and is in every way identical with natural *racemic* monobenzoyl arginine. Synthetic arginine nitrate, arginine copper nitrate, and arginine picrate are in every respect the same as the natural *racemic* products.

$\delta$ -Monobenzoylornithine (Fischer, *Ber.*, 1901, 34, 463), m. p. 285—288°, crystallises in rhomboidal or six-sided plates; with barium nitrite,  $\alpha$ -hydroxy- $\delta$ -benzoylamino-*n*-valeric acid is obtained, forming a colourless, crystalline mass of bundles of prismatic needles, m. p. 85°.

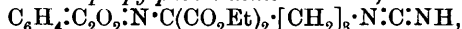
$\delta$ -Monobenzoylamino- $\alpha$ -guanidino-*n*-valeric acid,



forms a cheese-like precipitate, consisting of lumps of slender needles, m. p. 175°. When boiled with concentrated hydrochloric acid, it does not form  $\alpha$ -proline. On heating for three hours at 140—150° with 33% hydrochloric acid, the *hydrochloride* of  $\delta$ -amino- $\alpha$ -guanidino-*n*-valeric anhydride,  $\text{NH} \begin{array}{l} \text{CO} \text{---} \text{CH} \cdot [\text{CH}_2]_3 \cdot \text{NH}_2, 2\text{HCl} \\ \text{C}(\text{:NH}) \cdot \text{NH} \end{array}$ , is obtained

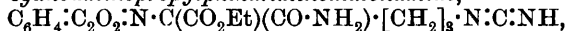
as colourless, prismatic crystals in stellar aggregates, m. p. 200°. The *picrate* forms long, yellow needles, m. p. 240—245°.

*Ethyl  $\gamma$ -cyanoaminopropylphthaliminomalonate,*



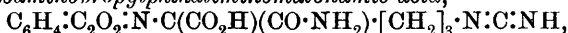
from ethyl  $\gamma$ -bromopropylphthaliminomalonate and sodium cyanamide, separates in well-formed colourless, short, stout, prismatic crystals, m. p. 191°; it can be titrated as a monobasic acid, using phenolphthalein.

*Ethyl  $\gamma$ -cyanoaminopropylphthaliminomalonamide,*



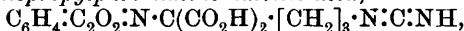
prepared by the action of concentrated ammonia on the above, crystallises in prismatic needles.

*γ* Cyanoaminopropylphthaliminomalonamic acid,



forms long, prismatic, obliquely-cut prisms. It behaves as a dibasic acid.

*γ*-Cyanoaminopropylphthaliminomalononic acid,



crystallises in stellar aggregates of microscopic needles; it is tribasic. On treatment of these compounds with aqueous ammonia, anhydrous ammonia, or ammonium salts, it was not possible under any conditions to obtain guanidino-compounds.

E. F. A.

**Hypiodous Amides.** ETIENNE BOISMENU (*Compt. rend.*, 1911, 153, 948—951. Compare *Abstr.*, 1911, i, 957).—Iodoacetamide,  $\text{CH}_3\cdot\text{CO}\cdot\text{NHI}$ , is obtained as a colourless substance, m. p.  $143^\circ$  (decomp.), by the alternate addition in small quantities of iodine (7 grams) and silver oxide to a solution of acetamide (1.475 grams) in ethyl acetate (100 c.c.), the liquid being finally evaporated to dryness, and the residue washed with chloroform. *Iodopropionamide* occurs in crystals, m. p.  $128^\circ$  (decomp.). *Iodoformamide*, m. p.  $95^\circ$  (decomp.), is less stable than the foregoing, and rapidly decomposes at the ordinary temperature, even in a vacuum. Iodobenzamide could not be obtained in the pure state. The substances described closely resemble the corresponding bromo-derivatives.

W. O. W.

**The Formation of Symmetrical Dialkylcarbamides by Heating the Corresponding Carbamates.** FRITZ FICHTER and BERNHARD BECKER (*Ber.*, 1911, 44, 3481—3485. Compare this vol., ii, 45).—The alkyl substituted ammonium carbamates when heated under pressure give, like ammonium carbamate, an equilibrium with the corresponding carbamide; the optimum temperature is, however, generally higher and the yield better than in the formation of the unsubstituted carbamide.

*Methylammonium methylcarbamate* was obtained from dry carbon dioxide and methylamine gas in crystalline crusts which smell strongly of methylamine and have m. p.  $105^\circ$ ; it is deliquescent, and its aqueous solution is strongly alkaline, owing to hydrolysis. After heating in a sealed glass tube and subsequent removal of unchanged methylcarbamate, practically pure *s*-dimethylcarbamide (m. p.  $96^\circ$ ) remains.

*Ethylammonium ethylcarbamate*, prepared similarly, is a white, crystalline salt, m. p.  $118^\circ$  (in sealed tube). On heating, it gives diethylcarbamide (m. p.  $106^\circ$ ), the optimum temperature being about  $150^\circ$ , the equilibrium mixture at this temperature containing 59—60% of the diethylcarbamide.

Benzylammonium benzylcarbamate, obtained by the action of carbon dioxide on a dry ethereal solution of benzylamine, separated as a gelatinous precipitate, which slowly changed to a crystalline mass, m. p.  $100^\circ$  (compare Tiemann and Friedländer (*Abstr.*, 1882, 56). On heating it yields dibenzylcarbamide.

*Benzhydrylammonium benzhydrylcarbamate*, formed by the action of carbon dioxide on benzhydrylamine in ethereal solution, is a white

substance which decomposes on warming with water, and has m. p.  $165^{\circ}$  (with decomp.). On heating, instead of the expected carbamide, there is formed *tribenzhydrylamine*,  $N(CHPh_2)_3$ ; this amine crystallises in needles, m. p.  $144^{\circ}$ , and forms a *picrate* insoluble in benzene.

*Diethylammonium diethylcarbamate* was produced by the combination of carbon dioxide with the vapour of diethylamine; it is a white, crystalline mass, melting at room temperature, and turning brown when kept. If carbon dioxide is led into diethylamine in the liquid or dissolved state, the product is *diethylammonium hydrogen carbonate*, which in a sealed tube melts and decomposes at  $70^{\circ}$ . If the above diethylcarbamate is heated, although the reaction product always possesses the characteristic odour of tetraethylcarbamide, no weighable quantity of this substance is isolable.

Hydrazine hydrazinecarboxylate is exceptional in its behaviour, and on heating under reflux at  $140^{\circ}$  gives a practically theoretical yield of carbohydrazide (compare Stollé and Hofmann, Abstr., 1905, i, 28); however, *ammonium hydrazinecarboxylate*, an unstable, deliquescent substance obtained by the action of ammonia on hydrazine hydrazinecarboxylate or on hydrazinecarboxylic acid, behaves analogously to the above-mentioned carbamates in being incompletely converted by heat into semicarbazide.

D. F. T.

**Storage of Calcium Cyanamide in the Tropics.** C. J. MILO (*Chem. Zentr.*, 1911, ii, 1655—1656; from *Med. Proefstat. Java-Suikerind.*, 1911, 3, 311—363).—When a concentrated aqueous extract of calcium cyanamide is kept for some days, a crystalline, basic calcium salt,  $C(N \cdot CaOH)_2$ , is obtained. The same salt is produced, along with cyanamide, dicyanamide, and carbamide when calcium cyanamide is kept for a long time in warm, damp air.

N. H. J. M.

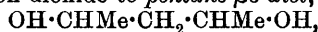
**Interaction of Thiocyanates and Bromine in Aqueous Solution.** W. KÖNIG (*J. pr. Chem.*, 1911, [ii], 84, 558—560).—2*N*-Bromine in 10% potassium bromide reacts quantitatively with aqueous potassium or ammonium thiocyanate in accordance with the equation:  $KSCN + 4Br_2 + 4H_2O = KBr + CNBr + H_2SO_4 + 6HBr$ ; so also does chlorine, but not iodine. The strengths of aqueous bromine or thiocyanate solutions, therefore, can be determined by titration with standard potassium hydroxide.

C. S.

**Constitution of Aliphatic Diazo-compounds and of Azoimide.** JOHANNES THIELE (*Ber.*, 1911, 44, 3336. Compare Abstr., 1911, i, 845).—The author acknowledges that Angeli has previously proposed a formula, which contains the group  $C:N:N$ , for a diazo-compound of indole; also that he has put forward the formulæ  $N:N:CH_2$  and  $N:N:NH$  for diazomethane and azoimide respectively.

H. W.

**1:2-Dimethylcyclopropane.** NICOLAI D. ZELINSKY and M. N. UJEDINOFF (*J. pr. Chem.*, 1911, [ii], 84, 543—548).—*a*-Acetylisopropyl alcohol (hydracetylacetone), for the preparation of which an improved method is described, is reduced by sodium amalgam and water in an atmosphere of carbon dioxide to *pentane- $\beta$ -diol*,

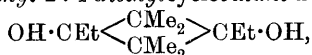


b. p. 197·5—198·5°/750 mm. or 97—98°/13 mm.,  $D_4^{20}$  0·9635,  $n_D^{20}$  1·4349, which is converted by phosphorus tribromide at 100°, and finally at 140°, into  $\beta\delta$ -dibromopentane, b. p. 60°/12 mm.,  $D_4^{20}$  1·6659, and  $n_D^{20}$  1·4987. By reduction with zinc dust and 80% alcohol in a freezing mixture, the dibromide yields 1:2-dimethylcyclopropane, b. p. 32—33°,  $D_4^{20}$  0·7025,  $D_4^{20}$  0·6806,  $n_D^{20}$  1·3763,  $n_D^{10}$  1·3823, which is oxidised by 1% potassium permanganate, and, in contrast to 1:1-dimethylcyclopropane, reacts slowly with bromine and is sparingly soluble in diluted sulphuric acid (2 vols. of acid to 1 vol. of water).

C. S.

**A Hydrocarbon of the cycloButane Series.** EDGAR WEDEKIND and M. MILLER (*Ber.*, 1911, **44**, 3285—3287).—An account of the synthesis of 1:1:3:3-tetramethyl-2:4-diethylcyclobutane.

1:1:3:3-Tetramethyl-2:4-diethylcyclobutane-2:4-diol,



obtained by the interaction of magnesium ethyl bromide and tetramethylcyclobutane-2:4-dione (Wedekind and Weisswange, *Abstr.*, 1906, i, 437; Staudinger and Klever, *ibid.*, i, 234) is an oil, having an aromatic odour, b. p. 128—130°/30 mm., and reacts with hydriodic acid to form the corresponding *di-iodo*-compound, which on account of its instability could not be obtained in a pure condition. When reduced with zinc and glacial acetic acid, this yields 1:1:3:3-tetramethyl-2:4-diethylcyclobutane,  $\text{CHEt}\begin{matrix} \text{CMe}_2 \\ \text{CMe}_2 \end{matrix}\text{CHEt}$ , which is a colourless, mobile liquid, b. p. 124—125°, and resembles in its chemical behaviour a saturated hydrocarbon of great stability.

1:1:3:3-Tetramethylcyclobutane-2:4-diol, obtained in small yield by the reduction of tetramethylcyclobutane-2:4-dione with sodium amalgam, and purified by means of its *diacetyl* derivative, is also mentioned.

F. B.

**The cycloOctane Series.** V. *cyclo*Octatetraene. RICHARD WILLSTÄTTER and ERNST WASER (*Ber.*, 1911, **44**, 3423—3445. Compare *Abstr.*, 1905, i, 515; 1907, i, 303; 1908, i, 407; 1910, i, 366).— $\alpha$ -Dedimethylgranatenine,  $\text{C}_8\text{H}_{11}\text{NMe}_2$ , was prepared by distilling in a vacuum the quaternary base obtained from *n*-methylgranatenine. It unites with methyl iodide to form a quaternary ammonium iodide, the hydroxide of which, on distillation, yields *cyclo*octatriene. Two series of attempts were made to prepare *cyclo*octatetraene from this. In the first series bromine was added, and the dibromocyclooctadiene so formed heated with quinoline. In this manner a hydrocarbon of the formula  $\text{C}_8\text{H}_8$  was obtained, which, however, on reduction in the presence of platinum black yielded a mixture of *dicyclo*octane ( $\text{C}_8\text{H}_{14}$ ) and *tricyclo*octane ( $\text{C}_8\text{H}_{12}$ ), thus showing that bridged rings had been formed during its preparation, probably owing to the rather high temperature employed. The second method was more successful. Dibromocyclooctadiene was converted into tetramethyldiaminocyclooctadiene. When the quaternary base obtained from this was heated in the vacuum of a Geryk oil pump, it was split up into trimethyl-

amine and *cyclooctatetraene*. When the distillation was carried out in the vacuum of a water-pump, the hydrocarbon formed contained considerable quantities of a dieyclic impurity.

*cycloOctatetraene*, in the presence of platinum black, readily unites with 4 molecules of hydrogen. It readily reduces permanganate and absorbs bromine. On treatment with nitrosulphuric acid it becomes resinified, but yields no nitro-derivative. It passes into more stable isomerides by the formation of bridged rings.

The contrast between the properties of *cyclooctatetraene* and benzene leads to a criticism of the formulæ proposed for the latter substance. The benzene formulæ of Kekulé and Thiele do not express these differences. The authors therefore prefer the centric benzene formula of Armstrong and von Baeyer, and consider that the centric equilibrium of the fourth carbon valencies does not occur in the



case of an eight-carbon ring because the distance of the carbon atoms from the centre is greater than in the case of rings of six-carbon atoms. Having preferred the centric formula for benzene, the authors are led to propose the appended formula for naphthalene.

The authors have also prepared  $\beta$ -dedimethylgranatenine by complete methylation of methylgranatenine. When treated with hydrochloric acid, it yields granatal ( $\Delta^2$ -*cyclooctenone*), together with a new base which has not been fully investigated.

*N*-Methylgranatenine was prepared by heating *N*-methylgranatoline with acetic acid and concentrated sulphuric acid at  $180^\circ$ . It crystallises readily, and has m. p.  $17.2$ — $17.4^\circ$ , b. p.  $62$ — $62.2^\circ/9$  mm., and  $186$ — $186.5^\circ/732$  mm. Ciamician and Silber (Abstr., 1894, i, 154) give the b. p.  $186^\circ$ . It has  $D_4^{20}$  0.961. Its *picrate*, which decomposes at  $286^\circ$ , *platinichloride*, m. p.  $221^\circ$  (decomp.), and *methiodide* were examined.

$\alpha$ -*Dedimethylgranatenine*,  $C_8H_{11}NMe_2$ , obtained by distilling the *quaternary ammonium base* from *N*-methylgranatenine under diminished pressure, is a colourless oil, which has b. p.  $71$ — $71.5^\circ/8$  mm.,  $D_4^{20}$  0.925,  $D_4^{20}$  0.910. When heated at the ordinary pressure, it becomes transformed into the  $\beta$ -base. Its *platinichloride* has m. p.  $168$ — $169^\circ$ , and decomposes at a higher temperature. The *methiodide* melts at  $172$ — $173^\circ$  (decomp.).

$\beta$ -*Dedimethylgranatenine* was prepared by the complete methylation of methylgranatenine. It is a colourless oil, b. p.  $218$ — $220^\circ/721$  mm. When exposed to air it become brown and gradually deposits a resin. On treatment with hydrochloric acid, it yields a base which has not been completely examined, together with granatal ( $\Delta^2$ -*cyclooctenone*) (compare Ciamician and Silber, Abstr., 1894, i, 154). The constitution of the latter follows from its reduction to *cyclooctanone*. The latter has b. p.  $78.6$ — $78.8^\circ/13$  mm. and  $200$ — $202^\circ$  (corr.)/ $713$  mm. It crystallises readily, and has m. p.  $29.5^\circ$ , which, by spreading on clay, is raised to  $32.3$ — $32.8^\circ$ . Wallach (Abstr., 1907, i, 602) gives the m. p.  $25$ — $26^\circ$ .

*cycloOctatriene*, obtained by distillation of the quaternary base derived from  $\alpha$ -dimethylgranatenine under diminished pressure, is a colourless, mobile oil, b. p.  $147.2$ — $148.2$ (corr.)/ordinary pressure,

31.2—31.8°/8 mm., and 33.5°/11 mm. Its density is much greater than that of *cyclooctadiene*, and somewhat higher than that of *tropilidene*. It has  $n_D^{20}$  1.52281,  $n_D^{20}$  1.52810,  $n_F^{20}$  1.54131, and  $n_G^{20}$  1.55322. On reduction with hydrogen in the presence of platinum black, it yielded *cyclooctane*, b. p. 149—150.3° (corr.), m. p. 11.6—11.8°. A former pure preparation had m. p. 14° (Abstr., 1910, i, 366). On oxidation with concentrated nitric acid, it yielded only pure hexane- $\alpha,\gamma$ -dicarboxylic acid.

*Dibromocyclooctadiene* was prepared by mixing chloroform solutions of *cyclooctatriene* and bromine. On evaporation of the solvent in a vacuum, the dibromide remains as a faintly brown-coloured mass, which appears to undergo a certain amount of transformation when distilled under diminished pressure. It has b. p. 129.5—130°/9 mm., 136—137.5°/14 mm. It is very susceptible to the action of air. When heated with dimethylamine it yields *tetramethyldiaminocyclooctadiene*, together with *dimethylaminocyclooctatriene*. The latter can be readily isolated by fractional distillation, and has b. p. 81—91°/10 mm.,  $D_4^0$  0.946,  $D_4^{20}$  0.936. Its *platinichloride* has m. p. 200° (decomp.), and its *methiodide*, m. p. 224—225° (decomp.).

*Tetramethyldiaminocyclooctadiene* is best prepared by the action of dimethylamine on the undistilled *dibromocyclooctadiene* dissolved in benzene. It is a pale yellow oil, which, on exposure to air, rapidly becomes dark brown. It has b. p. 126—127°/14 mm.,  $D_4^0$  0.944,  $D_4^{20}$  0.935. The product was probably not quite pure. Its *platinichloride* darkens at 210° and decomposes at 220°. Its *methobromide* has m. p. 195—196° (decomp.), and its *methiodide*, m. p. 170—171° (decomp.).

The *platinichloride* of the *diammonium* base,  $C_8H_{10}(NMe_3)_2Cl_6Pt$ , has no definite melting point, but darkens at 225°.

On reduction, *tetramethyldiaminocyclooctadiene* passes into *tetramethyldiaminocyclooctane*, a pale yellow oil, b. p. 259—261°/718 mm.,  $D_4^0$  0.926,  $D_4^{20}$  0.913.

By cautiously heating *dibromocyclooctadiene* with quinoline, a *hydrocarbon* was obtained, which had the following constants: b. p. 31.6—32.8°/10 mm., 142.8—143.8°/737 mm.,  $D_4^0$  0.927,  $D_4^{20}$  0.912,  $n_D^{20}$  1.53460,  $n_D^{20}$  1.54107,  $n_F^{20}$  1.55764,  $n_G^{20}$  1.57243. Analyses agreed with the formula  $C_8H_8$ , but the substance is probably not uniform, since, on reduction by hydrogen in the presence of platinum, it yields a mixture of approximately equal quantities of *dicyclooctane* ( $C_8H_{14}$ ) and *tricyclooctane* ( $C_8H_{12}$ ). The reduced hydrocarbon has b. p. 136°/728 mm.

For the preparation of *cyclooctatetraene*, the quaternary ammonium base of *tetramethyldiaminocyclooctadiene* was distilled in the vacuum of a Geryk oil pump. In this case a temperature of 85—95° sufficed for decomposition of the base, whilst, when a water pump was used, heating had to be continued to 110°. The hydrocarbon was obtained as a yellow oil of sweet, powerful odour. When exposed to air it deposits amorphous, white particles. Two specimens boiled at 36.2—36.4°/14 mm. and 42.2—42.4°/17 mm. respectively. It has  $D_4^0$  0.943,  $D_4^{20}$  0.925,  $n_D^{20}$  1.5389. On reduction with hydrogen in the presence of potassium black, it yields *cyclooctane*, b. p. 145—147°/720 mm.,  $D_4^0$  0.855,  $D_4^{20}$  0.841. Pure *cyclooctane* has b. p. 147—148°/720 mm.

720 mm. and  $D_4^{20}$  0.839. Since the *cyclooctane* also could not be crystallised, it was not perfectly pure. On oxidation it yielded hexane- $\alpha\zeta$ -dicarboxylic acid.

*cycloOctatetraene* was kept for three days and then reduced as above. The *cyclooctane* formed was found to contain *dicyclooctane*. The reduction of *cyclooctatetraene*, obtained by heating the quaternary base in the vacuum of a water pump, yielded still more unsatisfactory results. The product was a mixture of much *dicyclooctane* with but little *cyclooctane*.  
H. W.

**Two Methods of Treating the Problem of Substitution in the Benzene Nucleus.** ARNOLD F. HOLLEMAN (*Ber.*, 1911, **44**, 3556—3562).—Mainly polemical. A reply to Obermiller (*Abstr.*, 1911, i, 960). Holleman has based his laws of substitution on a study of the complete literature, showing that the position taken by a second substituting group in the benzene nucleus depends on the group already present, and, with but few exceptions, not on the nature of the entering group. This is also the case with a third substituting group.

E. F. A.

**Propenylbenzene from Cinnamylammonium Salts.** HERMANN EMDE (*Ber.*, 1911, **44**, 3224—3226).—Propenylbenzene,  $\text{CHPh}:\text{CHMe}$ , has been obtained by the reduction of quaternary cinnamylammonium salts with sodium amalgam (Emde, *Abstr.*, 1909, i, 708) with a b. p. as high as 176—177°. The possibility of the material so prepared containing allylbenzene or propylbenzene is considered; it was divided into four fractions, and each of these decomposed by ozone. In no case was phenylacetaldehyde or phenylacetic acid obtained, all four fractions yielding benzaldehyde or benzoic acid. Allylbenzene was, therefore, not present. E. F. A.

**Simultaneous Formation of Isomeric Substitution Products of Benzene. XVI. The Introduction of a Second Halogen Atom into Monohalogenated Benzenes.** ARNOLD F. HOLLEMAN and T. VAN DER LINDEN (*Rec. trav. chim.*, 1911, **30**, 305—380).—The authors have studied the chlorination of monochloro- and monobromobenzene, and their bromination also, directing the reaction so that only one halogen atom enters the benzene nucleus. The amount of each isomeride formed has been estimated, and the effect of certain catalytic agents ( $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ) on the proportions of the isomerides formed has also been studied.

The method employed for the quantitative estimation of the isomeric dihalogenated benzenes in their mixture from the halogenation consisted in (1) fractional distillation in a jacketed distilling flask, whereby almost all the unaltered monohalogenbenzene is removed. The residue is treated with 95.2% sulphuric acid, whereby the last trace of monohalogenbenzene is removed, whilst the dihalogenbenzene is unattacked by acid of this strength. It is essential that the acid be exactly this strength. This leaves behind a ternary mixture of the ortho-, meta-, and para-dihalogenbenzenes, the percentage of each isomeride being calculated after determining the initial point of solidification, when the para separates, and the second point of solidification, when the

whole mixture solidifies. Knowing these two values, the amounts of each isomeride in the mixture can be determined from tables and curves constructed previously from known mixtures of the pure substances.

Chlorobenzene was chlorinated at a temperature of 60—65°, slightly more than half the theoretical amount of chlorine being employed. In one set of experiments aluminium chloride was the catalyst, and in another ferric chloride. The amounts of the three isomerides present in the mixture differed considerably from the values given by Mouneyrat and Pouret (Abstr., 1899, i, 263). Only about 5.5% of the meta-compound was found, and its presence was confirmed by sulphonating the mixture, separating the barium salts of the sulphonic acids by fractional crystallisation, and from these preparing and identifying the corresponding sulphonamides. Two interesting microcrystalline reactions are quoted: one with rubidium chloride given by both the meta- and para-barium salts, and the other with sodium chloride given only by the para-salt.

Similar experiments were conducted with chlorine on bromobenzene and bromine on chloro- and bromo-benzene. For the removal of the last traces of bromobenzene a slightly different strength of sulphuric acid (95%) must be employed to that for chlorobenzene (95.2%).

It was found that the results obtained in different experiments, using aluminium chloride as catalyst, were not always in agreement. This is due to the fact that the aluminium chloride attacks the halogenated benzenes to a greater or less extent, and some benzene is produced. This is not the case with ferric chloride.

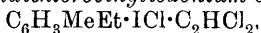
In chlorinating chloro- or bromo-benzene, aluminium favours the formation of the para-isomeride, iron, on the other hand, favouring the formation of the ortho. In bromination the reverse is the case. Without a catalyst the amounts of products obtained are situated between those with aluminium and those with iron. The substituent present in the compound has very little influence on the reaction, but the substituent entering seems to exert a great influence on the amounts of the three isomerides obtained. The amounts of ortho- and meta-isomerides seem to increase or diminish together, as opposed to the para-isomeride.

W. G.

**6-Iodo-1-methyl-3-ethylbenzene and its Derivatives containing Multivalent Iodine.** CONRAD WILLGERODT and MAX JAHN (*Annalen*, 1911, 385, 328—340).—By the usual method, 5-ethyl-*o*-toluidine is converted into 6-iodo-1-methyl-3-ethylbenzene,  $C_6H_3MeEtI$ , b. p. 242°, which reacts with chlorine in cold acetic acid to form 2-methyl-4-ethylphenyl iododichloride,  $C_6H_3MeEt \cdot ICl_2$ , yellow needles. 6-Iodoso-1-methyl-3-ethylbenzene,  $C_6H_3MeEt \cdot IO$ , decomp. 162°, obtained from the iododichloride and 10% sodium carbonate, forms a diacetate,  $C_6H_3MeEt \cdot I(OAc)_2$ , m. p. 104°, and is converted by distillation with steam into 6-iodoxy-1-methyl-3-ethylbenzene,  $C_6H_3MeEt \cdot IO_2$ , which explodes at 161°. Equal molecular quantities of the iodoso- and the iodoxy-compounds react with silver oxide and water at 40—50° to form ultimately a solution of di-2-methyl-4-ethylphenyliodonium hydroxide,  $OH \cdot I(C_6H_3MeEt)_2$ , from which the chloride, m. p. 148°, platinichloride, m. p. 163°, mercurichloride, m. p. 109—110°, bromide,

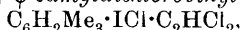
m. p. 162°, *iodide*, m. p. 134°, *nitrate*, m. p. 150° (decomp.), and *dichromate*, decomp. 132°, have been prepared. *Iododi-2-methyl-4-ethylphenyliodonium hydroxide*,  $C_6H_3MeEt \cdot I(OH) \cdot C_6H_2MeEtI$ , the sulphate of which is obtained by the careful addition of the preceding iodo-*o*-compound to concentrated sulphuric acid cooled by a freezing mixture, forms a *chloride*, m. p. 88°, *platinichloride*, m. p. 110—111° (decomp.), *mercurichloride*, m. p. 87°, *bromide*, m. p. 101°, *iodide*, m. p. 82°, and *dichromate*, m. p. 52°, resolidifying at 87°. *o-Tolyl-2-methyl-4-ethylphenyliodonium hydroxide*,  $C_6H_4Me \cdot I(OH) \cdot C_6H_3MeEt$ , obtained in solution from *o*-iodoxytoluene and 6-iodo-*o*-1-methyl-3-ethylbenzene and moist silver oxide, forms a *chloride*, m. p. 174°, *platinichloride*, m. p. 174° (decomp.), *mercurichloride*, m. p. 133°, *bromide*, m. p. 167°, *iodide*, decomp. 135°, and *dichromate*, decomp. about 138°.

*2-Methyl-4-ethylphenyldichlorovinylidodonium chloride*,



m. p. 144°, obtained by triturating 5-ethyl-*o*-tolyl iododichloride and acetylene silver chloride with water (compare Thiele and Haakh, *Abstr.*, 1909, i, 865), has been converted into the *platinichloride*, *mercurichloride*, m. p. 67°, *bromide*, m. p. 126°, *iodide*, decomp. 71°, *nitrate*, m. p. 93—94°, *hydrogen sulphate*, m. p. 56°, and unstable *dichromate*. C. S.

**5-Iodo- $\psi$ -cumene and its Derivatives.** CONRAD WILLGERODT and ROBERT MEYER (*Annalen*, 1911, 385, 341—351).—5-Iodo- $\psi$ -cumene,  $C_6H_2Me_3I$ , m. p. 37°, is most conveniently prepared by heating on the water-bath a mixture of  $\psi$ -cumene in petroleum, sulphur iodide, and nitric acid, D 1.34. It yields the following derivatives containing multivalent iodine.  $\psi$ -Cumyl iododichloride,  $C_6H_2Me_3 \cdot ICl_2$ , decomp. 66°; 5-iodo- $\psi$ -cumene,  $C_6H_2Me_3 \cdot IO$ , decomp. 171° (*acetate*, m. p. 123°); 5-iodoxy- $\psi$ -cumene,  $C_6H_2Me_3 \cdot IO_2$ , explodes at 210°; di- $\psi$ -cumyl-iodonium chloride,  $(C_6H_2Me_3)_2ICl$ , m. p. 107°, and the corresponding *platinichloride*, m. p. 159°, *aurichloride*, m. p. 90°, *bromide*, m. p. 118°, *iodide*, m. p. 120°, and *dichromate*, exploding at 120°; 5-iodo-di- $\psi$ -cumyliodonium chloride,  $C_6H_2Me_3 \cdot ICl \cdot C_6HMe_3I$ , m. p. 106°, and the corresponding *platinichloride*, m. p. 150°, *mercurichloride*, m. p. 108°, *aurichloride*, *bromide*, m. p. 105°, *iodide*, m. p. 112°, and *dichromate*, decomp. 113°; phenyl- $\psi$ -cumyliodonium chloride, m. p. 186°, and the corresponding *platinichloride*, *aurichloride*, m. p. 117°, *mercurichloride*, m. p. 161°, *bromide*, m. p. 173°, *iodide*, decomp. 147°, and *dichromate*, exploding at 184°; p-tolyl- $\psi$ -cumyliodonium chloride, m. p. 171°, and the corresponding *platinichloride*, *aurichloride*, m. p. 71°, *mercurichloride*, m. p. 81°, *bromide*, m. p. 148°, *iodide*, decomp. 108°, and *dichromate*, decomp. 149°;  $\psi$ -cumyldichlorovinylidodonium chloride,



m. p. 169°, and the corresponding *platinichloride*, *aurichloride*, m. p. 134° approx., *bromide*, m. p. 131°, and *iodide*, m. p. 96°.

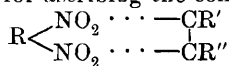
When chlorine is passed into an uncooled solution of 5-iodo- $\psi$ -cumene in chloroform, the product is 4:6-dichloro-5-iodo- $\psi$ -cumene,  $C_6Me_3Cl_2I$ , m. p. 188—189°; derivatives of this, containing multivalent iodine, cannot be prepared. C. S.

**Nitroalkylates.** IWAN OSTROMISLENSKY (*J. pr. Chem.*, 1911, [ii], 84, 495—506. Compare this vol., i, 1).—The colorations produced by

the addition of aliphatic nitro-compounds to organic substances containing ethylenic linkings are due probably to members of a new class of additive compounds, which are analogous to the picrates and which the author proposes to call nitroalkylates.

The tetranitromethanates of pyrene, acenaphthene, anthracene, and naphthalene are relatively the most stable, and are precipitated together with their components by the addition of water to their dilute alcoholic solutions. The cryoscopic behaviour of their dilute solutions in nitrobenzene indicates that the tetranitromethanates are almost completely dissociated into their components.

Reasons are advanced for ascribing the constitution :



to the nitroalkylates. The following are described: *anthranilic acid* 1 : 3 : 5 - *trinitrobenzenate*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_3$ , m. p. 186—187°, orange needles; *aminoazobenzene* 1 : 3 : 5 - *trinitrobenzenate*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{NPh} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_3$ , m. p. 156—157°, orange leaflets; *phenylhydrazine* 1 : 3 : 5 - *trinitrobenzenate*,  $\text{NHPh} \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2)_3$ , orange needles; *fluorene*  $\beta$ -1 : 3 : 6 : 8 - *tetranitronaphthalenate*,  $\text{C}_{18}\text{H}_{10} \cdot 2\text{C}_{10}\text{H}_4(\text{NO}_2)_3$ ,

m. p. 154—155°, brownish-yellow needles; *aniline* *p*-*hydroxynitrobenzenate*,  $\text{PhNH}_2 \cdot \text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , m. p. 41—42°, pale yellow prisms.

A list is given of nineteen substances which unite with 2 molecules of picric acid or other nitro-compound. It is claimed that the molecules of the picric acid, picryl chloride, trinitrobenzene, tetranitronaphthalene, or other nitro-compound are combined, not with the whole complex of the ethylenic molecule, but at a definite portion thereof, namely, at the ethylenic linking. It is shown, by Zerewitinoff's method with magnesium methyl iodide, that the  $\text{NH}_2$  or  $\text{NH}$  groups in nitroalkylates containing such groups do not experience any change, and still retain two and one active hydrogen atoms respectively.

C. S.

**$\alpha\kappa$ -Diphenyldecane and the Preparation of  $\omega\omega'$ -Diarylated Fatty Hydrocarbons.** WALTHER BORSCHKE and J. WOLLEMAN (Ber., 1911, 44, 3185—3188).—Sebacyl chloride combines with benzene to form diphenyldecanedione,  $\text{COPh} \cdot [\text{CH}_2]_8 \cdot \text{COPh}$  (Auger, Ann. Chim. Phys., 1891, [vi], 22, 361), in presence of aluminium chloride,  $\omega$ -benzoylnonoic acid, m. p. 85—86° (Auger, loc. cit.), being also formed. The dioxime of the ketone is readily reduced by sodium to the diamine, which on distillation of its phosphate forms  $\alpha\kappa$ -diphenyl- $\Delta^{\alpha\alpha}$ -decadiene; this, when shaken in methyl-alcoholic solution with colloidal palladium and hydrogen, is reduced to  $\alpha\kappa$ -diphenyl-*n*-decane.

$\alpha\kappa$  - *Dioximino* -  $\alpha\kappa$  - *diphenyldecane*,  $\text{OH} \cdot \text{N} : \text{CPh} \cdot [\text{CH}_2]_8 \cdot \text{CPh} : \text{N} \cdot \text{OH}$ , forms yellowish-white crystals, m. p. 120—121°; it slowly decomposes when kept.

$\alpha\kappa$ -*Diamino*- $\alpha\kappa$ -*diphenyldecane* is a colourless oil, b. p. 260°/18 mm., with a characteristic basic odour; the *dibenzoate* forms a colourless powder, m. p. 198—199°. *Dicarbamidodiphenyl decane* separates in microscopic needles, m. p. 183—184°.  $\alpha\kappa$  - *Diphenyl* -  $\Delta^{\alpha\alpha}$  - *decadiene*,  $\text{CHPh} : \text{CH} \cdot [\text{CH}_2]_6 \cdot \text{CH} : \text{CHPh}$ , forms large needles, m. p. 53°. With

two molecules of bromine,  $\alpha\beta\gamma\delta$ -tetrabromo- $\alpha\kappa$ -diphenyldecane is obtained as a colourless, crystalline mass, m. p. 164—165°.

$\alpha\kappa$ -Dihydroxy- $\alpha\kappa$ -diphenyldecane,  $\text{OH}\cdot\text{CHPh}\cdot[\text{CH}_2]_8\cdot\text{CHPh}\cdot\text{OH}$ , obtained by reduction of diphenyldecanedione with sodium and ethyl alcohol, forms colourless, matted needles, m. p. 70—72°.

$\alpha\kappa$ -Diphenyl- $n$ -decane is a transparent, strongly refractive oil, b. p. 234°/12 mm., solidifying to colourless crystals, m. p. 16—17°.

E. F. A.

**Some Secondary Aromatic Amines Related to Diisopropylamine.** M. C. DE LEEUW (*Rec. trav. chim.*, 1911, 30, 239—269).—The behaviour of some secondary amines, in which one or more of the methyl groups of diisopropylamine are replaced by phenyl, as compared with that of diisopropylamine itself, has been studied. The amines experimented with were  $\alpha$ -phenylethylisopropylamine, di- $\alpha$ -phenylethylamine, diphenylmethylisopropylamine, diphenylmethyl- $\alpha$ -phenylethylamine, and di-diphenylmethylamine. These were all prepared by Hofmann's method, namely, the condensation of an alkyl halide (1 mol.) with an amine (2 mols.).

$\alpha$ -Phenylethylisopropylamine,  $\text{CHMePh}\cdot\text{NH}\cdot\text{CHMe}_2$ , is obtained by heating together  $\alpha$ -phenylethylamine (2 mols.) and isopropyl iodide (1 mol.) in sealed tubes at 100°. The hydrochloride forms colourless crystals, m. p. 235·5°. By treatment with potassium hydroxide, it yields the base, a colourless, mobile liquid, b. p. 90·5—92°/20 mm.,  $D_4^{14}$  0·905,  $n_D^{14}$  1·4996. The picrate has m. p. 157·5°. The nitrite, m. p. 122°, when warmed with water, yields the corresponding nitrosoamine, a pale yellow liquid, b. p. 162°/19 mm.,  $D_4^{15·7}$  1·034,  $n_D^{15·7}$  1·52657.

Di- $\alpha$ -phenylethylamine,  $\text{NH}(\text{CHMePh})_2$  (compare Busch and Leeftink, *Abstr.*, 1908, i, 151), was obtained from  $\alpha$ -phenylethylamine and  $\alpha$ -phenylethyl bromide. With sodium nitrite, it yields a nitrosoamine, which was not, however, isolated.

Diphenylmethylisopropylamine,  $\text{CHPh}_2\cdot\text{NH}\cdot\text{CHMe}_2$ , is prepared by the condensation of diphenylmethylamine and isopropyl iodide as a highly refractive, colourless liquid, which crystallises on cooling, m. p. 11·5°, b. p. 181·5—182°/25 mm.,  $D_4^{13}$  1·001,  $n_D^{13}$  1·56015. It yields a hydrochloride, m. p. 213—214°, which crystallises from water with  $1\text{H}_2\text{O}$ . The nitrite, m. p. 107°, is very unstable, decomposing if heated in benzene solution above 55°, and yielding if heated to fusion the corresponding nitrosoamine, m. p. 75°. The picrate has m. p. 189—190°, and acetyl derivative, m. p. 89·5°.

Diphenylmethyl- $\alpha$ -phenylethylamine,  $\text{CHPh}_2\cdot\text{NH}\cdot\text{CHMePh}$ , results from the condensation of  $\alpha$ -phenylethylamine and diphenylmethyl bromide. It is a colourless liquid, b. p. 234·5—235°/19 mm.,  $D_4^{13·6}$  1·060,  $n_D^{13·6}$  1·59824, and yields a hydrochloride, m. p. 232·5—234°. No nitrite could be isolated, but from a solution of the hydrochloride in absolute alcohol by treatment with sodium nitrite, the nitrosoamine, m. p. 80·5°, was obtained. The picrate, m. p. 184·5°, crystallises with 1 mol. of benzene.

Di-diphenylmethylamine,  $\text{NH}:(\text{CHPh}_2)_2$  (compare Friedel and Balsohn, *Abstr.*, 1881, 279), was obtained by the action of diphenylmethylamine on diphenylmethyl bromide. The hydrochloride has m. p. 200—202°.

It is noticeable that the melting points, boiling points, specific gravities, and refractive indices of the bases rise as the base contains more phenyl and fewer methyl groups. The basic character diminishes with increase in the number of phenyl groups in the substance, as is shown by the stability of the hydrochlorides and nitrites towards water. None of the bases yielded a picryl derivative with picryl chloride, thus resembling diisopropylamine itself.

W. G.

**Optically Active Amino-oxides.** JAKOB MEISENHEIMER (*Annalen*, 1911, 385, 117—155).—The existence of substances of the type  $\alpha:Nbcd$  in enantiomorphous configurations, previously exemplified by the methylethylaniline oxides (Abstr., 1909, i, 20), has been substantiated by the isolation of the active forms of  $\beta$ -naphthylmethylethylamine oxide and of kairolin oxide. According to Jones (Trans., 1903, 83, 1400; 1907, 91, 1821), substances of the type  $>C:Nbcd$  exist in only one form. The author suggests that in these cases the double linking stands in the place of two of the non-ionisable groups, whilst in the amino-oxides it is in the place of the linking binding the acid group and one of the other four linkings (*loc. cit.*).

Further information is given regarding the methylethylaniline oxides. The *d*-base is obtained most conveniently by resolving the racemic base by means of *d*-tartaric acid. The active and the racemic modifications of the base have been obtained anhydrous and crystalline; their composition corresponds with the formula:  $O:NMeEtPh$ . The active forms have  $[M]_D + 24^\circ$  in 1—2% aqueous solution, and  $\pm 8^\circ$  in 1—2% benzene solution. *d*-Hydroxyphenylmethylethylammonium *d*-tartrate,  $C_9H_{13}ON, C_4H_6O_6$ , has m. p.  $134$ — $135^\circ$  and  $[M]_D$   $81.9^\circ$  in alcohol.

[With MARTHA HOFFHEINZ.]—*r*- $\beta$ -Naphthylmethylethylamine oxide,  $O:NMeEt \cdot C_{10}H_7, 3H_2O$ , m. p.  $70^\circ$ , colourless leaflets, is obtained by oxidising methylethyl- $\beta$ -naphthylamine by Caro's acid at the ordinary temperature. It is not resolved by *d*-bromocamphorsulphonic acid; the *bromocamphorsulphonate* obtained has decomp.  $135^\circ$ , after repeated crystallisation, and  $[M]_D + 282^\circ$ , as against the initial value  $+ 273^\circ$ . The resolution is accomplished by means of the tartaric acids. The racemic base and *d*-tartaric acid in alcoholic solution yield *d*-hydroxy- $\beta$ -naphthylmethylethylammonium *d*-tartrate,  $C_{13}H_{15}ON, C_4H_6O_6$ , m. p.  $132$ — $135^\circ$ , decomp.  $135^\circ$ ,  $[M]_D + 107.8^\circ$ , whilst *l*-hydroxy- $\beta$ -naphthylmethylethylammonium *l*-tartrate, obtained in a similar manner by means of *l*-tartaric acid, has m. p.  $132$ — $135^\circ$ , decomp.  $135^\circ$ , and  $[M]_D - 107.8^\circ$  in aqueous solution. Each of these tartrates is converted through the *picrate*, decomp.  $118$ — $119^\circ$ , and the *chloride* into the free base,



m. p.  $67$ — $70^\circ$ , needles; the *d*-base and the *l*-base have  $[M]_D + 38^\circ$  and  $-39^\circ$  respectively in aqueous solution.

[With JACOB DODONOW.]—Kairolin is oxidised by 3% hydrogen peroxide at  $60$ — $65^\circ$  to *r*-kairolin oxide,  $C_{10}H_{13}ON$ , m. p.  $124^\circ$  (decomp.), which is isolated in the form of the *hydrochloride*,  $C_{10}H_{13}ON, HCl$ , m. p.  $144^\circ$  (decomp.) (*platinichloride*, m. p.  $153^\circ$  decomp.), or better as the *picrate*, m. p.  $122^\circ$  (decomp.). The resolution of the *r*-base is effected with extraordinary ease. An alcoholic solution is treated

with alcoholic *d*-tartaric acid, the crystals of *l*-hydroxykairolinium *d*-tartrate which are deposited in 90% yield, are removed, the filtrate is freed from the excess of *d*-tartaric acid by the addition of ammonium chloride, and is then concentrated and treated with aqueous ammonium *d*-bromocamphorsulphonate, whereby *d*-hydroxykairolinium *d*-bromocamphorsulphonate is obtained in 80% yield. This salt has decomp.  $165^{\circ}$  and  $[M]_D + 362^{\circ}$ , and is converted as usual through the *d*-picrate, m. p.  $126^{\circ}$  (decomp.), and *d*-chloride, decomp.  $138^{\circ}$ ,  $[M]_D + 88^{\circ}$ , into *d*-kairoline oxide,  $C_{10}H_{13}ON, H_2O$ , hygroscopic plates, which has  $[M]_D + 45^{\circ}$  in water and (anhydrous)  $+ 134^{\circ}$  in benzene. *l*-Hydroxykairolinium *d*-tartrate, m. p.  $145^{\circ}$  (decomp),  $[M]_D - 48^{\circ}$ , is converted through the *l*-picrate, m. p.  $126^{\circ}$  (decomp.), and *l*-chloride, decomp.  $138^{\circ}$ ,  $[M]_D - 88^{\circ}$ , into *l*-kairoline oxide,  $C_{10}H_{13}ON, H_2O$ ,  $[M]_D - 45^{\circ}$  in water and (anhydrous)  $- 137^{\circ}$  in benzene.

*r*-Kairoline oxide reacts with methyl iodide in the presence of methyl alcohol to form a *periodide*,  $C_{10}H_{13}ONI_2$ , decomp.  $145^{\circ}$ , dimethyltetrahydroquinolinium iodide, and kairoline; the last substance is optically inactive even when the experiment is performed with *l*-kairoline oxide. Similar products are obtained when methyl sulphate is used.

C. S.

**Salts and Esters of Alkylaminodithiocarbamic Acids.** ERNEST FOURNEAU and VILA (*Bull. Soc. chim.*, 1911, [iv], 9, 985—989. Compare Abstr., 1911, i, 528).—It has been shown (Abstr., 1911, i, 528) that alkylaminoacetic acids react with carbon disulphide to give the corresponding dithiocarbamates. It is now shown that, if an arylaminoacetic acid is employed, the product is a thiothiazolone.

When ethyl or bromophenylacetate reacts with methylamine in benzene solution it yields *ethyl methylaminophenylacetate*, an oil readily saponified by boiling water, b. p.  $136^{\circ}/10$  mm. This ester reacts in ether with carbon disulphide to form 2-thio-4-phenyl-3-methylthiazolone,  $CHPh \begin{matrix} \swarrow NMe \cdot CS \\ \searrow CO - S \end{matrix}$ , voluminous prisms, m. p.  $137^{\circ}$ . This, when

treated with ammonia, does not yield the amide of the corresponding dithiocarbamic acid, but methylaminophenylacetamide. When warmed with sodium hydroxide in alcoholic solution, it yields the *sodium* derivative,  $CO_2Na \cdot CHPh \cdot NMe \cdot CS_2Na$ . The *potassium* derivative is prepared in a similar manner. If to a solution of the sodium salt in water freshly precipitated mercuric oxide is added, the unstable compound,  $(CO_2Na \cdot CHPh \cdot NMe \cdot CS_2)_2Hg$ , is precipitated in the form of pale yellow crystals. Organo-mercury compounds, such as mercury aniline, behave in the same way as the mercuric oxide.

If a solution of antimony trichloride is added to a solution of the potassium salt in water, there results an ill-defined compound, which should theoretically be  $(CO_2K \cdot CHPh \cdot NMe \cdot CS_2)_3Sb$ , but, judged by the estimation of the antimony, seems to correspond more nearly with the formula  $(CO_2K \cdot CHPh \cdot NMe \cdot CS_2)_2Sb \cdot OH$ . This substance is of therapeutic interest.

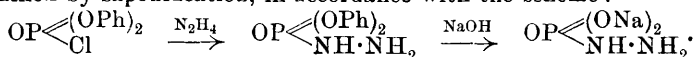
W. G.

**Diamidothiophosphoric Acid.** FRITZ EPHRAIM (*Ber.*, 1911, 44, 3414—3416. Compare Abstr., 1911, i, 284).—Diamidothiophosphoric

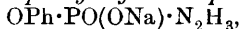
acid is obtained from the compound  $\text{PCl}_2 \cdot \text{OPh}$  by the addition of sulphur, replacement of the chlorine atoms by the amino-group, and saponification of the resulting ester.

*Phenyl dichlorothiophosphate*,  $\text{PSCl}_2 \cdot \text{OPh}$ , is formed when the compound  $\text{PCl}_2 \cdot \text{OPh}$  (1 mol.) is heated with sulphur (1 atom) for half an hour in a sealed tube at  $220-230^\circ$ . Fractional distillation of the product gives a colourless, highly refractive liquid, possessing a slight but unpleasant odour, b. p.  $260^\circ$  (decomp.) or  $133^\circ/22$  mm. Owing to its insolubility in aqueous solutions, it is practically unacted on by dilute acids or concentrated sodium hydroxide. Nitric acid (D 1.4) gives rise to phenyl or else nitrophenyl phosphate. When dissolved in alcohol and treated with aqueous ammonia (D 0.82), crystals of *phenyl diamidothiophosphate*,  $\text{PS}(\text{NH}_2)_2 \cdot \text{OPh}$ , are readily obtained, m. p.  $118^\circ$ . This compound cannot be hydrolysed by boiling with aqueous sodium hydroxide. To bring about hydrolysis, it is necessary to mix it with 2.3 mols. of solid sodium hydroxide and add a few drops of water; the heat of solution of the sodium hydroxide starts the hydrolysis. Addition of acetic acid and alcohol then precipitates an oil, which is doubtless *diamidothiophosphoric acid*,  $\text{PS}(\text{NH}_2)_2 \cdot \text{OH}$ . It is very unstable, gradually decomposing with evolution of hydrogen sulphide, so that it could not be obtained pure. The *silver* salt is characteristic. T. S. P.

**Hydrazidophosphoric Acid.** FRITZ EPHRAIM and M. SACKHEIM (*Ber.*, 1911, 44, 3416—3423).—In order to prepare monohydrazidophosphoric acid,  $\text{PO}(\text{OH})_2 \cdot \text{N}_2\text{H}_3$ , the authors wished to nitrate amidophosphoric acid,  $\text{PO}(\text{OH})_2 \cdot \text{NH}_2$ , and from the nitroamide so produced, obtain the hydrazide by reduction (compare the analogous process for the derivatives of sulphuric acid, *Abstr.*, 1911, ii, 286). Since free amidophosphoric acid is very unstable, the nitration experiments were carried out with the phenyl ester, but it was found that nitration always took place in the phenyl group, the amido-group being split off at the same time. The following method was therefore used: Diphenyl chlorophosphate was transformed into the hydrazide, from which salts of hydrazidophosphoric acid could be obtained by saponification, in accordance with the scheme:



*Diphenyl hydrazidophosphate*,  $\text{PO}(\text{O} \text{Ph})_2 \cdot \text{N}_2\text{H}_3$ , is obtained by the interaction of diphenyl chlorophosphate (1 mol.) and hydrazine hydrate (1 mol.) in alcoholic solution. A precipitate of the hydrochloride is first formed, and water is then added until the precipitate dissolves and the liquid becomes milky. On cooling, crystals of the desired compound are obtained, m. p.  $112^\circ$ . On hydrolysis with solid sodium hydroxide and a few drops of water (compare the previous abstract), *sodium phenyl hydrazidophosphate*,

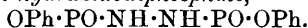


is produced; it crystallises in needles from alcohol. The *disodium hydrazidophosphate*,  $\text{PO}(\text{ONa})_2 \cdot \text{N}_2\text{H}_3$ , results when the reaction mixture is heated for ten minutes, after hydrolysis with the formation of the monosodium salt is complete. It is best prepared by hydrolysis

of the diphenyl ester with 25% sodium hydroxide under reflux. *Sodium hydrogen hydrazidophosphate*,  $\text{ONa}\cdot\text{PO}(\text{OH})\cdot\text{N}_2\text{H}_3$ , on account of its sparing solubility, is precipitated from a solution of the normal salt by the careful addition of acetic acid. The *normal potassium salt* and the *potassium hydrogen salt* are prepared similarly to the sodium salts. *Ammonium* and *barium phenyl hydrazidophosphates*,  $\text{OPh}\cdot\text{PO}(\text{O}\cdot\text{NH}_4)\cdot\text{N}_2\text{H}_3$  and  $[\text{PO}(\text{OPh})(\text{N}_2\text{H}_3\cdot\text{O})_2]_2\text{Ba}$ , are obtained from the diphenyl ester by hydrolysis with concentrated ammonium hydroxide and barium hydroxide respectively. Barium hydrazidophosphate could not be obtained pure. The *lead salts* of hydrazidophosphoric acid and of phenylhydrazidophosphoric acid are obtained by double decomposition of the corresponding sodium salts with lead acetate.

Free hydrazidophosphoric acid, as also its phenyl ester, were obtained in solution by interaction of the lead or barium salts with hydrogen sulphide or sulphuric acid. The solutions reduce silver nitrate and Fehling's solution with difficulty at the ordinary temperature, somewhat more quickly on boiling. The solid acids could not be isolated.

When diphenyl hydrazidophosphate is heated gradually to  $150^\circ$ , 1 mol. of hydrazine is lost from 2 mols. of ester, with the formation of *diphenyl hydrazidodiphosphate*,



This compound forms microscopic needles; it does not react with aldehyde, nor does it reduce alcoholic ammoniacal silver nitrate, so that it probably does not possess the formula  $\text{NH}_2\cdot\text{N}[\text{PO}(\text{OPh})_2]_2$ . It is changed by boiling water in some way, the solution then readily reducing silver nitrate. When the hot alcoholic solution is precipitated with water, hydrazine is split off, the precipitate consisting of monophenyl phosphate,  $\text{PO}(\text{OH})_2\cdot\text{OPh}$  (compare Rapp, Abstr., 1884, 1337).

Nitration of diphenyl amidophosphate gives rise to a mixture of *o*- and *p*-dinitrophenyl phosphates,  $\text{OH}\cdot\text{PO}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ , which melts to a turbid liquid at  $95-97^\circ$ , the fusion clearing suddenly at  $165-167^\circ$  (compare Rapp, *loc. cit.*). The mixture contains only a very small proportion of the ortho-compound (about 0.2%). *Sodium p-dinitrophenyl phosphate* forms light yellow, slender needles; the *silver salt* forms slender, white needles.

T. S. P.

**The Reactions of 4-Nitrosophenol, 2:6-Dibromo-4-nitrosophenol, and 6-Nitroso-*m*-cresol with Bromine.** HENRI VAN ERP (*Rec. trav. chim.*, 1911, 30, 270-304. Compare Bridge, Abstr., 1894, i, 25; Raiford and Heyl, Abstr., 1910, i, 273, 730).—A determination of the products obtained by the action of bromine on solutions of phenol containing nitrosophenol. From his experiments the author draws the conclusion that, when nitrosophenol is treated with excess of bromine, the principal product is 2:4:6-tribromophenol, probably formed according to the equation:  $\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{OH} + 8\text{Br} + 2\text{H}_2\text{O} = \text{C}_6\text{H}_2\text{Br}_3\cdot\text{OH} + \text{HNO}_3 + 5\text{HBr}$ . Other products are 4:6-dibromo-2-nitrophenol, 2:6-dibromo-4-nitrophenol, and 2:6-dibromo-*p*-benzoquinone in small quantity.

2:6-Dibromo-4-nitrosophenol was prepared both from the nitroso-

phenol and bromine (Fischer and Hepp, Abstr., 1888, 456), and by the action of hydroxylamine on 2:6-dibromo-*p*-benzoquinone, and, contrary to Kehrman's results (compare Abstr., 1889, 243), the products in the two cases were identical.

2:4:6-Tribromo-*m*-cresol yields an *acetate* and a *benzoate*, m. p. 87°.

The *diacetate* of 2:6-dibromoquinol is obtained in colourless prisms, m. p. 116·5°; the *dibenzoate* has m. p. 136°.

*Dibromodianilino-p-benzoquinone* is obtained by the addition of aniline, dissolved in alcohol, to a warm solution of 2:6-dibromo-*p*-benzoquinone in alcohol. It forms an olive-coloured, microcrystalline powder, which does not melt at 300° (compare Niemeyer, Abstr., 1885, 1065).

By the action of bromine in excess on 4-nitrosophenol in alcoholic solution and subsequent distillation in steam, there resulted (1) a non-volatile product, which was shown to be 2:6-dibromo-4-nitrophenol; (2) a volatile portion, which formed the major part of the products, and consisted chiefly of 2:4:6-tribromophenol with a little 4:6-dibromo-2-nitrophenol.

Working with water as a solvent instead of alcohol, the products were the same, but in this case some 2:6-dibromo-*p*-benzoquinone was also isolated. In each case the hydrogen bromide obtained from the reaction was in excess of the amount demanded by the equation. This the author considers was due to the formation of brominated resinous by-products and consequent generation of hydrogen bromide.

That the 2:6-dibromo-4-nitrophenol does not result by isomeric change from 4:6-dibromo-2-nitrophenol, or vice versa, in this reaction is shown by taking solutions of each of these separately in acetic acid, gradually adding sodium nitrite, and allowing the solutions to remain. After three days the starting materials can be recovered unchanged without any trace of the isomeride being present.

2:4:6-Tribromophenol is the product of the action of bromine in excess on an alcoholic solution of 2:6-dibromo-4-nitrosophenol. With 6-nitroso-*m*-cresol, bromine yields 2:4:6-tribromo-*m*-cresol.

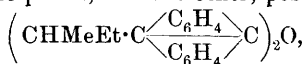
W. G.

### Action of Magnesium Ethyl Bromide on Anthraquinone.

LATHAM CLARKE and PAUL WHITTIER CARLETON (*J. Amer. Chem. Soc.*, 1911, 33, 1966—1973).—It has been shown by Clarke (Abstr., 1908, i, 330) that magnesium ethyl bromide reacts with anthraquinone with formation of 9:10-dihydroxy-9:10-diethyldihydroanthracene. A further study of this reaction has shown that when the magnesium ethyl bromide is in excess, dihydroxydiethyldihydroanthracene is formed, but that when the anthraquinone is in excess, ethyloxanthranol is produced.

9:10-Dihydroxy-9:10-diethyldihydroanthracene has m. p. 172°, and its *dimethyl ether*, m. p. 178°; the *diethyl ether* has also been prepared. When the compound is treated with acetyl chloride, a cream-coloured *substance*, C<sub>16</sub>H<sub>17</sub>O, m. p. 135·5—136°, is produced which crystallises in needles and dissolves in methyl alcohol to form a solution with a blue fluorescence. By the action of zinc dust and glacial acetic acid, the dihydroxy-compound is converted into diethyl-

anthracene. When the compound is heated with dilute hydrochloric acid, a mixture of two isomeric *substances*,  $C_{36}H_{34}O$ , is obtained. One of these compounds, probably  $(CHMe:C \begin{smallmatrix} \diagup C_6H_4 \diagdown \\ \diagdown C_6H_4 \diagup \end{smallmatrix} CEt)_2O$ , m. p.  $161^\circ$ , forms yellow, rhombic plates, and the other, possibly



m. p.  $226^\circ$ , crystallises in yellow prisms, and gives fluorescent solutions. These substances are also formed as by-products in the preparation of 9 : 10-dihydroxy-9 : 10-diethyldihydroanthracene. E. G.

**Synthesis of Butein.** A. GÖSCHKE and J. TAMBOR (*Ber.*, 1911, 44, 3502—3505).—The authors will describe shortly a method of synthesising polyhydroxychalkones. Amongst others, butein (Perkin and Hummel, *Trans.*, 1904, 85, 1459) has been obtained by treating a boiling alcoholic solution of equal molecular quantities of proto-catechualdehyde and resacetophenone with 50% potassium hydroxide. The product, which is obtained by acidification and purified through the tetra-acetyl derivative, is shown to be identical with natural butein by direct comparison. The 4' : 5'-methylene ether,



m. p.  $185^\circ$ , yellow needles, prepared in a similar manner from piperonal and resacetophenone, yields 2 : 4-dimethoxy-4' : 5'-dioxy-methylenechalkone, m. p.  $168^\circ$ , by treatment with warm methyl sulphate and 50% potassium hydroxide. C. S.

**$\alpha$ -isodypnopinacolin.** MAURICE DELACRE (*Bull. Soc. chim.*, 1911, [iv], 9, 1024—1025).—In this preliminary communication it is shown that dehydrodypnopinacolin,  $C_{32}H_{24}O$ , can be obtained by the oxidation of  $\alpha$ -isodypnopinacolin,  $C_{32}H_{26}O$ , with bromine (compare Abstr., 1896, i, 662). Oxidation with chromic acid in acetic acid gives rise to dehydrodypnopinacone,  $C_{32}H_{26}O_2$ . The latter by dehydration furnishes dehydrodypnopinacolin, and this on treatment with sodium amalgam gives a *substance*,  $C_{32}H_{26}O$ , isomeric with dypnopinacolin, but which behaves as an alcohol, and with acetyl chloride gives a hydrocarbon, which may be isodypnopinacolene (da Costa, *Thèse*, 1911).

T. A. H.

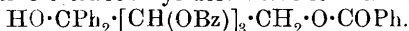
**Cholesterol.** III. LEO TSCHUGAEFF and P. KOCH (*Annalen*, 1911, 385, 352—358. Compare Abstr., 1910, i, 734).—Recently several investigations of the behaviour of cholesterol and its immediate derivatives towards ozone (Molinari and Fenaroli, Abstr., 1908, i, 882; Dorée, *Trans.*, 1909, 95, 638; Diels and Abderhalden, Abstr., 1904, i, 880; Diels, *ibid.*, i, 728) have thrown doubt on the usually accepted view that the molecule of cholesterol contains only one ethylenic linking. The authors, therefore, have determined the molecular refractions of cholesterol, cholestane, cholestene,  $\alpha$ -cholesterylene, methyl cholesterylxanthate, and methyl dihydrochol-

esteryl xanthate in benzene, and have obtained values which agree closely with those calculated on the assumption that only one ordinary ethylenic linking is present in the molecule of cholesterol.

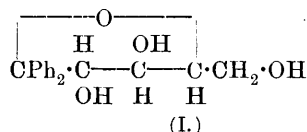
C. S.

**Synthesis of  $\alpha\alpha$ -Diaryl Substituted Arabitol.** CARL PAAL and MAX KINSCHER (*Ber.*, 1911, 43, 3543—3555. Compare Abstr., 1906, i, 802).—On treatment of triacetyl-*l*-arabonolactone with magnesium phenyl bromide and decomposition of the product with dilute acids,  $\alpha\alpha$ -diphenyl-*l*-arabitol is obtained. In a similar manner,  $\alpha\alpha$ -di-*p*-tolyl- and  $\alpha\alpha$ -dibenzyl-arabitol have been prepared.

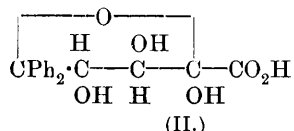
On benzoylation of diphenylarabitol, which is strongly dextro-rotatory, an inactive tetrabenzoyle derivative is obtained,



Diphenylarabitol is converted on oxidation into benzophenone and aliphatic compounds, of which only mesotartaric acid could be isolated. Dilute nitric and other mineral acids eliminate water, forming



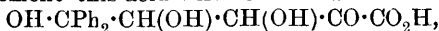
anhydrodiphenyl-*l*-arabitol,  $\text{C}_{17}\text{H}_{18}\text{O}_5$ . This does not react with aldehyde or ketone reagents, and when oxidised with potassium permanganate yields an acid,  $\text{C}_{17}\text{H}_{16}\text{O}_6$ , without the elimination of the phenyl groups as benzophenone.



Accordingly, constitution (I), namely, 3 : 4-*dihydroxy*-2 : 2-*diphenyl*-5-*methyl-ol*tetrahydrofuran, is assigned to the anhydro-compound, whilst the acid is 3 : 4 : 5-*trihydroxy*-2 : 2-*diphenyl*tetra-

*hydrofuran*-5-*carboxylic acid* (constitution II).

On rearrangement this acid will form an  $\alpha$ -ketonic acid,



as witnessed by the formation of a dark red, oily hydrazone or osazone on treatment with phenyl hydrazine.

*Triacetyl-l-arabonolactone* forms large, transparent, well-formed, prismatic crystals with many faces, m. p. 52—54°,  $[\alpha]_D^{18.5} = 60.45^\circ$ .

$\alpha\alpha$ -*Diphenyl-l-arabitol* separates in small, colourless, flat needles, grouped concentrically, m. p. 171°,  $[\alpha]_D^{20} = 85.6^\circ$ .

$\beta\gamma\delta$ -*Tetrabenzoyle- $\alpha\alpha$ -diphenylarabitol* crystallises in colourless, silky, glistening needles, m. p. 181—182°, which are optically inactive.

*Anhydrodiphenylarabitol* crystallises in transparent, large, thin plates, m. p. 172—174°,  $[\alpha]_D^3 = 114.8^\circ$ .

3 : 4 : 5-*Trihydroxy*-2 : 2-*diphenyl*tetrahydrofuran-5-*carboxylic acid* forms short, stunted needles, which sinter at 111°, m. p. 117°,  $[\alpha]_D^{17} = 201.7^\circ$ .

$\alpha\alpha$ -*Di-p-tolyl-l-arabitol* crystallises in small, glass-like, colourless, flat prisms with oblique end faces, in renniform aggregates. It has a faint aromatic odour, m. p. 186—187°,  $[\alpha]_D^{18} = 71.62^\circ$ .

$\alpha\alpha$ -*Dibenzyl-l-arabitol* forms transparent, colourless needles, m. p. 156—157°,  $[\alpha]_D^{19} = 31.5^\circ$ .

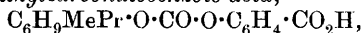
E. F. A.

**The Polymorphism of *allo*Cinnamic Acid.** JULIUS MEYER (*Zeitsch. Elektrochem.*, 1911, 17, 976—984).—A more detailed account of results already published (compare Abstr., 1911, i, 975).

T. S. P.

**Acylated Salicylic Acids.** ALFRED EINHORN, LEO ROTHLAUF, and RUDOLF SEUFFERT (*Ber.*, 1911, 44, 3309—3313).—Contrary to the experience of Lassar Cohn and Löwenstein (Abstr., 1908, i, 984), Einhorn and Seuffert find that benzoylsalicylic acid [*o*-benzoyloxybenzoic acid] may be readily prepared by the interaction of benzoyl chloride and salicylic acid in pyridine solution or by the action of benzoyl chloride on sodium salicylate. It crystallises in needles, m. p. 132°. The sodium salt was also analysed. The pyridine method was also found available for the preparation of *o*-isovaleryloxybenzoic acid, m. p. 95°, and of *o*-cinnamoyloxybenzoic acid, m. p. 150—152°.

Einhorn and Rothlauf have prepared *o*-thymylcarbonatobenzoic acid,  $C_6H_3MePr \cdot O \cdot CO \cdot O \cdot C_6H_4 \cdot CO_2H$ , m. p. 118°, by the action of thymolcarbonyl chloride on salicylic acid and dimethylaniline in benzene solution, and *o*-menthylcarbonatobenzoic acid,



m. p. 121·5°, by mixing sodium salicylate and menthylcarbonyl chloride in acetone solution.

None of these compounds gives a coloration with ferric chloride.

H. W.

**$\alpha$ -Chloro- $\beta$ -phenyl-lactic Acid and Phenylacetaldehyde.** BERTHOLD RASSOW and FRITZ BURMEISTER (*J. pr. Chem.*, 1911, [ii], 84, 473—489).—By passing carbon dioxide into an aqueous solution of potassium hypochlorite and potassium cinnamate and subsequently acidifying, the authors obtain crystallised  $\alpha$ -chloro- $\beta$ -phenyl-lactic acid without a trace of oily by-product (compare Erlenmeyer and Lipp, Abstr., 1883, 992). The hydrated acid containing  $H_2O$  has m. p. 56—57°. By keeping over sulphuric acid, it changes to a labile, anhydrous acid, m. p. 86°, which in time is converted into a stable modification, m. p. 102—103°; the last is also obtained by repeatedly crystallising the hydrated acid from dry chloroform. The ammonium salt, m. p. 185° (decomp.), and the aniline salt, m. p. 82°, are described. Phenylacetaldehyde is best obtained by neutralising an aqueous solution of  $\alpha$ -chloro- $\beta$ -phenyl-lactic acid with sodium hydroxide and subsequently heating; it resinifies by keeping, and yields a crystalline substance,  $C_7H_7O$ , m. p. 148°.

C. S.

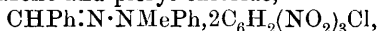
**The Anhydride of Mandelic Acid.** KARL STUTZ (*Ber.*, 1911, 44, 3485—3487. Compare Biedermann, Abstr., 1892, 473; Bischoff and Walden, Abstr., 1894, i, 525; Staudinger, Abstr., 1911, i, 308).—The vitreous amorphous anhydride of mandelic acid can also be obtained by heating the acid with a little sulphuric or hydrochloric acid in the steam-oven; obtained thus, it is soluble in ether, but insoluble in cold water and sodium hydrogen carbonate solution.

Although analysis and the equivalent weight indicate the formula  $C_{22}H_{26}O_9$ , the fact that the action of ammonia yields a larger quantity

of the amide than this formula would indicate leads the author to the opinion that either mandelic acid gives, like salicylic acid, several anhydrides, of which the vitreous substance is a mixture, or that the vitreous product represents the lactide,  $C_8H_6O_2$ , which, on account of its amorphous nature, has not yet been obtained free from water.

D. F. T.

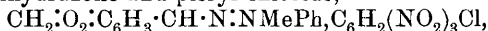
**Additive Products of Derivatives of Trinitrobenzene with Some Nitrogenous Aromatic Substances.** ROBERTO CIUSA and L. VECCHIOTTI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 377—383. Compare Abstr., 1911, i, 810; Sudborough and Beard, *Trans.*, 1910, 97, 773; Ciusa and Agostinelli, *Abstr.*, 1907, i, 553; Ciusa, *Abstr.*, 1906, i, 962).—In addition to the additive products with picryl chloride formerly described, other compounds have now been prepared. Benzaldehyde-*p*-nitrophenylhydrazone and picryl chloride form a *compound*,  $CHPh:N:NH \cdot C_6H_4 \cdot NO_2, 2C_6H_2(NO_2)_3Cl$ , which crystallises in carmine-red needles, m. p.  $132^\circ$ . The *compound* of benzaldehyde-phenylmethylhydrazone and picryl chloride,



crystallises in dark red needles, m. p.  $65^\circ$ . The compound of cinnamaldehydephenylhydrazone and picryl chloride has m. p.  $122-123^\circ$  (formerly given incorrectly by printer's error). The *compound* of *m*-nitrobenzaldehydephenylhydrazone and picryl chloride,



forms dark red needles, m. p.  $98^\circ$ . The *compound* of piperonaldehyde-phenylmethylhydrazone and picryl chloride,



crystallises in black needles with a violet lustre, and has m. p.  $115^\circ$ .

The *compound* of benzaldehydephenylhydrazone with trinitrotoluene,  $CHPh:N:NHPh, 2C_6H_2Me(NO_2)_3$ , forms dark red needles, m. p.  $84^\circ$ .

The *compound* of benzaldehydephenylhydrazone and trinitrophenol,  $CHPh:N:NHPh, 2C_6H_2(NO_2)_3 \cdot OH$ , crystallises in violet-black needles, m. p.  $117^\circ$ .

The *compound* of *o*-nitrobenzaldehydephenylhydrazone with trinitrobenzene,  $NO_2 \cdot C_6H_4 \cdot CH:N:NHPh, C_6H_3(NO_2)_3$ , crystallises in dark red needles, m. p.  $132^\circ$ .

The *compound* of benzaldehydephenyl-*p*-tolylhydrazone with trinitrobenzene,  $CHPh:N:NH \cdot C_6H_4 \cdot Me, 2C_6H_3(NO_2)_3$ , forms lustrous, black scales, m. p.  $142^\circ$ .

The *compound* of cinnamaldehydephenylhydrazone and trinitrobenzene,  $C_{15}H_{14}N_2, 2C_6H_3(NO_2)_3$ , crystallises in reddish-brown needles, m. p.  $167^\circ$ .

The *compound* of *m*-nitrobenzaldehydephenylhydrazone with trinitrobenzene,  $NO_2 \cdot C_6H_4 \cdot CH:N:NHPh, C_6H_3(NO_2)_3$ , forms dark red needles, m. p.  $136^\circ$ .

The *compound* of *m*-nitrobenzaldehydephenylhydrazone and trinitrotoluene,  $NO_2 \cdot C_6H_4 \cdot CH:N:NHPh, C_6H_2(NO_2)_3Me$ , crystallises in red needles, m. p.  $105-106^\circ$ .

The *compound* of *p*-nitrobenzaldehydephenylhydrazone and trinitrobenzene,  $NO_2 \cdot C_6H_4 \cdot CH:N:NHPh, C_6H_3(NO_2)_3$ , forms dark red, lustrous scales, m. p.  $144^\circ$ .

The compound of anisaldehydephenylhydrazone with trinitrobenzene,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH:N}\cdot\text{NHPH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_3$ , crystallises in reddish-brown scales, m. p.  $113^\circ$ .

The compound of piperonaldehydephenylhydrazone and trinitrobenzene,  $\text{CH}_3\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH:N}\cdot\text{NHPH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_3$ , crystallises in almost black needles with a violet lustre, and has m. p.  $147^\circ$ .

The compound of benzaldehyde-*p*-nitrophenylhydrazone and trinitrobenzene,  $\text{CHPh:N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2\cdot\text{C}_6\text{H}_3(\text{NO}_2)_3$ , forms red needles, m. p.  $164\text{--}165^\circ$ .

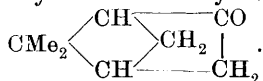
Additive compounds of a very unstable kind were also obtained with trinitrophenol and benzaldehydephenylmethylhydrazone, piperonaldehydephenylmethylhydrazone, and *m*-nitrobenzaldehydephenylmethylhydrazone, as well as from *m*-nitrobenzaldehydemethylhydrazone and picryl chloride.

R. V. S.

**Derivatives of cyclopentanone.** MARCEL GODCHOT and FELIX TABOURY (*Compt. rend.*, 1911, 153, 1010—1011. Compare Abstr., 1911, i, 385).—The ketone prepared by the catalytic hydrogenation of cyclopentanone is shown to be  $\alpha$ -cyclopentylcyclopentanone by the fact that on reduction, it gives  $\alpha$ -cyclopentylcyclopentanol,  $\text{C}_5\text{H}_9\cdot\text{C}_5\text{H}_8\cdot\text{OH}$ , needles, m. p.  $20^\circ$ , b. p.  $125\text{--}126^\circ/15\text{ mm.}$ ; the phenylurethane has m. p.  $88\text{--}89^\circ$ . This substance has also been prepared by acting on cyclopentanone with sodium ethoxide and reducing the resulting compound with alcohol and sodium (Wallach, Abstr., 1896, i, 572).

W. O. W.

**Products of the Dry Distillation of Calcium Pinate.** WALDEMAR BONSDORFF (*Ber.*, 1911, 44, 3208—3210).—Calcium pinate was expected to yield on dry distillation a cyclic ketone,



The actual product was an oil, distilling between  $50^\circ$  and  $100^\circ/8\text{ mm.}$ , which formed a semicarbazone,  $\text{C}_9\text{H}_{15}\text{ON}_3$ , crystallising in colourless plates, and yielded an unsaturated ketone on decomposition, probably

1-isopropylene-2-cyclopentanone,  $\text{CMe}_2\cdot\text{C} \begin{array}{c} \diagup \text{CO-CH}_2 \\ \diagdown \text{CH}_2\cdot\text{CH}_2 \end{array}$ . This is a transparent oil, b. p.  $69\text{--}71^\circ/8\text{ mm.}$ ,  $D_4^{20}$  0.9355,  $n_D$  1.4666. E. F. A.

**Fluorescence in the *p*-Benzoquinone Group.** M. M. RICHTER (*Ber.*, 1911, 44, 3469—3473).—When chloranil and potassium cyanide react in solution in methyl alcohol, there is formed the potassium salt of "cyananilic" acid,  $\text{C}_8\text{O}_4\text{N}_2\text{K}_2$ ; the same substance is obtained when chloranilic acid is used instead of chloranil. These methods of preparation, together with the properties, show the free acid substance to be 2:5-dicyano-3:6-dihydroxy-*p*-benzoquinone. It is a brown solid, which does not crystallise well, and contains two firmly attached molecules of water of crystallisation; on heating, it carbonises without melting. It is a strong acid, and has a feeble quinone-like odour. Towards reducing and hydrolytic agents it is surprisingly stable. It is sparingly soluble in most solvents, but all the solutions show a strong fluorescence, the colour of which varies with the solvent. This fluorescence

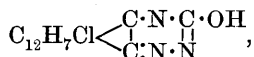
(the first case with a *p*-benzoquinone derivative) leads the author to prefer the peroxide to the diketone structure for this compound (compare Kauffmann, Abstr., 1907, ii, 215). The *ammonium* salt, which exhibits a more beautiful fluorescence than the other salts, is precipitated from solution by concentrated ammonia solution as a dark brown, amorphous powder; the *silver* salt is also brown.

Monochloro-, 2:5-dichloro-, and trichloro-*p*-benzoquinone also react with potassium cyanide, yielding intensely fluorescent solutions; the product from the last-named is probably identical with cyananilic acid. D. F. T.

**Phenanthrene Series. XXXII. Transition from the Phenanthraquinone to the Phenanthrene Series.** JULIUS SCHMIDT and EBERHARD SAUER (*Ber.*, 1911, 44, 3241—3255. Compare Abstr., 1911, i, 626).—When reduced with phosphorus and fuming hydriodic acid at 140°, 3-nitrophenanthraquinone yields two isomeric 3-aminophenanthrene hydriodides, of which the less soluble modification forms lustrous, rhombohedral crystals, m. p. 140°, whilst the more soluble isomeride, which forms the main product, crystallises in slender, white needles, m. p. 244—245°. Both isomerides on treatment with aqueous sodium hydroxide yield the same 3-aminophenanthrene, m. p. 87° (Werner, Abstr., 1902, i, 437).

2:9:10-Trichlorophenanthrene, prepared by heating phenanthraquinone with phosphorus pentachloride at 200°, crystallises in white needles, m. p. 144—145°, and on oxidation with chromium trioxide in aqueous acetic acid solution yields 2-chlorophenanthraquinone. This forms yellowish-red needles, m. p. 252—253°, and reacts with *o*-phenylenediamine hydrochloride in alcoholic solution, yielding 9-chlorophenanthraphenazine,  $\begin{matrix} \text{C}_6\text{H}_3\text{Cl} \cdot \text{C}:\text{N} \\ \text{C}_6\text{H}_4 - \text{C}:\text{N} \end{matrix} > \text{C}_6\text{H}_4$ , crystallising in white leaflets, m. p. 238°; the *oxime*,  $\text{C}_{14}\text{H}_8\text{O}_2\text{NCl}$ , m. p. 170—175°, and *semicarbazone*,  $\text{C}_{15}\text{H}_{10}\text{O}_2\text{N}_3\text{Cl}$ , slender, pale yellow needles, m. p. 220°, are described.

6-Chloro-3-hydroxyphenanthratiazine,  $\text{C}_{12}\text{H}_7\text{Cl} < \begin{matrix} \text{C}:\text{N} \cdot \text{C}:\text{O} \\ \text{C}:\text{N} \cdot \text{NH} \end{matrix}$  or



prepared by the interaction of the preceding oxime and semicarbazide hydrochloride in alcoholic solution, has m. p. 288° (decomp.).

2-Chlorophenanthraquinone is oxidised by potassium dichromate and dilute sulphuric acid to 4-chlorodiphenic acid (Schmidt and Schall, Abstr., 1907 i, 26), which forms a *silver* salt, m. p. 270° (decomp.). When boiled with fuming nitric acid, it yields 2-chlorodinitrophenanthraquinone,  $\begin{matrix} \text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Cl} \cdot \text{CO} \\ \text{NO}_2 \cdot \text{C}_6\text{H}_3 - \text{CO} \end{matrix}$ , which forms lustrous, yellow crystals, m. p. 274°, and is oxidised by potassium dichromate and sulphuric acid to 2-chlorodinitrodiphenic acid,  $\text{C}_{14}\text{H}_7\text{O}_8\text{N}_2\text{Cl}$ , m. p. 269°.

2-Chlorodinitrophenanthraphenazine,  $\begin{matrix} \text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Cl} \cdot \text{C}:\text{N} \\ \text{NO}_2 \cdot \text{C}_6\text{H}_3 - \text{C}:\text{N} \end{matrix} > \text{C}_6\text{H}_4$ , prepared from 2-chlorodinitrophenanthraquinone and *o*-phenylenediamine

hydrochloride in alcoholic solution, forms a white, crystalline powder, m. p. 357°.

The interaction of 9:9-dichloro-10-phenanthrene (Schmidt and Lump, Abstr., 1909, i, 34) or 9-chloro-10-hydroxyphenanthrene and alcoholic potassium sulphide yields *di-9-hydroxy-10-phenanthryl sulphide*,  $\left[ \text{C}_6\text{H}_4 \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{C}(\text{OH}) \end{array} \text{C} \right]_2\text{S}$ . This forms a light brown, crystalline powder, m. p. 223—224° (decomp.); the *dibenzoyl* derivative has m. p. 262—263°.

F. B.

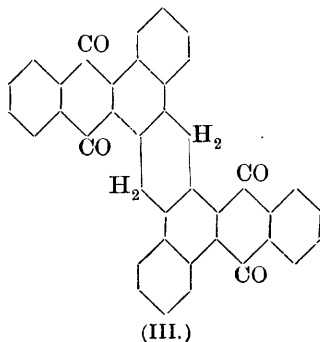
**The Methyl-1:2-benzanthraquinone Group.** I. ROLAND SCHOLL and WALTER TRITSCH (*Monatsh.*, 1911, **32**, 997—1018. Compare Bally and Scholl, Abstr., 1911, i, 676, 1097).—The authors have attempted with partial success to extend the anthraflavone and pyranthrone syntheses to the above group (compare Scholl, Abstr., 1910, i, 271).

*2'-Methyl- $\alpha$ -naphthoylbenzoic acid* and the *4'-methyl* isomeride were obtained by the action of phthalic anhydride and aluminium chloride on 2- and 1-methylnaphthalene respectively; the former product has m. p. 190—191°, and the latter 167—169°.

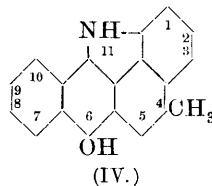
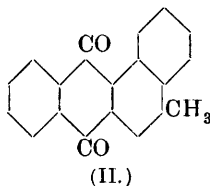
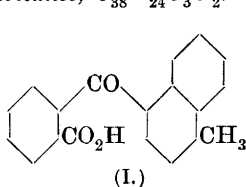
The latter substance (formula I), on reduction with zinc and acetic acid, yields the *lactone* of  $\omega$ -hydroxy- $\omega$ -4'-methyl- $\alpha$ -naphthyl-o-toluic acid, m. p. 163—164°. On the other hand, reduction by sodium hydroxide and zinc dust gives  $\omega$ -4'-methyl- $\alpha$ -naphthyl-o-toluic acid, a white, crystalline substance, m. p. 183—184°; the ammonium salt, unlike that of the parent ketonic acid, is easily soluble in water. The ammonium salt of the ketonic acid, when heated with strong sulphuric acid, condenses to 5-methyl-1:2-benzanthraquinone (formula II), consisting of yellow needles, m. p. 176—177°. By heating the last with alkali and a little anhydrous sodium acetate, simultaneous oxidation and condensation occur, with formation of 1:2:1':2'-dibenzanthraflavone (formula III); this gives orange-red crystals from nitrobenzene; with alkali and sodium hyposulphite it gives a vat which dyes unmordanted cotton yellow.

By careful nitration of 3-methyl-1:2-benzanthraquinone, there is obtained 1-nitro-5-methyl-1:2-benzanthraquinone in yellowish-brown crystals, m. p. 248—251°. Bromination produces 5-bromomethyl-1:2-benzanthraquinone, yellowish-green crystals, m. p. 219—221°, which by methyl-alcoholic potash is also condensed to dibenzanthraflavone (see above). Further bromination gives rise to a pentabromo-5-methyl-1:2-dibenzanthraquinone. Careful nitration of the monobromo-compound yields 1-nitro-5-bromo-methyl-1:2-benzanthraquinone, m. p. 215—225° (decomp.).

If 1-nitro-5-methyl-1:2-benzanthraquinone be reduced by phenylhydrazine there is formed 6-hydroxy-4-methyl-



*dihydroindoloanthrene* (formula IV); this substance, which is green, yields brown solutions. Air oxidises these solutions, giving a violet-brown precipitate of 4-methylindoloanthrone, which remains unmelted even at 360°. The last substance resembles benzoquinone in its behaviour as an oxidising agent, for example, towards phenylhydrazine and sulphurous acid. In certain aqueous solvents two molecules combine with one molecule of water to form a black substance,  $C_{38}H_{24}O_3N_2$ .



D. F. T.

**Determination of Unsaturation in Hydroaromatic Substances.** ISIDOR J. KLIMONT and WILHELM NEUMANN (*Chem. Zentr.*, 1911, 82, ii, 953; from *Pharm. Post*, 44, 587—588).—A decigram of the terpene is dissolved in chloroform, and a known volume of an aqueous solution of potassium bromate (1 mol.) and potassium bromide (5 mols.) is added, followed by sulphuric acid (50%). Potassium iodide is added in known excess, and the iodine liberated is titrated.

T. A. H.

**Catalytic Reactions at High Pressures and Temperatures.** XXIV. **Hydrogenation of the Terpenes.** WLADIMIR IPATIEFF and G. BALATSCHINSKY (*Ber.*, 1911, 44, 3461—3466).—The experiments were carried out with nickel oxide as catalyst, the initial pressure of the hydrogen being 100—130 atmospheres.

In the hydrogenation of the terpene ketones the double linkings add on hydrogen at 220—240°, irrespective of whether they are situated in the nucleus or in the side-chain. The reduction of the carbonyl group takes place at 260—280°; in the menthol series the temperature must not exceed 260°, otherwise menthane is formed. The optical rotation of the compounds produced is all the greater the lower the temperature of hydrogenation.

The above conclusions are drawn from the following experiments: at 280°, carvone gives carvomenthol, from which a mixture of two menthenes was obtained by loss of water in the pressure apparatus at 365°, with alumina as the catalyst. At 220° and 240°, carvomenthone was formed from carvone, the specific rotation of the product being greater at 220° than at 240°. At 280° pulegone gives menthane, but at 220—240° menthone is produced. At 250°, menthone gives menthol on prolonged hydrogenation. Thymol gives *i*-menthol at 260°, m. p. 9°,  $D_{20}$  0.8970,  $n_D$  1.45659.

T. S. P.

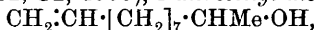
**Action of Nitrosyl Chloride on the Essential Oil of Bupleurum fruticosum.** Nitroso-chlorides. Derivatives and Decomposition Products. Dihydrocuminaldehyde. III. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 388—392. Compare Abstr., 1911, i, 1000).—When the nitroso-

chloride previously described is warmed with 25% acetic acid a vigorous decomposition occurs, accompanied by the evolution of gas, chiefly hydrogen chloride. When the product is distilled with steam the non-volatile portion is a nitrogenous *substance*, m. p. 68°. The part volatile with steam is an oil, a portion of which readily yields a bisulphite compound, and behaves in other respects as an aldehyde. On oxidation with silver oxide, it yields cuminic acid, and is regarded by the authors as a *dihydrocumininaldehyde*. It has the formula  $C_{10}H_{14}O$ , b. p. 136—140°/15 mm.,  $D^{13}_D$  0.9825,  $n_D$  1.5280—1.5305, and is dextrorotatory. The *semicarbazone* crystallises in silvery laminæ, m. p. 197—198°. The *aldazine*,  $(C_{10}H_{14}N)_2$ , forms yellow plates, m. p. 111—112°. The *phenylhydrazone*,  $C_{16}H_{20}N_2$ , has m. p. 123—126°. The *p-bromophenylhydrazone*,  $C_{16}H_{19}N_2Br$ , crystallises in pale yellow laminæ, m. p. 127—129°. The semicarbazone and especially the two hydrazones are phototropic, and all the compounds mentioned are dextrorotatory.

R. V. S.

**Essential Oil of Litsea odorifera Leaves.** PIETER VAN ROMBURGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 325—327).—The oil, known as “trawas oil” in Java, has  $D^{15}_D$  0.836—0.846,  $\alpha_D$  -10' to -7° in a 20 cm. tube, and boils mostly at 120—125°/10 mm. pressure or at 233°/760 mm.; it is pale yellow and possesses a disagreeable odour.

The oil contains *l*-methyl-*n*-nonylcarbinol,  $\alpha_D$  -5°40' (compare Power and Lees, *Trans.*, 1902, 81, 1593), *l*-undecenyl alcohol,



$D^{10}_D$  0.835, b. p. 233°,  $\alpha_D$  -5°10', and *undecenone*,  $CH_2:CH[CH_2]_7\cdot COMe$ , m. p. -7°, b. p. 235°,  $D^{11.5}_D$  0.848,  $MR=52.47$  (calc. for  $C_{11}H_{20}O=52.51$ ), which yields a *semicarbazone*, m. p. 116°, and a *di bromide*, b. p. 204°/15 mm. From the latter the unsaturated ketone can be recovered by treatment with zinc dust and alcohol.

T. A. H.

**Essential Oil of Santolina chamæcyparissus. III. Formula of Santolinone,  $C_{10}H_{16}O$ .** LUIGI FRANCESCONI and P. SCARAFIA (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 383—387. Compare *Abstr.*, 1911, i, 1001).—The authors discuss the constitution of the ketone,  $C_{10}H_{16}O$ , obtained from this essential oil, and assign to it the formula of  $\Delta^{1:7}$ -menthene-2-one.

R. V. S.

**Fresh Dammar Resin from Central Borneo.** EM. GOTTLIEB (*Arch. Pharm.*, 1911, 249, 701—705).—This variety of dammar is known in Borneo as “Dammar Daging,” and is possibly derived from *Retinodendron Rassak*. The figures in brackets give the percentage of the material dissolved by the solvents named: alcohol (82), methyl alcohol (70), acetone (60), chloroform (18). The resin had the following constants: acid number, direct, 140.0—142.0, indirect, 148.4—151.2; saponification value, cold, 159.6—162.4, hot, 163.5—165.2.

The portion soluble in ether yielded in turn to (a) sodium carbonate solution (1%), *dagingolic acid*,  $C_{24}H_{44}O_4$ , m. p.  $170^\circ$ , and (b) potassium hydroxide solution (1%), *digingolic acid*,  $C_{13}H_{26}O_3$ , m. p.  $125-126^\circ$ . The residue, freed from ether, yielded on steam distillation an essential oil and *dagingoresen*,  $C_{22}H_{28}O$ . The two acids and the resen give phytosterol-like colour reactions with the usual reagents. T. A. H.

**Recent Fossil Dammar Resin from Central Borneo.** EM. GOTTLIEB (*Arch. Pharm.*, 1911, 249, 705—710).—The following figures give the percentage solubilities of the resin in the solvents named: ether (65), acetone (40), turpentine oil (35), alcohol (28).

The portion soluble in ether yielded to (a) ammonium carbonate solution (1%), a resin acid,  $C_{16}H_{26}O_2$ , m. p.  $135^\circ$ , (b) sodium carbonate solution (1%), a resin acid,  $C_{14}H_{22}O_2$ , m. p.  $103-105^\circ$ , (c) potassium hydroxide solution (1%), a resin acid,  $C_{12}H_{18}O_2$ , m. p.  $120-122^\circ$ , and the residue on steam distillation furnished essential oil and an impure *resen*.

The portion insoluble in ether was dissolved, in part, on further addition of alcohol, and from this, by means of potassium hydroxide solution, a *substance*,  $C_{12}H_{22}O$ , was obtained, leaving a *resen*,  $C_{12}H_{22}O_2$ . The three acids and the resene all gave phytosterol-like colour reactions. The resin contained a bassorin-like substance. T. A. H.

**Decomposition of Gynocardin by the Enzyme of the Leaves of Pangium edule.** ANNE W. K. DE JONG (*Rec. trav. chim.*, 1911, 30, 220—221).—Gynocardin is decomposed at the ordinary temperature by the enzyme, giving dextrose and a *compound*,  $C_6H_8O_4$ , according to the equation:  $C_{18}H_{19}O_9N + H_2O = C_6H_{12}O_6 + HCN + C_6H_8O_4$ . This substance,  $C_6H_8O_4$ , is a diketone, and yields a *phenylhydrazone*, which decomposes at  $177^\circ$ .

If the fermentation takes place in a closed vessel, and the quantities of hydrogen cyanide and the diketone formed are estimated from time to time, the yields are a maximum after four hours, and then they diminish proportionately. The specific rotatory power also diminishes with the duration of the reaction. W. G.

**Saponins.** ERNST WINTERSTEIN and H. BLAU (*Zeitsch. physiol. Chem.*, 1911, 75, 410—442).—Saponin prepared from *Sapindus utilis* forms, on hydrolysis with sulphuric acid, lævulose, arabinose, and rhamnose; dextrose and galactose do not appear to be formed. Lævulose is split off by dilute mineral acids at low temperatures, and also a small quantity of an amorphous product which, by the action of stronger acids at higher temperatures, produces arabinose and rhamnose. This amorphous substance, "pentoside," still belongs to the group of the glucosides, and differs from saponin by being insoluble in water, and its great solubility in alcohol. Its decomposition by strong acids into arabinose and rhamnose is accompanied by the formation of a crystalline compound, to which the formula  $C_{18}H_{28}O_3$  has been given. This is the true sapogenin; it gives, on distillation

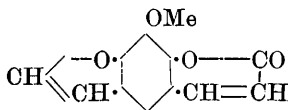
with zinc dust, higher hydrocarbons, and also a gas which consists partly of butylene.

Sapogenin forms a monomethyl and monoacetyl compound. By acetylation saponin is greatly affected in its chemical constitution and physiological action.

Saponin from horse chestnut gives, on hydrolysis, sapogenin, arabinose, dextrose, and lævulose.

H. B. H.

**The Constitution of Xanthotoxin and its Relationship to Bergaptene.** HERMANN THOMS [with HANS PREIS] (*Ber.*, 1911, 44, 3325—3332).—Two crystalline substances have been isolated from the residue left after the steam distillation of the fruit of *Fagara Xanthoxyloides*. One of these, m. p. 190—191°, has been shown to be identical with bergapten obtained from oil of bergamot. The second substance, *xanthotoxin*,  $C_{12}H_8O_4$ , has m. p. 145—146°. On nitration in acetic acid solution, xanthotoxin yields *nitroxanthotoxin*,  $C_{12}H_7O_6N$ , m. p. 233°, whilst, when treated with methyl iodide in methyl-alcoholic alkaline solution, it becomes transformed into *methyl-xanthotoxic acid*,  $C_{12}H_{11}O_3 \cdot CO_2H$ , m. p. 114—117°, and *methyl methylxanthotoxate*, m. p. 44°. When fused with potassium



hydroxide, xanthotoxin yields pyrogallolcarboxylic acid. From these experiments the annexed formula is proposed. A pharmacological comparison of the effect of xanthotoxin and bergapten on fishes shows the former to be the more powerful poison.

H. W.

**Chlorophyll. XVII. Absorption Spectra of the Components and of the Primary Derivatives of Chlorophyll.** RICHARD WILLSTÄTTER, ARTHUR STOLL, and MAX UTZINGER (*Annalen*, 1911, 385, 156—188).—The absorption spectra of the following substances in ether (0.03—0.04 gram per litre) have been measured: chlorophyll *a* and *b*, methylchlorophyllide *a* and *b*, phæophytin *a* and *b*, methylphæophorbide *a* and *b*, phytochlorin *e* and *f*, and phytorhodin *g*. The authors find that chemical methods are more sensitive than spectrum analysis for the examination of chlorophyll derivatives; thus the presence of a little chlorophyll *a* in chlorophyll *b*, or vice versa, cannot be detected by the spectrometer, neither are the changes through which chlorophyll passes in its conversion into the feebly basic products of hydrolysis betrayed by the absorption spectra; phytochlorin *e* and *f* show almost identical spectra in spite of their great chemical dissimilarity.

The absorption spectra of chlorophyll *a* and *b* respectively exhibit very slight differences from those of the methylchlorophyllides *a* and *b*. The same is true for the magnesium-free derivatives of the four substances, namely, the phæophytins *a* and *b* and the methylphæophorbides *a* and *b*. Willstätter and Benz's crystallised chlorophyll (*Abstr.*, 1908, i, 199) is a mixture of ethylchlorophyllides *a* and *b*, rich in the former.

The absorption bands in the spectrum of phytochlorin *e* show, in intensity, breadth, and position, a remarkable similarity to those in

the spectrum of phæophytin *a*; also the comparatively simple spectrum of phytorhodin *g* is nearly related to the far more complicated spectrum of phæophytin *b*, or of methylphæophorbide *b*. These similarities are very remarkable when the differences in the compositions of the substances are considered. The absorption spectra of phytochlorin *e*, phytorhodin *g*, and isochlorophyllins *a* and *b* (Abstr., 1911, i, 659) in dilute methyl-alcoholic potassium hydroxide are described, and the constitutions of chlorophyll derivatives containing potassium, zinc, iron, or copper in place of the magnesium of the natural product are discussed. C. S.

**Chlorophyll. XVIII. Reduction of Chlorophyll.** RICHARD WILLSTÄTTER and YASUHIKO ASAHINA (*Annalen*, 1911, 385, 188—225).—Malarski and Marchlewski have shown that chlorophyll-pyrrole and hæmopyrrole yield identical azo-compounds with diazonium salts (Abstr., 1910, i, 692). With the primary object of comparing these two pyrroles, the authors have reduced (i) hæmin by hydriodic acid, D 1·96, and phosphonium iodide by a modification of Nencki and Zaleski's method, (ii) hæmatoporphyrin by Piloty's method (Abstr., 1909, i, 539), and (iii) various chlorophyll derivatives (phytochlorins, phytorhodins, ethylchlorophyllides *a* and *b*, but best of all, phylloporphyrin) by both methods. In each case the reduction products are basified by sodium carbonate and distilled with steam, and the ethereal extract of the bases is freed quantitatively from pyrrolines and pyrrolidines by sodium dihydrogen phosphate, and is finally separated into three substances, hæmopyrrole, isohæmopyrrole, and phyllopyrrole, by fractional salt-formation with ethereal picric acid (compare this vol. i, 50, 56).

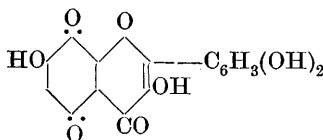
*Hæmopyrrole*,  $\text{NH} \begin{smallmatrix} \text{CMe}:\text{CEt} \\ | \\ \text{CH}=\text{CMe} \end{smallmatrix}$ , b. p. 198°/730 mm. or 86—87°/12 mm.,  $D_4^{20}$  0·930, and  $D_4^{20}$  0·918, which resembles most closely the "hæmopyrrole" of the literature, is a colourless liquid, which resinifies rapidly in the air, and responds to the pine-shaving and to Ehrlich's dimethylaminobenzaldehyde tests for pyrroles; it forms a *picrate*, m. p. 111° (corr.), *chloropicrate*, m. p. 123° (decomp.), and *styphnate*,  $\text{C}_8\text{H}_{13}\text{N}, \text{C}_6\text{H}_3\text{O}_3\text{N}_3$ , m. p. 120—121° (decomp.) (styphnic acid forms with pyrroles salts which are better suited than the picrolonates for the identification of the bases, on account of their stability, sparing solubility, and crystallisability), and reacts with nitrous acid to form an *oxime*, m. p. 201°, of methylethylmaleinimide.

*isoHæmopyrrole*,  $\text{NH} \begin{smallmatrix} \text{CMe}:\text{CMe} \\ | \\ \text{CH}=\text{CEt} \end{smallmatrix}$ , m. p. 16—17°, b. p. 198°/725 mm. or 88°/11—12 mm.,  $D_4^{20}$  0·915, is a colourless liquid with a characteristic odour. It exhibits the colour reactions of pyrroles, reddens and resinifies in the air, and forms a *picrate*, m. p. 119°, *chloropicrate*, m. p. 126°, and *styphnate*, m. p. 136°, decomp. 140°. With nitrous acid it forms an *oxime*, m. p. 221—222° (corr.), of methylethylmaleinimide. It is reduced by hydriodic acid and phosphorus at 240° to a mixture of the pyrroline and the pyrrolidine, which is completely reduced by hydrogen and platinum to *isohaemo-*

*pyrrolidine*,  $C_8H_{17}N$ , b. p. 155—156°/730 mm.,  $D_4^{20}$  0·845,  $D_4^{20}$  0·830 (*platinichloride*, m. p. 191—192°;  *$\alpha$ -naphthylcarbamide*, m. p. 138°).

*Phyllopyrrole*,  $NH \begin{smallmatrix} CMe:CMe \\ CMe:CEt \end{smallmatrix}$ , m. p. 63°, b. p. 213°/725 mm. or 92—93°/12 mm. (m. p. 66—67°, b. p. 88—90°/10 mm., when obtained from chlorophyll derivatives), white leaflets, resinifies rapidly in the air, and does not react with a pine-shaving or dimethylaminobenzaldehyde or with mercuric chloride. It forms a *picrate*, m. p. 95°, and yields by reduction (as above) *phyllopyrrolidine*,  $C_8H_{17}N$ , b. p. 160—164°,  $D_4^{20}$  0·824 ( *$\alpha$ -naphthylcarbamide*, m. p. 145°). C. S.

**Anthocyanins. I. An Anthocyanin-like Oxidation Product of Quercetin.** MAXIMILIAN NIERENSTEIN and MURIEL WHELDALÉ (*Ber.*, 1911, 44, 3487—3491. Compare this vol., ii, 80).—The red, violet and blue colouring matters of flowers are regarded as oxidation products of the tannins; they are also related to the yellow plant



dyes. On oxidation of quercetin with chromic acid in acetic acid solution, *quercetone* (annexed formula), crystallising in small, deep red needles, m. p. above 360°, is obtained. Like anthocyanin, it dissolves in alkali hydroxides with a blue, and in concentrated sulphuric acid with a red, coloration.

It could not be methylated or acetylated; the *tetrabenzoylquercetone*, prepared by the action of benzoyl chloride on quercetone dissolved in a mixture of quinoline and pyridine, crystallises in small, pointed needles, m. p. 281—283°. On fusion of quercetone with alkali, protocathechuic acid was obtained.

When heated with acetic anhydride and zinc dust, acetylated *hydroxyquercetin* is obtained as a colourless, amorphous powder, yielding on hydrolysis 1:3:4:3':4'-*pentahydroxyflavonol* (annexed formula). This crystallises in small, yellow, microscopic needles, which lose a molecule of water at

160°, m. p. 352—355°. Both alkali hydroxides and sulphuric acid dissolve it with a yellow coloration. 1:3:4:3':4'-*Pentamethoxyflavonol* forms small, colourless needles, which sinter at 136—138°, m. p. 147—149°. It is probably converted into veratric acid when heated with alcoholic potassium hydroxide at 170°. E. F. A.

**Melanins.** MAURICE PIETTRE (*Compt. rend.*, 1911, 153, 1037—1040. Compare Abstr., 1911, ii, 1006).—The melanin from *Sepia officinalis* on hydrolysis with sulphuric acid gives tyrosine, leucine, amorphous amino-acids, and an insoluble pigment. After alkali hydrolysis, alanine and amorphous amino-acids are obtained, together with a pigment which is readily soluble in alkalis. Artificial melanin, prepared by the action of *Russula* extract on tyrosine, gave no tyrosine on hydrolysis; leucine, however, was recognised amongst the products. The two melanins, therefore, resemble those already

examined, in containing a protein group united to a pigment. The name *melanin* is suggested for the latter substance. W. O. W.

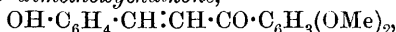
**The Composition of Tannin.** LEO F. ILJIN (*Ber.*, 1911, **44**, 3318—3319).—The author points out that the hygroscopic nature of tannin may account for the differences in the analytical results obtained by him and by Steinkopf and Sargarian (*Abstr.*, 1911, i, 1004). He quotes an experiment which shows the great readiness with which moisture is absorbed by tannin. H. W.

**Carboxonium Compounds.** FRIEDRICH KEHRMANN and JOSEPH KNOP (*Ber.*, 1911, **44**, 3505—3513).—The reaction between ethereal magnesium phenyl bromide and 3:6-dimethylxanthone in benzene leads ultimately to the formation of 9-phenyl-3:6-dimethylxanth-hydrol,  $C_6H_3Me \left\langle \begin{array}{c} CPh(OH) \\ O \end{array} \right\rangle C_6H_3Me$ , m. p. 152° (corr.). The fact that this substance forms an anhydrous, blackish-green, crystalline *iodide*,  $C_{21}H_{17}OI$  (and also the corresponding *bromide* and *chloride*), which is remarkably stable in the presence of water, is regarded as additional evidence that such coloured halides are oxonium salts, not quinonoid carbonium salts, as stated by Gomberg and Cone (*Abstr.*, 1910, i, 55). Still more stable is the *chloride* of methyl 9-phenyl-3:6-dimethylxanthonium-o-carboxylate,  $CO_2Me \cdot C_6H_4 \cdot C \left\langle \begin{array}{c} C_6H_3Me \\ C_6H_3Me \end{array} \right\rangle O \cdot Cl$ , orange-yellow needles, which is prepared by saturating a cold methyl-alcoholic solution of 3:6 dimethylfluoran with hydrogen chloride; the corresponding *bromide*, *iodide*, and *platinichloride* are described, as also are the *chloride*, *bromide*, and *platinichloride* of the corresponding *ethyl* ester.

9-Phenyl-2:7-dimethylxanth-hydrol, obtained by the oxidation of 9-phenyl-2:7-dimethylxanthene, forms oxonium salts, which are redder than those of the preceding isomeride, and are completely hydrolysed by water; the *ferrichloride*,  $C_{21}H_{17}OCl \cdot FeCl_3$ , crystallises in orange-red prisms. C. S.

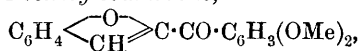
**Studies in the Coumarone Group.** JOSEF TAMBOR [with S. GÜNSBURG, O. KELLER, CHANSCHY-HERZENBERG, B. ROSENKNOPF, and J. LICHENTENBAUM] (*Ber.*, 1911, **44**, 3215—3223).—Alkyl ethers of 1-hydroxybenzoylcoumarone are obtained (1) by the action of alcoholic potassium hydroxide on *o*-acetoxychalkone dibromides; (2) by the interaction of coumarilyl chloride with phenol ethers and aluminium chloride (Zwayer and Kostanecki, *Abstr.*, 1908, i, 443), and (3) by the condensation of salicylaldehyde with  $\alpha$ -bromoacetophenone in alcoholic alkaline solution. A number of substituted 1-benzoylcoumarone derivatives have been prepared by these methods.

2-Hydroxy-2':5'-dimethoxychalkone,



from quinacetophenone dimethyl ether and salicylaldehyde, crystallises in orange prisms, m. p. 119.5°. Neither the acetate nor the dibromide is crystalline.

## 2' : 5'-Dimethoxy-1-benzoylcoumarone,



crystallises in yellow plates, m. p. 98°, which when moistened with concentrated sulphuric acid become dark red, and give an orange solution. The *phenylhydrazone* crystallises in slender needles, m. p. 161°.

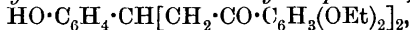
$\alpha$ -Bromo-3 : 5-dimethoxyacetophenone,  $\text{C}_6\text{H}_3(\text{OMe})_2 \cdot \text{CO} \cdot \text{CH}_2\text{Br}$ , from quinol dimethyl ether, bromoacetyl bromide, and aluminium chloride, crystallises in colourless needles, m. p. 91°. It condenses with salicylic aldehyde to form dimethoxybenzoylcoumarone.

2' : 4'-Diethoxy-1-benzoylcoumarone, from resorcinol diethyl ether and coumarilyl chloride, crystallises in almost colourless prisms, m. p. 87°. The crystals are coloured orange by concentrated sulphuric acid.

2-Hydroxy-2' : 4'-diethoxychalkone crystallises from dilute alcohol in greenish-yellow prisms, and from concentrated alcohol in sulphur-yellow needles, m. p. 164° (decomp. and green coloration) in each case. With concentrated sulphuric acid, the crystals become yellow.

2-Acetoxy-2' : 4'-diethoxychalkone forms small, colourless needles, m. p. 69°.

## 2-Hydroxybenzylidene-bis-2' : 4'-diethoxyacetophenone,

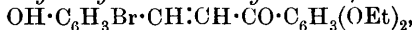


from salicylaldehyde and resacetophenone diethyl ether, separates in greenish-yellow needles, m. p. 75°.

On bromination of 2-acetoxydiethoxychalkone, 2-acetoxy-2' : 4'-diethoxy-5'-bromochalkone dibromide is obtained in colourless prisms, m. p. 139°.

5'-Bromo-2' : 4'-diethoxy-1-benzoylcoumarone, obtained by the action of potassium hydroxide on the foregoing and also on brominating diethoxybenzoylcoumarone, crystallises in colourless prisms, m. p. 143°.

Resacetophenone diethyl ether and 5-bromosalicylaldehyde condense to form 5-bromo-2-hydroxy-2' : 4'-diethoxychalkone,



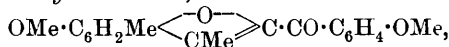
which crystallises in lustrous, yellow needles, m. p. 175° (decomp.). The *acetyl* derivative forms lustrous, light yellow needles, m. p. 112°.

5-Bromo-2-acetoxy-2' : 4'-diethoxychalkone dibromide gives colourless, rhombohedral crystals, m. p. 147°.

5-Bromo-2' : 4'-diethoxy-1-benzoylcoumarone forms colourless, rhombohedral crystals, m. p. 126°, which are coloured red by concentrated sulphuric acid; the compound is totally different from the isomeric 5'-bromo-derivative just described.

5-Methoxy-2 : 3-dimethylcoumarilyl chloride forms faintly green-coloured needles, m. p. 137°.

Condensed with anisole and aluminium chloride, 5 : 4'-dimethoxy-1-benzoyl-2 : 3-dimethylcoumarone,



yields lustrous, colourless needles, m. p. 145°.

5 : 3' : 4'-Trimethoxy-1-benzoyl-2 : 3-dimethylcoumarone forms lustrous, colourless needles, m. p. 156°.

5 : 2' : 4'-Trimethoxy-1-benzoyl-2 : 3-dimethylcoumarone crystallises in yellow needles, m. p. 115°.

5 : 2' : 5'-Trimethoxy-1-benzoyl-2 : 3-dimethylcoumarone separates in yellow cubes, m. p. 135°.

5 : 2' : 4' : 6'-Tetramethoxy-1-benzoyl-2 : 3-dimethylcoumarone crystallises in well-formed, yellow, prismatic columns, m. p. 196—197°.

5 : 2' : 3' : 4'-Tetramethoxy-1-benzoyl-2 : 3-dimethoxycoumarone forms slender, yellow needles, m. p. 158°.

5-Methoxy-2-methylcoumarilic chloride forms green needles, m. p. 104—105°. It has been condensed with phenol methyl ethers to form the following compounds :

5 : 4'-Dimethoxy-1-benzoyl-2-methylcoumarone forms pale yellow platelets, m. p. 140°.

5 : 3' : 4'-Trimethoxy-1-benzoyl-2-methylcoumarone crystallises in small, colourless platelets, m. p. 153—154°.

5 : 2' : 4' : 6'-Tetramethoxy-1-benzoyl-2-methylcoumarone crystallises in dark yellow, microscopic plates, m. p. 178°.

5 : 2' : 3' : 4'-Tetramethoxy-1-benzoyl-2-methylcoumarone forms pale yellow, clearly-defined needles, m. p. 72—73°.

These compounds are all coloured red by concentrated sulphuric acid. E. F. A.

Interaction of Homologous Phenols with Methylcoumaric Acid Dibromide. II. RICHARD STOERMER and C. FRIEMEL (*Ber.*, 1911, 44, 3256—3266).—In continuation of previous work (*Abstr.*, 1911, i, 632), the authors have studied the interaction of methylcoumaric (*o*-methoxycinnamic) acid dibromide and *m*-cresol. When equal parts of these substances are heated for ten minutes on the water-bath, the following products are obtained : (1)  $\beta$ -*o*-methoxyphenyl- $\alpha\beta$ -*di-p*-hydroxy-*o*-tolylpropionic acid,

$\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{C}_6\text{H}_3\text{Me} \cdot \text{OH}) \cdot \text{CH}(\text{C}_6\text{H}_3\text{Me} \cdot \text{OH}) \cdot \text{CO}_2\text{H}$ , which crystallises from dilute acetone in colourless needles, m. p. 274°, and yields a *methyl* ester, crystallising in small columns, m. p. 225°; the *di-p*-nitrobenzoyl derivative,  $\text{C}_{39}\text{H}_{32}\text{O}_{11}\text{N}_2$ , forms light yellow, rhombic plates, m. p. 216°. (2) 4-*o*-Methoxyphenyl-7-methylcoumarin,

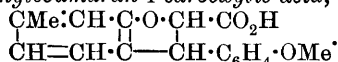
$$\text{CMe} : \text{CH} : \text{C} \begin{array}{c} \text{O} \\ | \end{array} \text{CO} \\ \text{CH} = \text{CH} : \text{C} \begin{array}{c} | \\ \text{C}(\text{C}_6\text{H}_4 \cdot \text{OMe}) \end{array} : \text{CH}$$

which crystallises from glacial acetic acid in rhombic columns, m. p. 220°, and is also obtained by the removal of hydrogen bromide from the compound (3) described below by means of quinoline. (3) 3-Bromo-4-*o*-methoxyphenyl-7-methyl-

hydrocoumarin,

$$\text{CMe} : \text{CH} : \text{C} \begin{array}{c} \text{O} \\ | \end{array} \text{CO} \\ \text{CH} = \text{CH} : \text{C} \begin{array}{c} | \\ \text{CH}(\text{C}_6\text{H}_4 \cdot \text{OMe}) \end{array} : \text{CHBr}$$

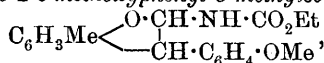
which crystallises in rectangular plates, m. p. 123°, and, when heated with strong aqueous sodium hydroxide, loses hydrogen bromide, yielding 2-*o*-methoxyphenyl-5-methylcoumaran-1-carboxylic acid,



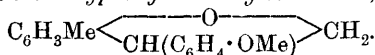
This crystallises in rhombic platelets, m. p. 199°, having a pale blue fluorescence, and yields a sparingly soluble, yellow sodium salt; the piperidide,  $\text{C}_{22}\text{H}_{25}\text{O}_3\text{N}$ , forms slender, colourless columns, m. p.

148—149°; the *methyl* ester crystallises in hexagonal plates, m. p. 75°. The *hydrazide*, prepared by heating the methyl ester with hydrazine hydrate in alcoholic solution, has m. p. 110°, and yields the corresponding *azoimide* when treated with sodium nitrite in aqueous acetic acid solution.

1-*Carbethoxyamino*-2-*o*-methoxyphenyl-5-methylcoumaran,

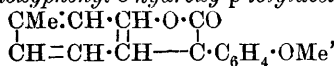


obtained by boiling an alcoholic solution of the azoimide, crystallises in very thin, colourless leaflets, m. p. 143—144°, and is converted on heating with concentrated hydrochloric acid and alcohol into 2-*o*-methoxyphenyl-5-methylcoumarone,  $\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \diagup \text{O} \\ \diagdown \text{C}(\text{C}_6\text{H}_4 \cdot \text{OMe}) \end{array} \text{CH}$ , which is an oil, b. p. 220—223°/25 mm., gives an intense orange-red coloration with sulphuric acid, and, on reduction with sodium in alcoholic solution, yields 2-*o*-methoxyphenyl-5-methylcoumaran,



This crystallises from alcohol in lustrous, silky needles, having a pale blue fluorescence, m. p. 96—97°.

The constitution of the two last-mentioned compounds has been established by their synthesis from *o*-methoxymandelonitrile and *m*-cresol. When heated with sulphuric acid, these condense to form the *lactone* of *o*-methoxyphenyl-*o*-hydroxy-*p*-tolylacetic acid,



which has m. p. 116—119°, and is converted into 2-*o*-methoxyphenyl-5-methylcoumarone by heating with phosphorus pentasulphide.

F. B.

**Corydalis Alkaloids. XI. Corytuberine.** JOHANNES GADAMER (*Arch. Pharm.*, 1911, 249, 641—669. Compare Dobbie and Lauder, *Trans.*, 1893, 63, 485; Gadamer and Wagner, *Abstr.*, 1902, i, 391; Schmidt, *Abstr.*, 1909, ii, 85, and Gadamer, *Abstr.*, 1911, i, 1011, 1012).—A general discussion of the constitutions and relationships of the corytuberine group of alkaloids has been given already (*Abstr.*, 1911, i, 1011), and in the present paper the experimental data on which the formula then assigned to corytuberine was based are given.

The alkaloid is best obtained by distilling the alcohol from an alcoholic extract of *Corydalis* roots, dissolving the residue in water, so that the aqueous mixture weighs twice as much as the weight of roots used, filtering, adding ammonia solution in very slight excess to the filtrate, shaking rapidly with ether, and removing the separated aqueous layer as quickly as possible. The aqueous liquid so treated continues to deposit impure crystals of corytuberine for several days. This may be purified by fractional precipitation by ammonia solution from the hydrochloride, washing with water, alcohol, and ether in turn, and finally recrystallising from boiling water. The alkaloid has the formula  $\text{C}_{19}\text{H}_{21}\text{O}_4\text{N}, 5\text{H}_2\text{O}$  (compare *loc. cit.*).

With benzoyl chloride, by the Schotten-Baumann method, it furnishes a crystalline *monobenzoyl* derivative, m. p. 211—214°,  $[\alpha]_D^{20} + 151.5^\circ$  in chloroform, and a *dibenzoyl* derivative, m. p. 135—140°,  $[\alpha]_D^{20} + 128.8$ —133.5° in chloroform, which is amorphous, but yields a crystalline *hydrochloride*. On boiling with benzoyl chloride a *tribenzoyl* (possibly *tetrabenzoyl*) derivative, m. p. 140—142° (approx.),  $[\alpha]_D^{20} = 0^\circ$ , crystallising in glandular masses of crystals, is formed.

On methylation with methyl sulphate by Pschorr and Karo's method (Abstr., 1906, i, 878), a mixture of two methylcorytuberine methosulphates with some corytuberine methosulphate is produced. With diazomethane a mixture of two methylcorytuberines with two methylcorytuberine methylhydroxides is formed. One of the methylcorytuberines is identical with corydine (see following abstract), and the other has been named *isocorydine* (*loc. cit.*). When diazomethane is generated in presence of corytuberine suspended in *isoamyl* ether, *dimethylcorytuberine* is produced; the *acid l-tartrate*, m. p. 219—224° (decomp.),  $[\alpha]_D^{20} + 150^\circ$  in water, crystallises in groups of needles. By applying methyl sulphate in excess to methylcorytuberine methosulphate and neutralising the solution from time to time as it becomes acid, complete methylation of the alkaloid was eventually secured, and from the *dimethylcorytuberine methosulphate* formed, a small amount of the corresponding *methochloride* was prepared; it crystallises as needles, m. p. 234—237° (decomp.),  $[\alpha]_D^{20} + 197.4^\circ$  in water, and gives an *aureochloride*, m. p. 160° (decomp.). The crude methosulphate on treatment with alkali gives *dimethylcorytuberimethine*,  $C_{22}H_{27}O_4N$ , the *hydrochloride* of which is crystalline and optically inactive. The methine base forms a *methiodide*, which melts above 260°, and a *methosulphate* (yellow needles); the latter, on treatment with alkali, furnishes trimethylamine and 3:4:5:6-*tetramethoxy-8-vinylphenanthrene*, m. p. 69°, which on bromination in chloroform yields a *pentabromo-derivative*,  $C_{20}H_{17}O_4Br_5$ , m. p. 175—178°, and a *hexabromo-compound*,  $C_{20}H_{16}O_4Br_6$ , m. p. 185° (decomp.); the latter, on recrystallisation from acetic acid, gives a *pentabromo-derivative*,  $C_{20}H_{17}O_4Br_5$ , m. p. 185° (decomp.). On distillation with zinc dust, *tetramethoxyvinylphenanthrene* yields  $\alpha$ -ethylphenanthrene (Pschorr and Karo, *loc. cit.*), and on oxidation with permanganate in acetone gives 3:4:5:6-*tetramethoxyphenanthrene-8-carboxylic acid*, m. p. 165—167°, crystallising in leaflets from alcohol, along with a small amount of a neutral substance, which is probably the corresponding glycol (compare Pschorr and Karo, *loc. cit.*).  
T. A. H.

**Corydalis Alkaloids. XII. Corydine. *iso*Corydine.** JOHANNES GADAMER (*Arch. Pharm.*, 1911, 249, 669—680).—In part IX of this series of papers (Abstr., 1911, i, 1011), formulæ for corydine and *isocorydine* were given, based on the fact that they are monomethyl ethers of corytuberine, and are produced by the methylation of the latter alkaloid with diazomethane (see preceding abstract). In this paper the experimental details of this work are given. In a previous paper (Abstr., 1902, i, 391) the formula  $C_{21}H_{23}O_4N$  or  $C_{21}H_{25}O_4N$

was assigned to corydine, but this is untenable in view of its relationship to corytuberine. New analyses of natural and synthetic corydine give results in agreement with the formula  $C_{20}H_{23}O_4N$ . When crystallised from alcohol, corydine contains  $\frac{1}{2}EtOH$ , and then melts at  $124-125^\circ$ ; on exposure in a vacuum desiccator and recrystallisation from ether, it melts at  $149^\circ$ . These two kinds of crystals are identical in form both for synthetic and natural corydine [ $a:c=1:0.39896$ ]. On treatment with methyl iodide in the cold, corydine gives a *methiodide*, m. p.  $190-191^\circ$ ,  $[\alpha]_D^{20} +157.3^\circ$  in 50% alcohol, crystallising in slender, voluminous needles with  $1\frac{1}{2}H_2O$ . If the mixture is heated, the methiodide formed has m. p. over  $200^\circ$ ,  $[\alpha]_D^{20} +154.6^\circ$ , and forms compact crystals with  $1\frac{1}{2}H_2O$ .

On treatment with iodine in alcohol, corydine furnishes *dehydrocorydine hydriodide*,  $C_{20}H_{19}O_4N, HI$ , which separates from water in yellow, compact crystals and gives a red coloration, and eventually a flocculent, red precipitate, with solutions of sodium hydroxide. On reduction with zinc and dilute sulphuric acid, it gives *dl-corydine*, m. p.  $165-167^\circ$ , which is somewhat less soluble in ether than the optically-active forms. The acid *d*-tartrate, on crystallisation from water, deposits *l-corydine hydrogen d-tartrate*, from which *l-corydine*,  $[\alpha]_D^{20} -206.2^\circ$  in chloroform, was prepared.

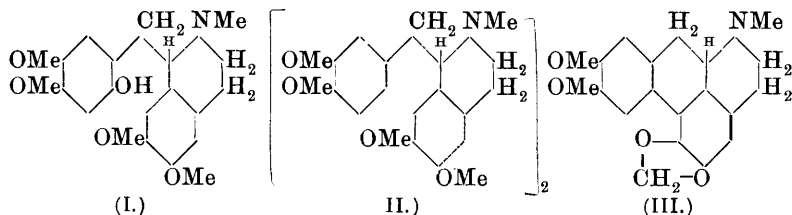
*isoCorydine*,  $C_{20}H_{23}O_4N$ , m. p.  $185^\circ$ ,  $[\alpha]_D^{20} +195.3^\circ$  in chloroform, prepared as described already (see preceding abstract), crystallises in glistening, four-sided tablets, and is less soluble in ether than corydine. In its colour reactions it resembles bulbocapnine rather than corydine. The *methiodide*, m. p.  $213-214^\circ$  (decomp.),  $[\alpha]_D^{20} +143.3^\circ$ , is crystalline, and, unlike the corresponding corydine derivative, is sparingly soluble in water. On treatment with iodine in alcohol, *isocorydine* gives a greenish-black product.

T. A. H.

**Corydalis Alkaloids. XIII. Glaucine Sub-group.** JOHANNES GADAMER (*Arch. Pharm.*, 1911, 249, 680-701).—Pschorr has described (*Abstr.*, 1904, i, 612) the synthesis of phenanthreno-*N*-methyltetrahydropapaverine from *dl*-aminolaudanosine (amino-*N*-methyltetrahydropapaverine), but the substance he described under this name was probably *dl*-laudanosine, since it gave a methiodide, m. p.  $215^\circ$ . The author has repeated Pschorr's work, and finds that phenanthreno-*N*-methyltetrahydropapaverine is actually produced in this synthesis, and is *dl*-glaucine; in addition, the *dl*-forms of laudanosine, hydroxylaudanosine, and dilaudanosine are also formed. Formulæ for aminolaudanosine, laudanosine, and glaucine have been printed already (*Abstr.*, 1900, i, 685; 1904, i, 612), and constitutions are now assigned to hydroxylaudanosine (I), dilaudanosine (II), and dicentrine (III), to which allusion is made later.

The solution resulting from the addition of copper powder to a diazotised solution of aminolaudanosine (Pschorr, *loc. cit.*) is reduced with zinc and dilute sulphuric acid; excess of ammonia is then added, and the solution shaken with ether, which removes all the alkaloids. The residue left on distilling the ether is separated into phenolic base (hydroxylaudanosine) and non-phenolic bases (laudanosine,

glaucine, and dilaudanosine) by solution in dilute hydrochloric acid and treatment of this liquid with excess of alkali hydroxide. Full



details of the isolation of these constituents from these two fractions are given.

*dl-Glaucine*,  $C_{21}H_{25}O_4N$ , m. p. 137—139°, gives a crystalline hydrochloride, which is less soluble than those of the *d*- and *l*-forms; the *methiodide*, m. p. 218—220°, is crystalline. *dl-Glaucine hydrogen d- or l-tartrate* crystallises in needles, and has  $[\alpha]_D \pm 33^\circ$ . On recrystallisation from water these tartrates yield the corresponding salts of *d*- and *l*-glaucine, from which the free bases are obtainable; the *d*-glaucine so obtained is identical with the natural alkaloid (Fischer, Abstr., 1901, i, 743).

*dl-Laudanosine*, obtained in this reaction, is identical with that described by Pictet and Athanasescu (Abstr., 1900, i, 685).

*dl-Hydroxyglaucine*,  $C_{21}H_{27}O_5N$ , m. p. 189—190·5° (decomp.), gives colour reactions resembling those of glaucine. By recrystallisation of the hydrogen tartrates it was separated into *d*- and *l*-forms. These crystallise in masses of long, colourless needles, and have m. p. 188—190·5° and  $[\alpha]_D \pm 50^\circ$ . The *nitrates* crystallise well, and are sparingly soluble.

*dl-Laudanosine*,  $C_{42}H_{52}O_8N_2$ , is amorphous; it is produced in very small quantity in this synthesis, and was not obtained pure. Its chief colour reactions are described.

Dicentrine, isolated by Asahina (Abstr., 1909, i, 601), closely resembles glaucine in its colour reactions, physiological action, and chemical properties, and for that reason is regarded as glaucine, in which the -OMe groups in positions 5 and 6 are replaced by a dioxy-methylene group. A synthesis of dicentrine is being attempted.

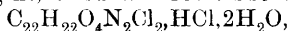
T. A. H.

**Isomerism of Corynanthine with Yohimbine.** ERNEST FOURNEAU and FIORE (*Bull. Soc. chim.*, 1911, [iv], 9, 1037—1040).—In view of the possible isomerism of these two alkaloids already referred to (Abstr., 1910, i, 501), the authors have re-examined yohimbine, and find that, like corynanthine, it has the composition represented by the formula  $C_{21}H_{26}O_3N_2$ . Yohimbine hydrochloride has  $[\alpha]_D^{20} + 105^\circ$ ; corynanthine hydrochloride has  $[\alpha]_D^{20} - 64\cdot15^\circ$ .

T. A. H.

**Red Compounds from Brucine.** JOSEF BURACZEWSKI and Z. ZBIJEWSKI (*Bull. Acad. Sci. Cracow*, 1911, A, 464—469).—Various reagents act on brucine to give red soluble compounds without oxidising or decomposing the brucine molecule.

By the action of dry chlorine on brucine, until the evolution of hydrogen chloride begins, a reddish-brown substance,



is obtained. When the action of the chlorine is prolonged until no more hydrogen chloride separates, a dark grey *powder* is obtained, soluble in water with a red coloration; this has the composition  $\text{C}_{21}\text{H}_{19}\text{O}_4\text{N}_2\text{Cl}_3, \text{HCl}, 2\text{H}_2\text{O}$ .

When bromine is allowed to act on brucine in absolute alcohol, a brownish-red *powder* is obtained, which is considered to be a mixture of  $\text{C}_{21}\text{H}_{22}\text{O}_4\text{N}_2\text{Br}, 2\text{H}_2\text{O}$  and  $\text{C}_{22}\text{H}_{24}\text{O}_4\text{N}_2\text{Br}, \text{HBr}, \text{H}_2\text{O}$ .

The production of a red coloration when the product of the action of dry chlorine on brucine is boiled with alcohol is characteristic of this alkaloid, and may be used for its detection. E. F. A.

**Hæmopyrrole.** HANS FISCHER and E. BARTHOLOMAUS (*Ber.*, 1911, 44, 3313—3317).—Knorr and Hess have recently published (*Abstr.*, 1911, i, 1019) a synthesis of 2:4-dimethyl-3-ethylpyrrole which they consider not to be identical with hæmopyrrole investigated by Piloty (*Abstr.*, 1910, i, 133). The main difference is a discrepancy of 23° in the melting point of the picrates.

The authors show that hæmopyrrole picrate has m. p. 120—122°, instead of 108.5° as previously described. In attempting to obtain 2:4-dimethyl-3-ethylpyrrole according to the method of Knorr and Hess, the authors obtained, in place of the expected hydrazone, a ketazine, the m. p. of which varied between 195° and 215°. This, on energetic reduction, yields an oil, the b. p. of which agreed with that given by Knorr and Hess, but the picrate melted indefinitely at 82—83°. This oil, when treated with benzenediazonium sulphate, yielded an *azo-dye*,  $\text{C}_{14}\text{H}_{17}\text{O}_3\text{N}_3\text{S}$ , which crystallises in red needles (compare this vol., i, 41, 56). H. W.

**Picrylpyridinium Chloride.** MAX BUSCH and WALTER KÖGEL (*J. pr. Chem.*, 1911, [ii], 84, 507—514).—When equal molecular quantities are heated in alcohol on the water-bath, picryl chloride and pyridine yield at first a little *picrylpyridinium picrate*, yellow needles, m. p. 223°, and finally, after cooling, almost colourless crystals of *picrylpyridinium chloride*,  $\text{C}_5\text{H}_5\text{N} \left\langle \begin{smallmatrix} \text{Cl} \\ \text{C}_6\text{H}_2(\text{NO}_2)_3 \end{smallmatrix} \right.$ , m. p. 128°; the latter changes to the former after long keeping, or after prolonged boiling in alcoholic solution. The chloride is converted by alcoholic potassium hydroxide into the *potassium* salt of a pyridine dye, probably  $\text{NO}_2\text{K}:\text{C}_6\text{H}_2(\text{NO}_2)_2:\text{NC}_4\text{H}_4\cdot\text{CHO}$ , which forms reddish-brown crystals with a green lustre. Picrylpyridinium picrate is decomposed almost quantitatively into pyridine and picric acid by boiling water, and yields with potassium iodide, *picrylpyridinium iodide*, m. p. 155°, orange leaflets. In ether, pyridine and picryl chloride (2 mols.) yield an additive compound,  $\text{C}_{11}\text{H}_7\text{O}_6\text{N}_4\text{Cl}, \text{C}_6\text{H}_2(\text{NO}_2)_3\text{Cl}$ , m. p. 151°, yellowish-green needles. C. S.

**New Derivatives of Dioxindole.** MORITZ KOHN and ALFONS OSTERSETZER (*Monatsh.*, 1911, 32, 905—916).—Various substituted dioxindoles with a tertiary hydroxyl group have already been obtained

by the application of the Grignard reagent to isatin (Kohn, Abstr., 1910, i, 697).

3-Phenyldioxindole by methylation with methyl sulphate gives 3-phenyl-1-methyldioxindole methyl ether; this forms leafy crystals, m. p. 83°. The action of acetic anhydride yields a monoacetyl compound, probably 1-acetyl-3-phenyldioxindole, which crystallises from benzene in short, columnar crystals, m. p. 141°.

3-Benzyl-1-methyldioxindole methyl ether, obtained analogously to the corresponding phenyl compound, forms needles, m. p. 97°.

3-Methyldioxindole, obtained by the action of magnesium methyl iodide on isatin, forms white, granular crystals, m. p. 160°; methylation gives 1:3-dimethyldioxindole methyl ether, cubical crystals, m. p. 78.5°; it yields a diacetyl derivative, m. p. 125°.

5-Bromo-3-phenyldioxindole is produced when magnesium phenyl bromide reacts with 5-bromoisatin; it forms thin rods, m. p. 243° with decomposition.

5-Bromo-3-methyldioxindole is obtained similarly from bromoisatin with magnesium methyl iodide, and also by the action of bromine water on 3-methyldioxindole; on heating it turns brown at 240°, and melts at 258°. When methylated, it produces 5-bromo-1:3-dimethyldioxindole methyl ether, needles, m. p. 142°.

D. F. T.

**Spirans. IV. History and Theory.** DAN RADULESCU (*Chem. Zentr.*, 1911, 82, ii, 1535; from *Bull. Soc. Sti. Bucuresti*, 1911, 20, 281—284. Compare Abstr., 1911, i, 497).—The chemical properties of a spiran ACB, composed of rings CA and CB of known structure and properties, are qualitatively the sum of those due to AC and CB, except where there are large accumulations of groups on the same carbon atom. With the exception of those formed from three or four atom rings, the spirans are stable. They show optical activity in some cases, although no asymmetric atom is present. Compounds in which two rings share a common nitrogen atom are quite different from the spirans, although they present a superficial resemblance to them.

T. A. H.

**Compounds of Ferric Salts with Antipyrine.** FILIPPO CALZOLARI (*Boll. chim. farm.*, 1911, 50, 763—767).—The molecular weight of antipyrine, determined cryoscopically in aqueous solutions, is normal, but when ferric chloride is present higher values are obtained, so that the red coloration which antipyrine gives with ferric chloride is probably due to the formation of a complex cation. Ferric fluoride gives only a pale yellow coloration with antipyrine, and corresponding with this the molecular weight of antipyrine is lower in this solution than in the presence of ferric chloride. The compound of ferric chloride and antipyrine is an orange-red, crystalline powder having the composition  $2\text{FeCl}_3 \cdot 3\text{C}_{11}\text{H}_{12}\text{ON}_2$ , and ferric bromide also yields a compound,  $2\text{FeBr}_3 \cdot 3\text{C}_{11}\text{H}_{12}\text{ON}_2$ , which forms reddish-brown crystals.

R. V. S.

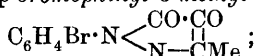
**1-Phenyl-3-methyl-5-pyrazolone and 4-Amino-1-phenyl-3-methyl-5-pyrazolone.** ALFRED HEIDUSCHKA and O. ROTHACKER (*J. pr. Chem.*, 1911, [ii], 84, 533—542).—The heating of 1-phenyl-

3-methyl-5-pyrazolone and *o*-, *m*-, or *p*-nitrobenzaldehyde at 140° for ten minutes yields a mixture of the nitrobenzylidene derivative and a bispyrazolone derivative, which is separated by means of benzene. 4-*o*-Nitrobenzylidene-1-phenyl-3-methyl-5-pyrazolone, m. p. 157°, crystallises in red needles; the corresponding *meta*- and *para*-isomerides have m. p. 162° and 171° respectively. 4:4'-*o*-Nitrobenzylidenebis-1-phenyl-3-methyl-5-pyrazolone,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{C}_{10}\text{H}_9\text{ON}_2)_2$ , m. p. 146° (decomp.), and the *meta*-isomeride, m. p. 150° (decomp.), form yellow leaflets.

When heated with zinc chloride at 140°, 1-phenyl-3-methyl-5-pyrazolone condenses with acetophenone to form 1-phenyl-4-*a*-phenylethylidene-3-methyl-5-pyrazolone,  $\text{CMePh} \cdot \text{C} \begin{smallmatrix} \text{CO-NPh} \\ \text{CMe:N} \end{smallmatrix}$ , m. p. 89°, orange crystals, and with benzophenone to form a corresponding substance,  $\text{C}_{23}\text{H}_{18}\text{ON}_2$ , m. p. 133°, orange-red leaflets.

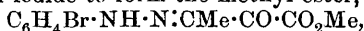
4-Amino-1-phenyl-3-methyl-5-pyrazolone reacts with cinnamaldehyde and with *o*-nitrobenzaldehyde to form the corresponding Schiff's bases,  $\text{C}_{19}\text{H}_{17}\text{ON}_3$ , m. p. 192°, and  $\text{C}_{17}\text{H}_{14}\text{O}_3\text{N}_4$ , m. p. 198°. Also with piperonal and with anisaldehyde it yields the substances,  $\text{C}_{44}\text{H}_{36}\text{O}_9\text{N}_6$ , m. p. 235°, and  $\text{C}_{44}\text{H}_{42}\text{O}_6\text{N}_6$ , m. p. 252°, respectively. C. S.

**Conversion of the Nitro- into the Keto-group.** WILHELM WISLICENUS and HERMANN GÖZ (*Ber.*, 1911, 44, 3491—3496).—The potassium salt of 4-oximino-1-phenyl-3-methyl-5-pyrazolone separates in lustrous, silky, deep yellow needles, m. p. 250—255°. By the action of bromine, 4-bromo-4-nitro-1-*p*-bromophenyl-3-methyl-5-pyrazolone is formed; this crystallises in well formed, small, dark yellow prisms, m. p. about 85°, to a red oil (decomp.). On heating, it is converted into 4-keto-1-*p*-bromophenyl-3-methyl-5-pyrazolone,



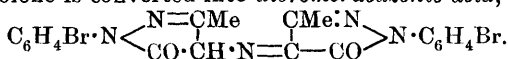
this separates in small, flat prisms, yellowish-red in transparent, bluish-red in reflected, light, m. p. after sintering 171—172°. On boiling with water, it forms colourless needles, probably indicating an additive product; a colourless additive product is formed also with sodium hydrogen sulphite.

When dissolved in sodium hydroxide or carbonate the keto-pyrazolone ring is opened; from the reddish-yellow solution a yellow acid is precipitated by strong mineral acids. This  $\alpha\beta$ -diketobutyric acid  $\beta$ -*p*-bromophenylhydrazone,  $\text{C}_6\text{H}_4\text{Br} \cdot \text{NH} \cdot \text{N} \cdot \text{CMe} \cdot \text{CO} \cdot \text{CO}_2\text{H}$ , crystallises in microscopic, canary-yellow prisms, m. p. 153—154° (decomp.). On boiling with acetic anhydride the deep red keto-*p*-bromophenyl-methylpyrazolone is re-formed. With phenylhydrazine a golden-yellow phenylosazone, m. p. 211°, is obtained. The yellow insoluble silver salt reacts with methyl iodide to form the methyl ester,



which crystallises in brownish-yellow, microscopic prisms, m. p. 165—170°.

When warmed for several days with acetic acid, keto-*p*-bromophenyl-methylpyrazolone is converted into dibromorubazonic acid,



This has m. p. 305—308°, and dissolves in alcoholic potassium hydroxide and in concentrated ammonia with a violet-red coloration.

4-Bromo-4-nitro-3-methyl-5-pyrazolone,  $\text{NH} \begin{smallmatrix} \text{N}=\text{CMe} \\ \text{CO} \cdot \text{CBr} \cdot \text{NO}_2 \end{smallmatrix}$ , obtained from the golden-yellow prisms of the potassium salt of 3-methyl-4-isouitro-5-pyrazolone, crystallises in small, yellowish-white prisms, m. p. 84—85° (decomp.). On heating, a red, amorphous substance is obtained, which could not be purified. E. F. A.

**Hydantoins. VII. Synthesis of 2-Thiohydantoin.** TREAT B. JOHNSON and BEN H. NICOLET (*J. Amer. Chem. Soc.*, 1911, **33**, 1973—1978).—2-Thiohydantoin has been synthesised by Komatsu (Abstr., 1911, i, 683) by the action of potassium thiocyanate on glycine in presence of acetic anhydride, and also by Wheeler, Nicolet, and Johnson (Abstr., 1911, i, 1031) by heating acylthiohydantoic acids with hydrochloric acid.

A large quantity of 2-thiohydantoin being required for certain investigations, Komatsu's method was employed, and it was found that the compound could be very easily prepared in this way. Komatsu's interpretation of the mechanism of the reaction is incorrect, and his statement that thiohydantoic acid is produced could not be confirmed. It is shown that acetylglycine is first produced, and combines with thiocyanic acid to form a thiocyanate, which undergoes re-arrangement to acetylthiohydantoic acid. This compound suffers an inner condensation, with formation of 2-thio-3-acetylhydantoin, which is subsequently converted into 2-thiohydantoin.

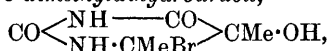
When glycine is heated with potassium thiocyanate and acetic anhydride, 2-thio-3-acetylhydantoin,  $\text{CH}_2 \begin{smallmatrix} \text{CO}-\text{NH} \\ \text{N} \cdot \text{Ac} \cdot \text{CS} \end{smallmatrix}$ , m. p. 175—176°, is produced, which crystallises in square blocks, and when heated with hydrochloric acid is converted quantitatively into 2-thiohydantoin. The compound can also be obtained by the action of potassium thiocyanate on acetylglycine (aceturic acid).

By the action of potassium thiocyanate on hippuric acid in presence of acetic anhydride (9 parts) and glacial acetic acid (1 part), 2-thio-3-benzoylhydantoin,  $\text{CH}_2 \begin{smallmatrix} \text{CO}-\text{NH} \\ \text{N} \cdot \text{Bz} \cdot \text{CS} \end{smallmatrix}$ , m. p. 165°, is obtained in a yield of 86%; it crystallises in square plates. When the compound is hydrolysed with concentrated hydrochloric acid, it yields 2-thiohydantoin, and when condensed with benzaldehyde in presence of glacial acetic acid and anhydrous sodium acetate, it is converted into 2-thio-4-benzylidenehydantoin. E. G.

**Condensation of Methyluracil and Formaldehyde.** WILHELM KIRCHER (*Annalen*, 1911, **385**, 293—314).—4-Methyluracil and 40% formaldehyde (3 mols.) condense in acid solution to form 4-methyl-5-hydroxymethyluracil,  $\text{CO} \begin{smallmatrix} \text{NH}-\text{CO} \\ \text{NH} \cdot \text{CMe} \end{smallmatrix} \gg \text{C} \cdot \text{CH}_2 \cdot \text{OH}$ , plates or needles, decomp. 305—310°; in alkaline solution, the same product is obtained in the form of the sodium salt,  $\text{C}_6\text{H}_7\text{O}_3\text{N}_2\text{Na}$ . The substance is

reconverted into its generators by boiling water, and is changed to a substance,  $C_{12}H_{14}O_5N_4$ , decomp.  $303-307^\circ$ , by boiling dilute hydrochloric acid. By reduction with tin and 36% hydrochloric acid at  $58-60^\circ$ , it yields 4:5-dimethyluracil and a substance,  $C_{11}H_{12}O_4N_4$ , decomp.  $302-307^\circ$ . 4:5-Dimethyluracil has also been prepared by passing the vapour of cyanic acid (3 mols.) in a current of dry carbon dioxide into an ethereal solution of methyl  $\beta$ -amino- $\alpha$ -methylcrotonate in a freezing mixture, boiling the product with 10% potassium hydroxide, and acidifying after the removal of the cyamelide by filtration. 4:5-Dimethyluracil is oxidised to acetylcarbamide and oxalic acid by 4% potassium permanganate, and when heated with aqueous potassium hydroxide, 95% alcohol, and methyl iodide yields a mixture of 1:3:4:5-tetramethyluracil, m. p.  $123-125.5^\circ$ , 1:4:5-trimethyluracil, m. p.  $220.5-222^\circ$ , and 3:4:5-trimethyluracil, m. p.  $172-174^\circ$ .

A suspension of 4:5-dimethyluracil is converted by bromine into 4-bromo-5-hydroxy-4:5-dimethyldihydrouracil,



m. p.  $226-227^\circ$  (decomp.), which changes to 4-bromo-4-methyl-5-methylenedihydrouracil at  $105^\circ$ , and to 4-bromo-5-ethoxy-4:5-dimethyldihydrouracil, m. p.  $225-226^\circ$  (decomp.), when boiled with alcohol. The last substance at  $105^\circ$  also yields 4-bromo-4-methyl-5-methylenedihydrouracil, which is converted by bromine water into 4-bromo-5-hydroxy-4-methyl-5-bromomethyldihydrouracil,  $C_6H_8O_3N_2Br_2$ , m. p.  $165-167^\circ$  (decomp.); the latter is also obtained by treating 4:5-dimethyluracil with bromine and subsequently boiling with water.

When 4-bromo-5-hydroxy-4:5-dimethyldihydrouracil is treated with 5% potassium hydroxide in the cold, a substance,  $C_6H_{10}O_4N_2 \cdot H_2O$ , m. p.  $168.5-169.5^\circ$  (decomp.), is obtained, which may be 4:5-dihydroxy-4:5-dimethyldihydrouracil or acetylmethylhydantoin (compare Bremer, Abstr., 1911, i, 160). C. S.

**Alkyl Derivatives of Methyluracil.** OSKAR BÜCKENDORFF (*Annalen*, 1911, 385, 314-327).—4-Methyl-3-ethyluracil (Hoebel, Abstr., 1907, i, 557) reacts with aqueous bromine to form 5:5-dibromo-4-hydroxy-4-methyl-3-ethyldihydrouracil,  $N\text{Et} \begin{array}{c} \text{CO} \text{---} \text{NH} \\ \text{CMe}(\text{OH}) \cdot \text{CBr}_2 \end{array} \text{CO}$ , m. p. about  $160^\circ$ , which is converted by 95% alcohol into 5-bromo-4-methyl-3-ethyluracil, m. p.  $234-236^\circ$  (decomp.); the latter reacts with aqueous ammonia at  $150-160^\circ$  to form 5-amino-4-methyl-3-ethyluracil, m. p.  $234-236^\circ$ . The following compounds are obtained from 4-methyl-1-ethyluracil by similar methods: 5:5-dibromo-4-hydroxy-4-methyl-1-ethyldihydrouracil, m. p. about  $160^\circ$ ; 5-bromo-4-methyl-1-ethyluracil, m. p.  $203-206^\circ$ ; 5-amino-4-methyl-1-ethyluracil, m. p.  $203-205^\circ$ . 4-Methyl-1-ethyluracil is converted by sulphuric and nitric acids on the water-bath into 5-nitro-1-ethyluracil-4-carboxylic acid,  $C_7H_7O_6N_3 \cdot H_2O$ , m. p.  $189^\circ$  (decomp.), and a substance,  $C_7H_6O_5N_4$ , decomp.  $180-220^\circ$ ; at  $140-150^\circ$  the former yields 5-nitro-1-ethyluracil, m. p.  $159-161^\circ$ , which is reduced by aqueous ammonia and aluminium amalgam to 5-amino-1-ethyluracil, m. p.  $171-172^\circ$ .

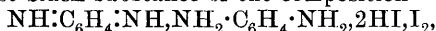
4-Methyl-3-propyluracil, m. p. 170—172°, and 4-methyl-1-propyluracil, m. p. 184°, are prepared and separated in a similar manner to the methylethyluracils (Hoebel, *loc. cit.*). Their constitutions are proved as follows: 4-Methyl-1-propyluracil by ethylation, and 4-methyl-3-ethyluracil by propylation, yield the same 4-methyl-3-ethyl-1-propyluracil, m. p. 63—65°. Also, 4-methyl-1-propyluracil by methylation, and 3:4-dimethyluracil by propylation, yield the same 3:4-dimethyl-1-propyluracil, m. p. 85—87°. Finally, 4-methyl-3-propyluracil by methylation, and 1:4-dimethyluracil by propylation, yield the same 1:4-dimethyl-3-propyluracil, m. p. 52—54°.

Methylallyluracils have been prepared and their constitutions proved by similar methods. 4-Methyl-1-allyluracil and 4-methyl-3-allyluracil have m. p. 180—182° and 168—169° respectively; 1:4-dimethyl-3-allyluracil and 3:4-dimethyl-1-allyluracil have m. p. 45—47° and 59—61° respectively.

Methylisobutyluracils, m. p. 195—196° and 133—135°, have been obtained, but have not yet been fully investigated. C. S.

**Phenylmethyltriazole. A Correction.** EUGEN BAMBERGER (*Ber.*, 1911, 44, 3564—3565).—It was previously stated (*Abstr.*, 1894, i, 23) that 1-phenyl-5-methyltriazole-3-carboxylic acid yielded phenylmethyltriazole, m. p. 191°, when heated in a stream of carbon dioxide. Pellizzari has shown that this compound is in reality cyanophenylacetamidine,  $\text{NPh}\cdot\text{CMe}\cdot\text{NH}\cdot\text{CN}$ . It was also stated that the compound was a base, but it is now shown to be an acid soluble in sodium hydroxide, and is precipitated in colourless needles, as stated by Pellizzari (*loc. cit.*). E. F. A.

**N-Quinhydrones.** M. M. RICHTER (*Ber.*, 1911, 44, 3466—3469).—The action of iodine on *p*-phenylenediamine in benzene solution gives rise to an almost black substance of the composition



a nitrogen analogue of the quinhydrones. This *N*-benzoquinhydrone dihydriodide periodide is an almost black substance, which loses iodine on warming. On account of its instability, the corresponding base could not be isolated.

Benzidine treated with iodine in a similar manner gives *N*-benzidine-quinhydrone dihydriodide periodide,  $\text{C}_{24}\text{H}_{22}\text{N}_4\cdot 2\text{HI}\cdot\text{I}_4$ , a greyish-black powder, which loses iodine even at the ordinary temperature.

*o*-Phenylenediamine treated with iodine behaves quite differently, and yields 2:3-diaminophenazine.

References are given to papers describing compounds which must be regarded as derived from the above bases or from bases of the same type. The author ascribes to all these bases a structure analogous to that which he has already attributed to the quinhydrones (*Abstr.*, 1911, i, 136), for example,  $\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2\cdot 2\text{HI}\cdot\text{I}_2$ .

D. F. T.

**Preparation of Solid Diazonium Salts by means of Nitrosyl Chloride.** M. STRUSZYŃSKI and WOJECIECH SVENTOSLAVSKY (*Bull. Acad. Sci. Cracov*, 1911, A, 459—463).—Nitrosyl chloride, which is now an

easily accessible product, is an energetic diazotising agent, and it is conveniently used for preparing solid diazonium salts in a state of purity.

The amine is dissolved in alcohol, and an alcoholic solution of hydrogen chloride containing 2.5—3 mols. of the acid added; the mixture is cooled in ice, and the solution of nitrosyl chloride in toluene added. Action is rapid and complete, and the insoluble diazonium salt separates. When sulphuric acid is substituted for hydrochloric acid, the corresponding sulphates are obtained. E. F. A.

**Cazeneuve's Diphenylcarbodiazone and Diphenylcarbazone.** EUGEN BAMBERGER (*Ber.*, 1911, **44**, 3743—3754).—From a comparison of the properties, the author shows that the diphenylcarbodiazone of Cazeneuve (*Abstr.*, 1901, i, 297) is identical with the betaine of diphenylhydroxytetrazolium hydroxide (Bamberger, *Abstr.*, 1899, i, 355); the latter name gives the correct description.

Reasons are also given for believing that whilst the formula  $N_2Ph \cdot CO \cdot NH \cdot NHPh$  correctly represents the structure of free diphenylcarbazone (compare Heller, *Abstr.*, 1891, 1212), the salts, which have a much more intense colour, are derived from the structure  $N_2Ph \cdot C(OH) : N \cdot NHPh$ . D. F. T.

**Hæmopyrrole.** LAD. LEYKO and LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1911, **A**, 345—349).—The hydrochlorides of dyes obtained by coupling hæmopyrrole with benzenediazonium chloride have been described previously (Leyko and Marchlewski, *Abstr.*, 1910, i, 144). To obtain the free base,  $N_2Ph \cdot C_8H_9N \cdot N_2Ph$ , the hydrochloride is decomposed with sodium acetate in alcoholic solution.

*Bisbenzeneazohaemopyrrole* forms fine, lustrous needles, m. p. 171—172°. In ethereal solution it shows two absorption bands in the visible region of the spectrum, whereas *biscymeneazopyrrole* and *bisbenzeneazopyrrole* are characterised by only one band. Taking into account Küster's proof that hæmopyrrole,  $C_8H_{13}N$ , yields methylethylmaleinimide on oxidation, the bisbenzeneazo-derivative is formulated as  $PhN_2 \cdot N \begin{cases} CMe = CEt \\ C(N_2Ph) : CMe \end{cases}$  [compare this vol., i, 41, 50]. E. F. A.

**The Changes in Physical Conditions of Colloids. XII. The Properties of the Protein Ions.** CARL SCHORR (*Biochem Zeitsch.*, 1911, **37**, 424—451).—According to the theory of Pauli, proteins act both as acids and bases, but under certain conditions of hydrogen ion concentration, the protein ions themselves exist in solution, and not protein salts of either acids or bases. The protein ions, according to the theory, differ from the protein salts in that the ions, as hydrophil colloids, are capable of existing as highly hydrated aggregates, from which the water is extracted only with some difficulty. This theory is supported by the fact that under such conditions the solution of protein contains protein not in form of salts; the protein is only slightly, if at all, precipitated by dehydrating agents, such as alcohol. Such solutions, furthermore, owing to the large aggregates, have a high viscosity, and also, owing to the large size of the hydrated

protein ions and their slow motion, have only a relatively small capacity for conducting electricity. In the presence of neutral salts, furthermore, the protein ions lose their electric charge, and all those properties disappear which are due to the presence of protein ions. In the presence of salts there is therefore a restitution of such properties as the precipitability by alcohol and a diminution of viscosity. The above theory is substantiated by numerous experiments on the precipitability of proteins in the presence of varying quantities of acids and bases, and by numerous physical measurements of the properties of the solutions under the varying conditions.

S. B. S.

**Action of Bromine and Iodine on Proteins.** A. KRZEMECKI (*Bull. Acad. Sci. Cracow*, 1911, A, 470—488).—Previous observers of the action of iodine or bromine on proteins have worked under conditions in which more or less oxidation took place. The experiments now described were made so as to alter the protein molecule as little as possible, merely introducing halogen partly in a very loosely bound condition.

Egg-albumin was found to retain 28.3—29.6% of iodine and 18% of bromine, serum-albumin 28.5% iodine and 20.5% bromine, casein 19.1 to 24.9% iodine, and plant protein 34.6% iodine. The halogen is attached to the protein molecule in several different ways, part being removed by boiling with acetic acid; thus, after treatment, egg-albumin contains 24.45% iodine, serum-albumin 24.5% iodine, and casein 17.37% iodine. Acetone at the ordinary temperature eliminates a further proportion of halogen, egg-albumin now containing 15.6% iodine, and serum-albumin 14%. Finally, treatment with sodium thiosulphate reduced the iodine in egg-albumin to 6.26%.

$\alpha$ -Hydroxyprotosulphonic acid, under similar conditions, was only able to take up 11.12% of iodine when made from egg-albumin, and 9.8% of iodine when prepared from serum-albumin. When the halogen proteins are heated with water, a large amount of decomposition takes place. The halogen proteins are digested both by trypsin and pepsin.

The halogens in ethereal solution were allowed to act on the protein, absorption being usually complete within a few hours in the case of iodine. Even better results were obtained, using methyl alcohol as solvent.

E. F. A.

**3:5-Di-iodotyrosine from Iodoprotein.** IV. Gorgonin and Spongin. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1911, 75, 353—362).—The iodoproteins differ in the relative proportions of fixed iodine and iodine eliminated as hydrogen iodide on decomposition with barium hydroxide (compare Oswald, *Abstr.*, 1911, 697, 812). Of the total iodine in gorgonin, 82% is fixed, and 18% can be eliminated; the amount of di-iodotyrosine isolated was 0.9%. Tyrosine is not the only iodine-fixing group of gorgonin. Spongin yields 64% of fixed iodine, 36% being eliminated on continued boiling; 15.7% of the total iodine was isolated in the form of di-iodotyrosine. Spongin is regarded as containing at least two forms of iodine compound.

E. F. A.

**The Physical Chemistry of the Bence-Jones Protein.** WOLFGANG PAULI (*Chem. Zentr.*, 1911, ii, 371; from *Zentr. Physiol.*, 1911, 25, 110—111).—The author, in view of the recent work of Hopkins and Savory on the Bence-Jones protein, calls attention to the fact that he has already explained the peculiar properties of this substance as regards its solubility in salt solutions as a special case of the general properties of proteins. S. B. S.

**Formation and Estimation of Methæmoglobin.** JOSEPH BARCROFT and FRANZ MÜLLER (*Proc. physiol. Soc.*, 1911, xx.; *J. Physiol.*, 43).—Methæmoglobin is formed quantitatively when potassium nitrite is added to blood, the amount of hæmoglobin converted containing an amount of dissociable oxygen equivalent to that necessary to convert nitrite into nitrate. Hydroxylamine sulphate acts similarly. Magnesium chlorate does not do so. Methæmoglobin in blood may be estimated by combining two operations: (1) a comparison of the oxygen capacity with that of a standard blood, and (2) colorimetric comparison of the blood for estimation with the same standard, the hæmoglobin in both being first turned into methæmoglobin. Two mild cases of methæmoglobin poisoning in cats produced no change in the dissociation curve of the blood. W. D. H.

**Preparation of Nucleic Acid.** AMOS W. PETERS (*J. Biol. Chem.*, 1911, 10, 373—379).—Barium hydroxide with sodium chloride is used for the extraction of the tissue. The alkalinity thus obtained is sufficient to decompose the nucleo-proteins. One advantage of this new method is the comparative insolubility of the barium compounds formed with constituents of the tissue, and so little protein goes into solution that a separate precipitation of protein is unnecessary. The solution of barium hydroxide and sodium chloride dissolves nucleic acid freely. Barium, proteins, and guanylic acid are absent from the final product. W. D. H.

**Tyrosine as an Agent for the Fixation of Iodine in the Preparation of Iodopeptones.** PAUL MACQUAIRE (*Compt. rend.*, 1911, 153, 1084—1085).—Di-iodotyrosine has been isolated from peptones which have been treated with iodine. W. O. W.

**Oxyprotosulphonic Acids.** I. JOSEF BURACZEWSKI and L. KRAUZE (*Zeitsch. physiol. Chem.*, 1911, 76, 37—43. Compare Abstr., 1911, i, 408).—Crude oxyprotosulphonic acid from egg-albumin, blood-serum, and casein is divided into fractions: ( $\alpha$ ) insoluble in hot acetic acid; ( $\beta$ ) crystallising from acetic acid solution in the cold; ( $\gamma$ ) soluble in acetic acid, insoluble in alcohol; ( $\gamma_2$ ) insoluble in cold alcohol; ( $\gamma_3$ ) soluble in alcohol, but precipitated by ether. Each of these fractions has been analysed completely; they differ in the intensity with which they show the biuret coloration, and also as regards the blackening with a lead salt due to sulphur in a loosely combined state. The intensity with each test falls from the  $\alpha$ - to the  $\gamma_3$ -acid, that is, with the increase in solubility, and possibly corresponds with the increased

oxidation of the protein. The  $\alpha$ -oxyprotosulphonic acid comprises more than one-half of the total product.

E. F. A.

**Hydrolytic Decomposition of Proteins by Pepsin, Trypsin, Acids, and Alkalis.** VALDEMAR HENRIQUES and J. K. GJALDBÆK (*Zeitsch. physiol. Chem.*, 1911, **75**, 363—409).—The hydrolysis of a number of proteins by pepsin and trypsin has been followed by Sørensen's method of titrating in presence of formaldehyde, the titration of the amino-acids being effected in four stages (Henriques and Sørensen, *Abstr.*, 1910, ii, 164, 466). The liquid is made neutral to litmus paper, phenolphthalein added, and then *N*/5-sodium hydroxide until a faint red coloration is obtained (stage 1); the addition is continued until the deep red colour of the control is matched (stage 2), when the neutral formaldehyde solution is added, and the titration continued until a faint red (stage 3) and a deep red (stage 4) colour are obtained. The ratio of the figure in stage 4, less the alkali used in the control, to the figure in stage 1 is calculated for each test. The other determinations made were the total nitrogen, the nitrogen as ammonia, and the nitrogen which could be titrated as formaldehyde expressed as a percentage of the total.

Pepsin contains about 25% of titratable nitrogen; trypsin some 28%. On auto-digestion these figures increase to 37% and 58% respectively.

Egg-white, casein, lean beef, edestin, gliadin, gelatin, and Witte peptone were incubated with pepsin or trypsin, and the above measurements made every few days. With pepsin, after about one hundred and seven days' action, from 30—38% of the total nitrogen can be titrated with formaldehyde. The action of the pepsin itself very soon falls off and stops altogether, subsequent digestion being due to the action of the acid; accordingly, fresh pepsin was occasionally added. It is evident that the products of very prolonged peptic action are in the main due to the action of the acid present.

Much evidence as to the nature of the hydrolysis is given by the ratio of the alkali required in the 4th and 1st stages of titration. In the case of glycine this is 48.9; for glycyl-glycine it is only 2.1. Alanine has a value of 64.7; arginine, lysine, cystine, and tryptophan have values below 10; the values for aspartic acid, 162, and glutamic acid, 194, are very high. The formation of amino-acids during hydrolysis will therefore be indicated by a large increase in the value of the ratio.

The experiments with pepsin show a low value, 2.1—2.7, for the ratio, which does not materially change during hydrolysis, indicating that the products of hydrolysis are polypeptides and not amino-acids. The amount of ammonia formed increases throughout hydrolysis; it differs considerably in magnitude in the six proteins investigated, but is far larger in the case of pepsin and hydrochloric acid than with trypsin.

The trypsin experiments show variations of from 25% in the case of gelatin to 60% in the case of egg-white in the amount of nitrogen which can be titrated in presence of formaldehyde. The titration

ratio is, as a rule, larger with trypsin, being markedly so in the case of egg white, and it tends to increase during the progress of hydrolysis, indicating the formation of amino-acids. The results show clearly the differences between the action of the two ferments.

The addition of pepsin to the products of a completed tryptic hydrolysis slightly increased the amount of nitrogen which could be titrated, and tended to lessen the titration ratio. The addition of trypsin to a completed peptic digestion caused the greatest total hydrolysis measured, and an increase in the titration ratio, which, however, did not become so large as in the case of the simple tryptic digestion owing to the presence of the peptide constituents.

For comparison, hydrolysis has also been effected by hydrochloric acid and by sodium hydroxide. The proportion of ammonia formed is greatest in the last case. The titration ratio indicates that acid hydrolysis is very similar to that caused by pepsin; possibly pepsin acts as a catalyst for the weak acid. The titration ratio is higher in hydrolysis by alkali, but not as great as with trypsin; probably the difference in the mode of action in the two agents depends mainly on the secondary changes produced by the alkali.

E. F. A.

**Inactivation of Trypsin by Dialysis against Distilled Water; Reactivation of the Diastase by Addition of Salts.** ALBERT FROUIN and ARTHUR COMPTON (*Compt. rend.*, 1911, 153, 1032—1034).—The proteolytic enzyme of pancreatic juice is rendered inactive when the liquid is submitted to dialysis for sixty-six to seventy-two hours, but can be activated by addition of certain salts, such as sodium chloride, bromide, iodide, fluoride, acetate, citrate, magnesium sulphate, and others, or by alkali hydroxides. If dialysis is prolonged beyond the period stated, the enzyme undergoes a permanent loss of activity.

W. O. W.

**Protection of Trypsin from Destruction by Heat.** D. H. DE SOUZA (*J. Physiol.*, 1911, 43, 374—378).—A temperature of 80° destroys trypsin in five minutes; the protective action of peptone in the solution is very slight, but rather greater if the reaction is acid or neutral. Lower temperatures (65—70°) take longer to destroy the enzyme, and the protective action of peptone is somewhat greater. The protection is too small to be of any value in sterilising enzymes by heat. Experiments without antiseptics are not trustworthy.

W. D. H.

**Tryptic Digestion of Silk.** I. W. S. HUBBARD (*J. Amer. Chem. Soc.*, 1911, 33, 2032—2035).—Experiments are described which show that silk is slowly hydrolysed by trypsin with formation of tyrosine, tryptophan, or a compound of this substance, and dextrorotatory tryptic peptones.

E. G.

**The Conditions for Optimal Action of Invertase.** ARISTIDES KANITZ (*Biochem. Zeitsch.*, 1911, 37, 50—51).—In view of various recent investigations on this subject, the author calls attention to his own work published in 1903, in which he showed that the optimal action

of invertin from *Aspergillus niger* takes place in a medium with hydrogen ion concentration of  $3.3 \times 10^{-3}$  to  $3.3 \times 10^{-4}$  at a temperature of  $56^\circ$  (compare Abstr., 1904, i, 158). S. B. S.

**Mechanism of the Destruction of Diastases by Light.** HENRI AGULHON (*Compt. rend.*, 1911, 153, 979—982. Compare this vol., ii, 243).—Enzymes are divisible into three classes according to their sensitiveness to light. Sucrase, tyrosinase, and laccase are destroyed by visible rays only in presence of oxygen; in a vacuum they are destroyed only by ultra-violet light. Probably in the absence of molecular oxygen, hydrogen peroxide is the effective agent of decomposition. Emulsin and catalase are destroyed by light of all wave-lengths, even in a vacuum, but more rapidly when oxygen is present. Rennet is an example of a third type, the activity of which is not impaired by visible rays, but is rapidly destroyed by ultra-violet radiation in a vacuum. W. O. W.

**The Mode of Action of Phosphatase.** A. VON LEBEDEFF (*Zeitsch. physiol. Chem.*, 1911, 75, 499—500).—Polemical against Euler and Kullberg (Abstr., 1911, i, 1057). The results obtained by these authors were vitiated by the use of impure yeast-extract.

H. B. H.

**The Influence of Temperature on the Action of Phosphatase.** HANS VON EULER and HJALMAR OHLSEN (*Biochem. Zeitsch.*, 1911, 37, 312—320).—The aqueous extract of yeast dried at  $50^\circ$  does not produce a synthesis of phosphoric esters of sugars from dextrose and phosphoric acid unless the former substance is previously partly fermented with living yeast. A synthetical enzyme can therefore be separated from other enzymes in yeast. The extract of dried yeast becomes more active synthetically if it is warmed to  $40^\circ$  before acting on the mixture of phosphate and partly fermented dextrose. The explanation of this phenomenon has not yet been found, but preliminary experiments indicate that it is not due to the destruction of inhibitory substances. S. B. S.

**5-Nitro-2-aminophenylarsinic Acid.** LUDWIG BENDA (*Ber.*, 1911, 44, 3293—3297).—It has been shown previously (Abstr., 1908, i, 591) that in the preparation of aminoarylarsinic acids from aromatic amines, the arsenic always enters the para-position to the amino-group, provided that this position is unoccupied. In the case of para-substituted amines, either the introduction of arsenic cannot be effected, or exceedingly small yields of o-aminoarylarsinic acids are obtained (Benda, Abstr., 1908, i, 747). An exception to this rule has been found in p-nitroaniline, which is readily converted into 5-nitro-2-aminophenylarsinic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{AsO}(\text{OH})_2$ , by heating it with arsenic acid at  $210^\circ$ . The acid crystallises in lustrous, orange-yellow prisms, m. p.  $235\text{—}236^\circ$  (decomp.), and yields an acetyl derivative and an almost colourless diazo-compound. The constitution of the acid has been established by its conversion into 2-iodo-4-nitroaniline (Michael and Norton, Abstr., 1878, 406) by the action of potassium iodide and sulphuric acid on the aqueous solution of its sodium salt.

When heated with aqueous sodium hydroxide, it yields 5-nitro-2-hydroxyphenylarsinic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{AsO}(\text{OH})_2$ . This forms stout, lustrous, pale amber-yellow crystals, m. p. 247—248° (decomp.), and yields a monopotassium salt,  $\text{C}_6\text{H}_5\text{O}_6\text{NKAs}_2\text{H}_2\text{O}$ , crystallising in almost colourless needles or leaflets; the dipotassium salt forms intensely yellow, felted needles.

3 : 5-Dinitro-2-hydroxyphenylarsinic acid,  
 $\text{OH} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{AsO}(\text{OH})_2$ ,

prepared by nitrating the mononitro-acid, crystallises in pale yellow needles, m. p. 237°.

Reduction of 5-nitro-2-hydroxyphenylarsinic acid by means of sodium hyposulphite yields 5 : 5'-diamino-2 : 2'-dihydroxyarsenobenzene, which forms a yellow powder, yields a microcrystalline dihydrochloride, and, when oxidised with sodium hypochlorite in alkaline solution in the presence of *p*-xylenol, gives a cornflower-blue solution of the corresponding indophenolarsinic acid. F. B.

**Constitution of the Isomeric Aminophenylarsinic Acids, and of Michaelis's Nitrophenylarsinic Acid.** ALFRED BERTHEIM and LUDWIG BENDA (*Ber.*, 1911, 44, 3297—3300).—*m*-Aminophenylarsinic acid has been prepared by eliminating the amino-group from 3-nitro-4-aminophenylarsinic acid (Abstr., 1911, i, 1055) and 5-nitro-2-aminophenylarsinic acid (preceding abstract), and found to be identical with the acid previously obtained (Berthelm, Abstr., 1908, i, 590) by the reduction of the nitrophenylarsinic acid prepared by Michaelis and Loesner (Abstr., 1894, i, 187) by directly nitrating phenylarsinic acid. Michaelis and Loesner's acid is accordingly *m*-nitrophenylarsinic acid.

The elimination of the amino-group from 3-nitro-4-aminophenylarsinic acid was accomplished by diazotisation and subsequent treatment of the resulting diazo-compound with hypophosphorous acid. In the case of 5-nitro-2-aminophenylarsinic acid, the replacement of the diazo-group was effected by means of copper bronze and alcohol. The *m*-nitrophenylarsinic acid thus obtained was isolated by means of the zinc salt, and reduced with sodium amalgam to *m*-aminophenylarsinic acid. F. B.

***p*-Phenylenediaminearsinic Acid.** LUDWIG BENDA (*Ber.*, 1911, 44, 3300—3304). — *p*-Phenylenediaminearsinic [2 : 5-diaminophenylarsinic] acid is prepared by reducing 5-nitro-2-aminophenylarsinic acid (preceding abstracts) in aqueous sodium hydroxide solution with ferrous chloride. It crystallises in slender needles, which become violet on exposure to air and light, and decompose at 210—215°. It reacts with only one molecule of nitrous acid to form a diazo-compound, which yields reddish-violet, yellowish-orange, and red azo-dyes with *R*-salt, resorcinol, and  $\beta$ -naphthol respectively. When the diazo-compound is treated with copper and alcohol, and the resulting monoaminophenylarsinic acid again diazotised and coupled with  $\beta$ -naphthol, a red azo-dye is obtained, which is reduced by sodium hyposulphite to *m*-aminophenylarsinic acid. The diazotisation of 2 : 5-diaminophenylarsinic acid therefore takes place at the amino-group in the 2-position.

Attempts to prepare *o*-aminophenylarsinic acid (see following abstract) by acetylating 2:5-diaminophenylarsinic acid, diazotising the resulting 2-amino-5-acetylaminophenylarsinic acid, and combining the *diazo*-compound thus obtained with  $\beta$ -naphthol, followed by hydrolysis and subsequent removal of the amino-group from the resulting *azo*-dye, were only partly successful. *o*-Aminophenylarsinic acid was identified in the product, but could not be isolated in a crystalline condition.

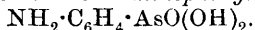
F. B.

***o*-Aminophenylarsinic (*o*-Arsanilic) Acid.** LUDWIG BENDA (*Ber.*, 1911, 44, 3304—3308).—5-Nitro-2-aminophenylarsinic acid (preceding abstracts) and oxalic acid react when heated with concentrated aqueous sodium hydroxide at 160—165° to form 4:4'-*di-nitro-oxanilide-2:2'-diarsinic acid*,

$\text{AsO(OH)}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{NH} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{AsO(OH)}_2$ , which is reduced by iron and acetic acid to 4:4'-*diamino-oxanilide-2:2'-diarsinic acid*. The amino-group is eliminated from the latter compound by diazotisation and treatment of the resulting *diazo*-compound with copper and alcohol.

The *oxanilide-2:2'-diarsinic acid*,

$\text{AsO(OH)}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO(OH)}_2$ , thus obtained crystallises in lustrous, silvery leaflets, and is hydrolysed by dilute sulphuric acid to *o*-aminophenylarsinic acid,



This crystallises in needles, m. p. 153°, and is distinguished from its isomerides by its much greater solubility in water and the ease with which the arsenic acid residue is removed. When heated with potassium iodide and dilute sulphuric acid at 80°, it is instantly converted into *o*-iodoaniline. Its toxicity is much greater than that of the *p*-isomeride. The crystalline *barium* and *silver* salts are described.

F. B.

**Nitrohydroxyarylarsinic Acids.** LUDWIG BENDA and ALFRED BERTHEIM (*Ber.*, 1911, 44, 3445—3448).—The nitration of *p*-hydroxyphenylarsinic acid and of 4-hydroxy-5-methylarsinic acid has been studied.

3 - Nitro - 4 - hydroxyphenylarsinic acid is formed when sodium *p*-hydroxyphenylarsinate dissolved in concentrated sulphuric acid is treated with the theoretical quantity of nitric acid (D 1.4), the temperature not being allowed to rise above 0°. It forms nearly white crystals, which decompose when heated. The *mono*-, *di*-, and *tri*-sodium salts were prepared, the last-named existing in two forms. Its *p*-toluenesulphonic ester, colourless leaflets, m. p. 171° previously sintering, was also investigated.

3:5-Dinitro-4-hydroxyphenylarsinic acid was prepared by nitrating sodium *p*-hydroxyphenylarsinate dissolved in concentrated sulphuric acid by means of nitric acid (D 1.52), the temperature being maintained at between 15° and 20°. It decomposes when heated. In alkaline solution it yields a deep red coloration on the addition of sodium thio-sulphate. The mononitro-acid shows no change in colour on similar treatment.

5-Nitro-6-hydroxy-*m*-tolylarsinic acid was prepared from 4-hydroxy-*m*-tolylarsinic acid according to the method used in the preparation

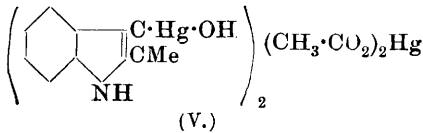
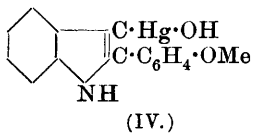
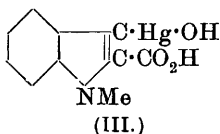
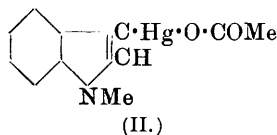
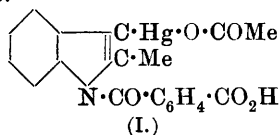
of 3-nitro-4-hydroxyphenylarsinic acid. It crystallises from 50% acetic acid in faintly yellow leaflets or needles. H. W.

**3-Nitro-4-hydroxyphenylarsinic Acid.** LUDWIG BENDA (*Ber.*, 1911, 44, 3449—3451).—Difficulties were encountered in applying the method given in the previous abstract to the technical preparation of 3-nitro-4-hydroxyphenylarsinic acid, the latter being required for the preparation of the drug salvarsan. Attempts were therefore made to prepare an azo-compound from crude *p*-hydroxyphenylarsinic acid, which, on reduction, would yield either 3-amino-4-hydroxyphenylarsinic acid or di-*m*-aminodi-*p*-hydroxyarsenobenzene (the base of salvarsan). The compounds obtained by coupling *p*-hydroxyphenylarsinic acid with *p*-nitrodiazobenzene or with diazobenzene were, however, found to be completely free from arsenic.

3-Nitro-4-hydroxyphenylarsinic acid was finally obtained in quantitative yield by warming 3-nitro-4-aminophenylarsinic acid (compare Berthelm, *Abstr.*, 1911, i, 1035) with potassium hydroxide and subsequent treatment with hydrochloric acid. When similarly treated, 5-nitro-6-amino-*m*-tolylarsinic acid yielded the corresponding 5-nitro-6-hydroxy-*m*-tolylarsinic acid. H. W.

**Preparation of Mercury Derivatives of Indoles.** C. F. BOEHRINGER & SÖHNE (D.R.-P. 236893).—The action of mercuric acetate on indole derivatives in alcoholic solution yields products which are readily decomposed by hot dilute mineral acids into their generators.

The following compounds were prepared: (I)  $C_{19}H_{15}O_3NHg$  (a red precipitate) from phthalylmethylindole; (II)  $C_{11}H_{11}O_2NHg$  (needles) from 1-methylindole; (III)  $C_{10}H_9O_3NHg$  from 1-methylindolecarboxylic acid; (IV)  $C_{15}H_{13}O_2NHg$  (a brown precipitate) from *anisylindole*, m. p.  $226^\circ$ , obtained by the action of zinc chloride on acetylanisolephenylhydrazone; (V)  $C_{22}H_{24}O_6N_2Hg_3$  (a yellow precipitate) from 2-methylindole.



F. M. G. M.

## Organic Chemistry.

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Three Normal Saturated Hydrocarbons: Triacontane, Tetratriacontane, and Hexatriacontane. ALBERT GASCARD (*Compt. rend.*, 1912, 154, 1484—1487).—Pentadecyl alcohol (Simonini, Abstr., 1892, 1301) was converted into *pentadecyl iodide*, brilliant scales, m. p. 24·5°. This was boiled with xylene and sodium for twelve hours, when *n-triacontane*,  $C_{30}H_{62}$ , was obtained as brilliant scales, m. p. 65·2—65·5°, isomeric, if not identical, with the hydrocarbons isolated from plants by Klobb (Abstr., 1910, ii, 1100), and from the products of electrolysis of potassium palmitate by Petersen (Abstr., 1906, i, 331).

Heptadecyl stearate was prepared by heating silver stearate with iodine. The compound crystallises in silky lamellæ, m. p. 64·7°, and on hydrolysis yields *n-heptadecyl alcohol*, pearly scales, m. p. 54°. *Heptadecyl iodide*, brilliant lamellæ, m. p. 33·6°, when treated with sodium gives *n-tetratriacontane*,  $C_{34}H_{70}$ , occurring as very brilliant scales, m. p. 73·2°.

Similarly, *octadecyl iodide*, m. p. 33·5°, has been converted into *n-hexatriacontane*,  $C_{36}H_{74}$ , a substance crystallising in brilliant lamellæ, m. p. 76°. W. O. W.

Catalytic Action. V. Friedel and Crafts' Reaction. JACOB BÖESEKEN (*Rec. trav. chim.*, 1911, 30, 381—391. Compare Abstr., 1910, i, 152).—In continuation of the previous work it is shown that dissociable chlorides, such as sulphuryl chloride, pentachloroethane, and chloral, act as a mixture of the non-decomposed molecule, in which the chlorine atoms are activated, and of its products of decomposition. The first-named chloride has been tried with benzene, toluene, and anisole. With the two former the products of reaction are those of the condensation of the non-dissociated molecule as well as those of the products of dissociation. The latter are in excess, since the equilibrium  $SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$  is displaced to the right by the catalyst. In the case of anisole the reaction only yields the substances formed from the products of dissociation, probably owing to the fact that the anisole is attacked so energetically by these products.

With pentachloroethane, it is only the activated chlorine in the undecomposed molecule which attacks benzene, although at the same time some of the pentachloroethane is decomposed into tetrachloroethylene and hydrogen chloride.

Chloral and benzene give a very complex reaction, a large number of substances being formed, owing to the fact that the products of decomposition of the chloral can re-combine to form other substances.

W. G.

Autoxidation of Trichloroethylene. ERNST ERDMANN (*J. pr. Chem.*, 1912, [ii], 85, 78—89).—Trichloroethylene was prepared by

the action of alcoholic potash on tetrachloroethane; it has b. p.  $85.8-86.0^{\circ}/741.6$  mm., m. p.  $-83^{\circ}$ ,  $D_4^{20}$  1.4649,  $D_4^{15}$  1.4695.

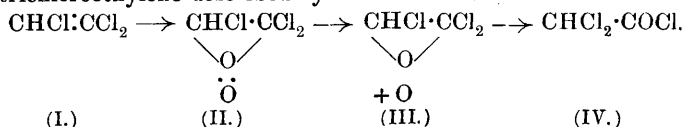
In contact with air this liquid undergoes autoxidation; at elevated temperatures and increased pressure, for example, in an autoclave, the reactions are complex, a mixture of halogen compounds boiling between  $100$  and  $240^{\circ}$  being obtained, due to polymerisations and secondary actions; at the ordinary pressure and below  $60^{\circ}$  the process is much simpler, the final products being hydrogen chloride, carbon monoxide, carbonyl chloride, and dichloroacetyl chloride, the latter being the only liquid product. In order to obtain measurable quantities of the products the experiment may have to extend over several weeks; the rate of reaction varies as the ratio of trichloroethylene to oxygen. With excess of oxygen, after twenty-eight days, the amount of oxygen removed is between 1 and 2 atoms for each molecule of trichloroethylene originally present, thus indicating the simultaneous reactions:  $\text{CHCl}:\text{CCl}_2 + \text{O} = \text{CHCl}_2\cdot\text{COCl}$  and  $\text{CHCl}:\text{CCl}_2 + \text{O}_2 = \text{CO} + \text{HCl} + \text{COCl}_2$ .

On passing ozonised oxygen through trichloroethylene, hydrogen chloride, carbonyl chloride, and carbon monoxide are formed, but no dichloroacetyl chloride. By using a solution of trichloroethylene in hexahydrotoluene at  $-79^{\circ}$ , the increase in weight due to ozonide formation could be directly determined and indicated an addition of one molecule of ozone to each molecule of trichloroethylene; the ozonide, which was too unstable and explosive to be examined in a pure state, is therefore formulated  $\begin{array}{c} \text{CHCl}\cdot\text{CCl}_2 \\ | \\ \text{O} \text{---} \text{O} \end{array}$ . The gases from an explosion

of the ozonide contained carbon monoxide, carbonyl chloride, hydrogen chloride, and an oxide of chlorine; the decomposition can be moderated by solution in chloroform or hexahydrotoluene, but the products are the same with the exclusion of the oxide of chlorine. In decomposition in the presence of water, hydrogen peroxide is formed. The spontaneous decomposition of the ozonide in a dilute solution (for example, excess of trichloroethylene), in the absence of water, indicates that an atom of oxygen is first removed, being chemically absorbed by the solvent, and after removal of excess of trichloroethylene in a vacuum, a pungent oil remains, to which is attributed the formula  $\begin{array}{c} \text{CHCl}\cdot\text{CCl}_2 \\ | \\ \text{O} \text{---} \text{O} \end{array}$ ;

it rapidly decomposes, giving carbon monoxide, hydrogen chloride, and carbonyl chloride, the first two of which can be regarded as the decomposition products of the intermediate formyl chloride. No indication of dichloroacetyl chloride was detected in any decomposition of the ozonide.

The author, therefore, suggests an explanation of the autoxidation of trichloroethylene described by the formulæ:



The method of formation of the dichloroacetyl chloride is thus explained. The nascent oxygen formed at (III), together with ordinary

oxygen, then attacks another molecule of trichloroethylene, like a molecule of ozone, giving the ozonide, which then decomposes as described above.

The possibility of autoxidation is not restricted to unsymmetrical substituted ethylenes (compare Demole, Abstr., 1878, 847; Demole and Dürr, Abstr., 1878, 846; Anschütz, Abstr., 1880, 98).

The action of other oxidising agents on trichloroethylene was also investigated; anhydrous ferric chloride attacks the substance in a sealed tube first at 85°, the former being reduced to the ferrous salt, whilst the latter gives pentachloroethane; at higher temperatures the last substance loses a molecule of hydrogen chloride, and the resultant tetrachloroethylene becomes further converted into hexachloroethane.

D. F. T.

**The Distillation of Methyl Alcohol.** GUSTAV BIRSTEIN, H. DENNELER, and ALFRED HEIDUSCHKA (*Zeitsch. angew. Chem.*, 1911, 24, 2429—2430).—Two series of experiments on the volatility of solutions of methyl alcohol have been carried out. In the first series, in which the solutions were distilled under constant pressure, it was shown that even dilute solutions of methyl alcohol yielded distillates comparatively rich in methyl alcohol. In the second series, in which the temperature was kept approximately constant, and air drawn through the solution, the concentration of alcohol in the distillate was found to be invariably slightly greater than in the original solution. The bearing of these results on the commercial preparation of formaldehyde is discussed.

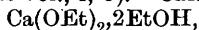
H. W.

**Action of Potassium Hydroxide on Primary Alcohols; Preparation of the Corresponding Acids.** MARCEL GUERBET (*Compt. rend.*, 1912, 154, 1487—1489; *J. Pharm. Chim.*, 1912, [vii], 5, 58—64).—Dumas and Stas (*Ann. Chim. Phys.*, 1840, [2], 73, 113) found that potassium hydroxide acts on methyl, ethyl, and amyl alcohols at 200—230°, transforming them into the corresponding acids, with liberation of hydrogen. It is now shown that in the case of the lower alcohols, dehydration also occurs with formation of ethylenic hydrocarbons. The higher alcohols, however, form only hydrogen and the potassium salt of the acid. This method of oxidation is very advantageous for alcohols above the  $C_6$  terms, since it is unnecessary to employ sealed tubes, and the yield is practically theoretical.

$\beta$ -Methylpentanol gives a 95% yield of the corresponding acid, which was characterised by conversion into its *amide*, m. p. 85°.  *$\beta$ -Heptylhexoamide*,  $CH_3 \cdot [CH_2]_3 \cdot CH(C_7H_{15}) \cdot CH_2 \cdot CO \cdot NH_2$ , has m. p. 108°.

W. O. W.

**Calcium Ethoxides.** ROBERT DE FORCRAND (*Compt. rend.*, 1912, 154, 1441—1444. Compare Abstr., 1895, i, 259; Doby, Abstr., 1903, i, 546; Chablay, this vol., i, 3).—Calcium ethoxide,



when allowed to remain over concentrated sulphuric acid, slowly loses alcohol. A specimen prepared in 1905 now approximates in com-

position to the formula  $3\text{CaO}, \text{EtOH}, 2\text{H}_2\text{O}$  or  $\text{Ca}(\text{OEt})_2, 5\text{CaO}, 5\text{H}_2\text{O}$ . The suggestion is put forward that a process of catalytic decomposition occurs, calcium oxide, the active agent, behaving as the thorium dioxide in Sabatier and Mailhe's experiments (Abstr., 1910, i, 294). Calcium ethoxide is analogous to the hypothetical compound  $\text{ThO}(\text{OEt})_2$ , losing ethylene or ether like this substance, but having greater stability at the ordinary temperature. W. O. W.

**The Crystallographic Distinctions of Nitroglycerol.** SIGURD NAUCKHOFF (*Zeitsch. Scheiss. Sprengstoffw.*, 1911, 6, 124—125).—The paper contains sketches and measurements of two forms of nitroglycerol crystals; they are of the bipyramidal class of the rhombic system, but when obtained from supercooled nitroglycerol have a flattened, tabular habit, whilst those deposited from saturated ethereal solution are of rhombic character; their optical properties are also described.

The author discusses the work of Kast (*Atti VI Cong. Internaz. chim. appl. IIIb*), and considers that the m. p. of nitroglycerol is  $-12.5^\circ$ , instead of  $-13.5^\circ$  (Kast). F. M. G. M.

**Transformations of Thio- and Seleno-phosphoric Esters.** P. PISTSCHIMUKA (*J. pr. Chem.*, 1911, [ii], 84, 746—760; from *Mem. Inst. agr. forest., Novo Alexandria*, 1911, 1—148).—The esters of thiophosphoric acid should exist in two isomeric forms,  $\text{PO}(\text{OR})_2\cdot\text{SR}$  and  $\text{PS}(\text{OR})_3$ , but, hitherto, only the latter series have been prepared. It is found that the esters of this series combine with a large number of metallic salts, yielding additive compounds, which undergo decomposition, either at the ordinary temperature or when heated, with the formation of derivatives of isothiophosphoric acid,  $\text{PO}(\text{OH})_2\cdot\text{SH}$ ; thus, the additive compounds of the alkyl esters with silver nitrate,  $\text{PS}(\text{OR})_3\cdot\text{AgNO}_3$ , readily lose one molecule of alkyl nitrate and form salts of the composition  $\text{PO}(\text{OR})_2\cdot\text{SAg}$ . The isomeric esters are obtained from these salts by the action of alkyl iodides.

A similar transformation into derivatives of the isomeric acid is caused by alkalis, alkyl oxides, alkyl halides, and ammonia, although the formation of intermediate additive products with these compounds could not be observed. The transformation is, however, not confined to esters of monothiophosphoric acid, but is common to all esters of the type  $\text{PS}(\text{XR})_2\cdot\text{OR}$  (where  $\text{X}=\text{O}$  or  $\text{S}$ ), derivatives of  $\text{PO}(\text{XH})_2\cdot\text{SH}$  being produced.

Esters of selenophosphoric acid,  $\text{PSe}(\text{OR})_3$ , have also been prepared and converted into the isomeric forms by methods similar to those employed in the case of the thiophosphates.

The alkyl thiophosphates of the type  $\text{PS}(\text{OR})_3$  were prepared by the method described previously (Abstr., 1909, i, 5); the ethyl ester has b. p.  $106^\circ/20$  mm.,  $D_4^{20}$  1.0944; the *propyl* ester, b. p.  $133$ — $134^\circ/20$  mm.,  $D_4^{20}$  1.0409; the *isobutyl* ester, b. p.  $155^\circ/20$  mm.,  $D_4^{20}$  0.9907. On treatment with nitric acid, they yield esters of phosphoric acid, and are converted by sodium into the corresponding alkyl phosphites.

The compound,  $\text{PSCl}_2\cdot\text{SEt}$ , obtained by heating the acid chloride,

$\text{PCl}_2 \cdot \text{SEt}$ , with sulphur, has b. p.  $92^\circ/10 \text{ mm.}$ ,  $D_0^{20} 1.4453$ ; it reacts with sodium ethoxide, yielding *ethyl dithiophosphate*,  $\text{PS}(\text{OEt})_2 \cdot \text{SEt}$ , b. p.  $130^\circ/20 \text{ mm.}$ ,  $D_0^{20} 1.1340$ .

*Ethyl trithiophosphate*, obtained from the chloride  $\text{PSCl}_2 \cdot \text{OEt}$  and sodium ethylmercaptide, is a liquid, b. p.  $155^\circ/20 \text{ mm.}$ ,  $D_0^{20} 1.1716$ .

The following *additive* compounds with mercuric chloride were prepared:  $\text{PS}(\text{OMe})_3 \cdot 2\text{HgCl}_2$ , transparent needles, melting at  $102^\circ$ , and simultaneously losing methyl chloride, forming the *compound*,  $\text{PO}(\text{OMe})_2 \cdot \text{SHgCl} \cdot \text{HgCl}_2$ , which passes at  $150^\circ$  into the *compound*,  $\text{SHgCl} \cdot \text{PO}(\text{OMe}) \cdot \text{OHgCl}$ ;  $\text{SHgCl} \cdot \text{PO}(\text{OEt})_2 \cdot \text{HgCl}_2$ , forms stout, transparent prisms, m. p.  $66^\circ$ , which at  $85^\circ$  yield the *compound*,



$\text{PS}(\text{OPr}^e)_3 \cdot 2\text{HgCl}_2$ ;  $\text{PS}(\text{OCH}_2\text{Pr}^e)_3 \cdot 2\text{HgCl}_2$ ;  $\text{PS}(\text{SEt})_2 \cdot \text{OEt} \cdot 2\text{HgCl}_2$ , white needles, m. p.  $81^\circ$ ;  $\text{PS}(\text{SEt})_3 \cdot 2\text{HgCl}_2$ , m. p.  $84^\circ$ . All additive compounds of the type  $\text{PS}(\text{XR})_2 \cdot \text{OR} \cdot 2\text{HgCl}_2$  lose one molecule of alkyl chloride at a relatively low temperature.

The esters of thiophosphoric acid form with ferric chloride *additive* compounds of the general formula  $3\text{PS}(\text{OR})_3 \cdot 2\text{FeCl}_3$ , which lose three molecules of alkyl chloride when heated; the *methyl* compound forms large, yellow prisms, m. p.  $125^\circ$ ; the *ethyl* compound is crystalline; the *propyl* and *isobutyl* compounds are oils.

The ethyl esters of di- and tri-thiophosphoric acid yield with ferric chloride oily *additive* compounds having a similar composition. Compounds of the same type are formed with ferric bromide, but only the *methyl* compound,  $3\text{PS}(\text{OMe})_3 \cdot 2\text{FeBr}_3$ , m. p.  $99^\circ$ , is crystalline.

Ethyl thiophosphate combines with platinic chloride, yielding the *compound*,  $3\text{PS}(\text{OEt})_3 \cdot 2\text{PtCl}_4$ , orange-yellow needles, m. p.  $103^\circ$ . The crystalline *compound* of methyl thiophosphate and auric chloride has m. p.  $110^\circ$ .

Silver nitrate dissolves in methyl thiophosphate, yielding methyl nitrate and the *silver* salt,  $\text{PO}(\text{OMe})_2 \cdot \text{SAg}$ , and in ethyl thiophosphate to form the *additive* compound,  $\text{PS}(\text{OEt})_3 \cdot \text{AgNO}_3$ , which decomposes slowly at the ordinary temperature into ethyl nitrate and the *silver* salt,  $\text{PO}(\text{OEt})_2 \cdot \text{SAg}$ , m. p.  $82^\circ$ .

Similar *compounds* are formed by the propyl and *isobutyl* esters. The phenyl ester reacts with silver nitrate, yielding *o*-nitrophenol and the *compound*,  $\text{PO}(\text{OPh})_2 \cdot \text{SAg}$ . The behaviour of silver nitrite resembles that of the nitrate.

Mercuric iodide combines with the alkyl thiophosphates,  $\text{PS}(\text{OR})_3$ , to form additive compounds, which are derivatives of the isomeric ester,  $\text{PO}(\text{OR})_2 \cdot \text{SR}$ . Thus, ethyl thiophosphate, when heated with mercuric iodide at  $180^\circ$ , yields the *compound*,  $\text{PO}(\text{OEt})_2 \cdot \text{SEt} \cdot 2\text{HgI}_2$ .

Similar compounds are formed by the esters of di- and tri-thiophosphoric acid. The interaction of alcoholic ammonia and ethyl thiophosphate yields ethylamine and the *compound*,  $\text{NH}_2 \cdot \text{PO}(\text{OEt})_2$ .

Sodium hydroxide, sodium ethylmercaptide, and sodium alkyl-oxides react with the alkyl thiophosphates to form sodium salts of the composition  $\text{PO}(\text{OR})_2 \cdot \text{SNa}$ . The action of sodium hydroxide and sodium alkyloxides on the esters of di- and tri-thiophosphoric acids leads to the formation of a mercaptan or alkyl sulphide, together

with sodium salts containing a smaller number of atoms in the molecule. Sodium ethylmercaptide, on the other hand, gives rise to the *sodium* salts,  $\text{SNa} \cdot \text{PO}(\text{SEt}) \cdot \text{OEt}$  and  $\text{PO}(\text{SEt})_2 \cdot \text{SNa}$ .

The isomeric thiophosphoric esters of the type  $\text{PO}(\text{OR})_2 \cdot \text{SR}$  are obtained by the action of alkyl iodide on the above-mentioned silver salts,  $\text{PO}(\text{OR})_2 \cdot \text{SAg}$ , in alcoholic solution. The methyl ester has b. p.  $107^\circ/20$  mm.,  $D_0^\circ 1.2685$ ; the *ethyl* ester, b. p.  $122^\circ/20$  mm.,  $D_0^\circ 1.1245$ ; the *propyl* ester, b. p.  $156^\circ/20$  mm.,  $D_0^\circ 1.0532$ ; the *isobutyl* ester, b. p.  $170^\circ/20$  mm.,  $D_0^\circ 1.0102$ .

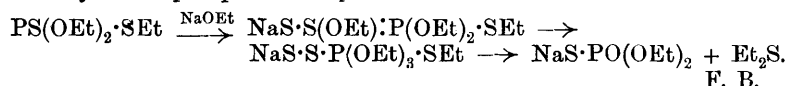
The esters of selenophosphoric acid of the formula  $\text{PSe}(\text{OR})_3$  are formed by the combination of "molecular" selenium and esters of phosphorous acid; the *methyl* ester is a liquid, b. p.  $95^\circ/20$  mm.,  $D_0^\circ 1.5387$ ; the *ethyl* ester has b. p.  $117^\circ/20$  mm.,  $D_0^\circ 1.3189$ .

The following *additive* compounds were prepared:  $\text{PSe}(\text{OMe})_3, \text{HgCl}_2$ ;  $\text{PSe}(\text{OEt})_3, \text{HgCl}_2$ ;  $\text{PSe}(\text{OMe})_3, \text{HgI}_2$ , m. p.  $66^\circ$ , and is simultaneously transformed into its *isomeride*,  $\text{PO}(\text{OMe})_2 \cdot \text{SeMe}, \text{HgI}_2$ ;  $\text{PSe}(\text{OEt})_3, \text{HgI}_2$ , large, yellow prisms, m. p.  $32^\circ$ , which pass at  $75^\circ$  into the *isomeride*,  $\text{PO}(\text{OEt})_2 \cdot \text{SeEt}, \text{HgI}_2$ , m. p.  $95^\circ$ , and when warmed under diminished pressure lose ethyl iodide, yielding the *compound*,  $\text{PO}(\text{OEt})_2 \cdot \text{SeHgI}$ .

Ethyl selenophosphate and sodium ethyl mercaptide react to form the *sodium* salt,  $\text{PO}(\text{OEt})_2 \cdot \text{SeNa}$ , m. p.  $196^\circ$ ; the corresponding *lead* salt is unstable, and yields with ethyl iodide the *ester*,  $\text{PO}(\text{OEt})_2 \cdot \text{SeEt}$ , a liquid, b. p.  $140^\circ/20$  mm.,  $D_0^\circ 1.3593$ .

Esters of the type  $\text{PS}(\text{XR})_2 \cdot \text{OR}$  are transformed by prolonged heating with an excess of alkyl iodide into their *isomerides*. Thus, ethyl thiophosphate,  $\text{PS}(\text{OEt})_3$ , is converted by ethyl iodide into its *isomeride*,  $\text{PO}(\text{OEt})_2 \cdot \text{SEt}$ , and by *isobutyl* iodide into the *ester*,  $\text{PO}(\text{OEt})_2 \cdot \text{S} \cdot \text{CH}_2\text{Pr}^2$ .

With respect to the mechanism of the above-mentioned transformations the author considers that, in all cases, *additive* compounds containing either a quadrivalent or sexavalent sulphur or selenium atom are first produced, and that these subsequently undergo tautomeric change and decomposition; the action of sodium ethoxide on ethyl dithiophosphate is represented as follows:



**Complex Compounds of Platinous Bromide with Organic Sulphides.** LEO A. TSCHUGAEFF and (Mlle.) D. FRAENKEL (*Compt. rend.*, 1912, 154, 33—35. Compare Abstr., 1910, i, 354).—When an aqueous solution of potassium platinobromide is treated with ethylenedithioglycol ether, the *compound*,  $[\text{Pt}2\text{C}_2\text{H}_4(\text{SEt})_2]\text{PtBr}_4$ , separates as a grey, microcrystalline precipitate, m. p.  $157^\circ$ . At  $100^\circ$  this substance changes into a yellow *isomeride* having the same m. p., but a greater solubility in water and chloroform. The above constitution is assigned to the substance on the ground that it unites with Reiset's bromide, forming the salt,  $[\text{Pt}4\text{NH}_3]\text{PtBr}_4$ , together with a yellow *compound*, m. p.  $157$ — $158^\circ$ . The latter has the constitution  $[\text{C}_2\text{H}_4(\text{SEt})_2]_2\text{PtBr}_2$ , since it can also be prepared by mixing the grey salt with ethylenedi-

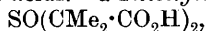
thioglycol ether and potassium platinobromide in equimolecular proportions.

Potassium platinobromide reacts with methyl sulphide, giving an unstable grey compound,  $[\text{Pt}_4\text{Me}_2\text{S}]\text{PtBr}_4$ , m. p.  $160^\circ$ . On crystallisation from chloroform this changes into Blomstrand's salt,  $(\text{Me}_2\text{S})_2\text{PtBr}_2$ .

Platinoiodides do not form derivatives with organic sulphides.

W. O. W.

**Intramolecular Rearrangements of Aliphatic Sulphoxides.** THOMAS P. HILDITCH (*Ber.*, 1911, **44**, 3583—3589).—By treatment with alcoholic hydrogen chloride or with boiling acetic anhydride, *diisoamyl*-sulphoxide is converted into *isoamyl* mercaptan and *isovaleraldehyde*; by the former reagent, thionylacetic acid is decomposed into thioglycollic and glyoxylic acids. *a-Thionyl-diisobutyric acid*,



m. p.  $186^\circ$ , is unchanged by alcoholic hydrogen chloride.

An explanation of these decompositions is given which assumes the intermediate formation of thionium compounds.

C. S.

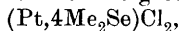
**Complex Compounds of Platinum with Organic Selenides.** I. E. FRITZMANN (*Zeitsch. anorg. Chem.*, 1911, **73**, 239—255).—The isomerism of the compounds of platinous chloride with organic sulphides has been discussed by Tschugaeff and Subbotin (*Abstr.*, 1910, i, 354). The corresponding selenium compounds have not been examined, with the exception of those derived from ethyl selenide (Petren, *Zeitsch. anorg. Chem.*, 1899, **20**, 62).

The isomerism observed is similar to that of the sulphur compounds. The  $\alpha$ -compounds are more soluble than the  $\beta$ -compounds, and are darker in colour. The former are to be regarded, in accordance with Werner's views, as *cis*-modifications, and the latter as *trans*-modifications. The  $\gamma$ -compounds are less stable than those of sulphur.

A 4% solution of potassium platinochloride (1 mol.) is shaken with the alkyl selenide (2 mols.) until decolorised. The  $\alpha$ -compound is then chiefly obtained. In order to prepare the  $\beta$ -compound, 4 mols. of selenide are used, and the mixture is digested at  $70$ — $75^\circ$  in a closed vessel until all is dissolved. The cooled solution is evaporated in a vacuum over calcium chloride and solid paraffin or rubber, and potassium chloride is then removed by washing. For analysis, the compound is decomposed with sulphuric acid, and heated in hydrogen to remove selenium, the residual platinum being weighed. Selenium is estimated by boiling with aqua regia in a quartz vessel, evaporating, and precipitating the slightly acid solution with a hot saturated solution of hydrazine sulphate. The precipitated mixture of platinum and selenium is collected, dried at  $100^\circ$ , and weighed, and the selenium is then removed by heating in hydrogen.

*Methyl selenide platinous chloride*,  $\text{PtCl}_2\cdot 2\text{Me}_2\text{Se}$ , has m. p.  $163$ — $163.5^\circ$ . The  $\alpha$ -form is partly converted into the  $\beta$ -form by repeated crystallisation from chloroform, and the reverse change is also observed. At a

low temperature it is possible to obtain the  $\gamma$ -modification, but it can only be isolated in the form of the green Magnus salt,



by the addition of a solution of Reiset's salt,  $(\text{Pt}, 4\text{NH}_3)\text{Cl}_2$ .

*Methyl selenide platinous bromide*,  $\text{PtBr}_2 \cdot 2\text{Me}_2\text{Se}$ , is red, and has m. p.  $171^\circ$  (decomp.). Propyl selenide forms the compound,  $\text{PtCl}_2 \cdot 2\text{Pr}_2\text{Se}$ , m. p.  $42.5-43^\circ$ ; only the  $\alpha$ -modification has been obtained. *n*-Butyl selenide only yields an oily product. *iso*Amyl selenide yields an  $\alpha$ -compound,  $\text{PtCl}_2 \cdot 2(\text{C}_5\text{H}_{11})_2\text{Se}$ , m. p.  $97-97.5^\circ$ , and a  $\beta$ -compound, m. p.  $115-116^\circ$ . The phenyl selenide  $\alpha$ -compound has m. p.  $180^\circ$ , and the  $\beta$ -compound, m. p.  $178-179^\circ$ .

Diethyl trimethylene diselenide forms an  $\alpha$ - and a  $\beta$ -compound,  $2\text{PtCl}_2 \cdot 2\text{CH}_2(\text{CH}_2 \cdot \text{SeEt})_2$ , both of which have m. p.  $176-176.5^\circ$ . A  $\gamma$ -modification has been recognised by conversion into the Magnus salt.  
C. H. D.

**Chemico-crystallographic Notes.** L. WAGNER (*Zeitsch. Kryst. Min.*, 1911, 50, 47-56).—Phosphonium iodide,  $\text{PH}_4\text{I}$ ; tetragonal, D 2.860. Tetramethylphosphonium iodide; tetragonal,  $a:c=1:0.7310$ , D 1.746. Calcium formate,  $\text{Ca}(\text{CHO}_2)_2$ ; orthorhombic (bipyramidal) [ $a:b:c=0.7599:1:0.9363$  (Plathan)], D 2.023. Strontium formate,  $\text{Sr}(\text{CHO}_2)_2$ ; orthorhombic (bisphenoidal),  $a:b:c=0.7846:1:0.8292$ , D 2.693. Mixed crystals of calcium and strontium formate resemble those of either one or other of the simple salts, but they also show an intermediate tetragonal form; the two salts are therefore isotri-morphous. Strontium formate forms the hydrate,  $\text{Sr}(\text{CHO}_2)_2 \cdot 2\text{H}_2\text{O}$ , D 2.259; but calcium formate forms no hydrate. Anhydrous oxalic acid; orthorhombic,  $a:b:c=0.8301:1:0.7678$ , D 1.900. Nitrobenzene; monoclinic (domatic?),  $a:b:c=1.280:1:1$ ;  $\beta=117^\circ 21'$ , m. p.  $3.8^\circ$ .

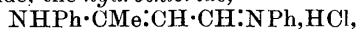
L. J. S.

**Direct Synthesis of the Glycerides.** GIUSEPPE GIANOLI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 653-654. Compare Abstr., 1911, i, 349; Bellucci and Manzetti, *ibid.*, i, 259).—Polemical.

R. V. S.

**Formation of Cork.** MAX VON SCHMIDT (*J. pr. Chem.*, 1911, [ii], 84, 830-832).—A reply to Zeisel's criticism (Abstr., 1911, i, 768) of previous work of the author (Abstr., 1910, i, 540). F. B.

**Derivatives of Tetrolaldehyde and its Acetal [Diethoxybutinene].** PAUL L. VIGUIER (*Compt. rend.*, 1911, 153, 1231-1233. Compare Abstr., 1909, i, 691).—On treating diethoxybutinene with aniline hydrochloride, the *hydrochloride*,



is obtained as yellow crystals decomposing at  $160^\circ$ . No definite compound was obtained from aniline, and phenylmethylpyrazole was the only definite product with phenylhydrazine. Urethane combines with the acetal, in presence of hydrogen chloride, giving the compound,  $\text{CMe} \cdot \text{C} \cdot \text{CH}(\text{NH} \cdot \text{CO}_2\text{Et})_2$ , slender needles, m. p.  $188-189^\circ$ . The acetal unites with alcohol, in presence of sodium ethoxide, forming

*ααγ-triethoxy-Δ<sup>2</sup>-butylene*,  $\text{OEt} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CH}(\text{OEt})_2$ , b. p. 190—195°, under ordinary pressure, 82—86°/15 mm.,  $D^{21}_D$  0.908,  $n^{21}_D$  1.430.

Exposure to air converts triethoxybutylene into  $\beta$ -ethoxycrotonic acid. On hydrolysis, it appears to form acetoacetaldehyde, but this rapidly polymerises to triacetylbenzene. When treated with semicarbazide hydrochloride, it yields a compound, m. p. 127—128°, having the constitution 
$$\begin{array}{c} \text{CH} \cdot \text{CMe} \\ | \\ \text{CH} = \text{N} \end{array} > \text{N} \cdot \text{CO} \cdot \text{NH}_2.$$
 W. O. W.

**Action of Monochlorocarbamide on Ketones.** AUGUSTE BÉHAL and A. DETÈUF (*Compt. rend.*, 1911, 153, 1229—1231. Compare Abstr., 1911, i, 957).—On allowing chlorocarbamide to act on the calculated amount of an aliphatic ketone in aqueous solutions for three to five days, an excellent yield of a monochloro-ketone is obtained. Symmetrical ketones give the halogen derivative, in which the chlorine is next to the carbonyl group, whilst unsymmetrical ketones give two halogen derivatives, the secondary one predominating.

On boiling the semicarbazones of chloro-ketones with water, hydrogen chloride is eliminated and a ketol formed; thus the semicarbazone of  $\beta$ -chloropropane- $\gamma$ -one gives  $\beta$ -hydroxypropane- $\gamma$ -one.

Chlorocarbamide and methyl hexyl ketone give a *chloro-octanone*, m. p. -25°, b. p. 104—108°/20 mm.,  $D$  1.0034; the *semicarbazone* has m. p. 133°. Acetophenone forms only  $\omega$ -chloroacetophenone; cyclic ketones also undergo chlorination. W. O. W.

**Action of Dilute Nitric Acid on Starch and on Dextrin.** WILLIAM OECHSNER DE CONINCK and ALBERT RAYNAUD (*Rev. gen. Chim. pure appl.*, 1910, 14, 169—170).—An investigation on the action of dilute nitric acid on dextrin and starch. The dilution of the nitric acid varied from 1 to 5 c.c. of acid (36°Bé) in 50 c.c. water, and the results indicated that the amounts of dextrose formed during the same interval of time increased with the concentration of the acid, but that this increase was less rapid with dextrin than with starch.

With low concentrations, more dextrin than starch underwent hydrolysis, but at the highest concentration dextrin yielded 87.7% dextrose as compared with 90% from starch, indicating that in the former oxidation had to some extent interfered with saccharification.

F. M. G. M.

**Modifications Undergone by Nitrated Celluloses and Powders Derived from them, under the Influence of Heat.** R. FRIC (*Compt. rend.*, 1912, 154, 31—32).—The changes produced in nitrated celluloses by heat can be followed by measuring the viscosity of an acetone solution in the usual way. The effect of heating the solid at 110° is to diminish the viscosity of the solution.

W. O. W.

**The "Cause" of the Beckmann Rearrangement.** PIETER J. MONTAGNE (*Chem. Weekblad*, 1911, 8, 968—976. Compare Abstr., 1910, i, 623).—In the author's opinion, the Beckmann rearrangement

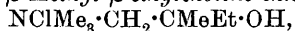
is a simple exchange of position between the alkyl group attached to carbon and that attached to nitrogen. The assumption of the intermediate formation of an oxime-ester is at variance with the experimental facts.

A. J. W.

**New Compounds of the Choline Type.** G. A. MENGE (*J. Biol. Chem.*, 1911, 10, 399—406).—The *chloride* of  $\alpha$ -methylcholine,  $\text{NCI Me}_3 \cdot \text{CH Me} \cdot \text{CH}_2 \cdot \text{OH}$ , has been prepared as follows: allyl chloride was converted into the chlorohydrin, and then into the corresponding acetate; this by treatment with hydrochloric acid was converted into the acetate-chloride, and saponified to give the desired chlorohydrin,  $\text{CH Me Cl} \cdot \text{CH}_2 \cdot \text{OH}$ . On heating at  $100^\circ$  in a sealed tube with trimethylamine dissolved in alcohol, the choline was obtained as a viscous, yellow oil, from which a hygroscopic, colourless solid separated on cooling. The yellow *platinichloride* decomposes at  $254$ — $255^\circ$ ; the *aurichloride* is definitely crystalline: it sinters above  $180^\circ$ , m. p.  $198$ — $199.5^\circ$ .

By condensing monochloroacetone with magnesium alkyl halides, the chlorohydrins of  $\beta$ -methylpropylene  $\alpha\beta$ -glycol and  $\beta$ -methylbutylene  $\alpha\beta$ -glycol are obtained. With trimethylamine these yield  $\beta$ -disubstituted cholines.

$\beta$ -Dimethylcholine chloride,  $\text{NCI Me}_3 \cdot \text{CH}_2 \cdot \text{C Me}_2 \cdot \text{OH}$ , is obtained as a colourless, hygroscopic solid. The *platinichloride* crystallises in yellow, short, individual prisms or foliated clusters, which blacken at  $240^\circ$ , decomp.  $245^\circ$ .  $\beta$ -Methyl- $\beta$ -ethylcholine chloride,



forms a *platinichloride*, which sinters at  $240^\circ$ , m. p.  $242$ — $243^\circ$  (decomp.).

E. F. A.

**Stereoisomeric Cobalt Compounds.** ALFRED WERNER (*Annalen*, 1911, 386, 1—272).—The author's investigations on the stereoisomeric cobalt compounds have now reached such a stage, that stringent proofs have been obtained for the stereochemical conceptions, and methods which are free from objections have been devised for the determination of the configurations of the various isomerides. A summary of the methods used, and of the results obtained, is given in the present paper, the greater part of the work consisting of hitherto unpublished investigations.

The general results arrived at may be briefly summarised as follows: The investigation of inorganic compounds containing the complex radicle  $\text{CoA}_6$  has shown that in all these compounds the six groups  $A$  are in direct connexion with the central cobalt atom. Any space formula used to represent these compounds must be such that positions occupied by the groups  $A$  are all equivalent; this follows from the fact that no stereoisomerides are known having the formula  $\left[ \text{Co} \begin{smallmatrix} A_5 \\ B \end{smallmatrix} \right]$ . It has hitherto been impossible to prepare more than two stereoisomerides of the formula  $\left[ \text{Co} \begin{smallmatrix} A_4 \\ B_2 \end{smallmatrix} \right]$ , so that the groups

*A* and *B* must occupy the corners of an octahedron, the cobalt atom being in the centre; the plane formula and prism formula would each give three possible isomerides. The groups *B* in the stereoisomerides  $\left[ \text{Co} \begin{smallmatrix} \text{A}_4 \\ \text{B}_2 \end{smallmatrix} \right]$  must consequently occupy the *cis*- and *trans*-positions.

Investigation has shown that in all cases when the two groups *B* are replaced by a bivalent group, giving three-, four-, five-, or six-membered rings, the same compound results, no matter whether the *cis*- or *trans*-isomeride was used in the preparation. It appears, therefore, that there is only one position in the complex (the *cis*-position) favourable to the formation of such rings, this being in accordance with the octahedral arrangement of the groups, and in analogy with the formation and non-formation of anhydrides from organic *cis*- and *trans*-isomerides. Use has been made of this result in the determination of the configuration of the various stereoisomerides, but great caution is necessary in drawing conclusions, owing to the ready transformation of one isomeride into the other

*Diaquo*-salts,  $\left[ \begin{smallmatrix} \text{H}_2\text{O} \\ \text{H}_2\text{O} \end{smallmatrix} \text{Co en}_2 \right] \text{X}_3$ .—The *cis*-isomerides have been characterised by their preparation from the carbonato-salts, as also from the hexol- and diol-dicobaltic salts. The *cis*-compounds only are known in the tetrammine series, whereas both *cis*- and *trans*-compounds of the ethylenediamine series have been prepared. The configuration of the *hydroxo-aquo*-salts,  $\left[ \begin{smallmatrix} \text{HO} \\ \text{H}_2\text{O} \end{smallmatrix} \text{Co en}_2 \right] \text{X}$ , is deduced from that of the *diaquo*-salts because of their formation from the latter by loss of a molecule of acid. Both *cis*- and *trans*-isomerides are known.

*Dihalogeno*-salts,  $\left[ \text{X}_2 \text{Co en}_2 \right] \text{X}_2$ .—The two stereoisomeric dichloro-salts are known, both in the tetrammine and diethylenediamine series. The *cis*-isomeride (*violeto*-salt) is the first product of the action of concentrated hydrochloric acid on the carbonato-salt; it readily changes into the *trans*-isomeride (*praseo*-salt) under the influence of concentrated hydrochloric acid. The *cis*-dibromotetra-mmine salts are not known. Stereoisomeric *halogeno-aquo*-salts,  $\left[ \begin{smallmatrix} \text{X} \\ \text{H}_2\text{O} \end{smallmatrix} \text{Co en}_2 \right] \text{X}_2$ , are not known; in all cases the *cis*-isomeride is alone formed.

*Halogeno-isothiocyanato*-salts,  $\left[ \begin{smallmatrix} \text{H} \\ \text{SCN} \end{smallmatrix} \text{Co en}_2 \right] \text{X}$ .—Stereoisomeric chloro- and bromo-*isothiocyanato*-salts are known. Their configuration has to be decided chiefly by their colour (see later), since they so readily undergo transformation. The *isothiocyanate* group deepens the colour of the cobaltammines, and it follows that the violet chloro-salts and indigo-blue bromo-salts are the *trans*-isomerides, the *cis*-isomerides being red and bluish-red respectively. Similar results hold for the *isothiocyanato-aquo*-salts,  $\left[ \begin{smallmatrix} \text{SCN} \\ \text{H}_2\text{O} \end{smallmatrix} \text{Co en}_2 \right] \text{X}_2$ , the violet salts forming the *trans*-, and the orange the *cis*-isomerides. The configuration of the *halogeno-amminediethylenediamine* salts,  $\left[ \begin{smallmatrix} \text{X} \\ \text{H}_3\text{N} \end{smallmatrix} \text{Co en}_2 \right] \text{X}_2$ , has been determined by oxidation of the corresponding *halogeno-isothio*-

cyanato-salts with hydrogen peroxide; both the chloro- and bromo-salts have been prepared. The constitution of the *aquo-ammine-diethylenediamine* salts,  $\left[ \begin{smallmatrix} \text{H}_2\text{O} \\ \text{H}_3\text{N} \end{smallmatrix} \text{Co en}_2 \right] \text{X}_3$ , is determined by their transformation into the halogeno-ammine-salts by interaction with the halogen acids. The stereoisomeric *diisothiocyanato*-salts,  $\left[ \begin{smallmatrix} \text{SCN} \\ \text{SCN} \end{smallmatrix} \text{Co en}_2 \right] \text{X}$ , have already been described (Abstr., 1900, i, 86), but the wrong configuration given to them. The *cis*-isomerides are those which were formerly characterised as dithiocyanato-salts, as may be deduced by their oxidation with hydrogen peroxide and subsequent evaporation with hydrochloric acid, whereby the *cis*-chloro-ammine salts are formed. The *trans*-isomerides on oxidation with chlorine yield *trans*-diamminediethylenediaminecobaltic salts, and were formerly characterised as *diisothiocyanato*-salts. The configuration of the *diamminediethylenediamine* salts,  $\left[ \begin{smallmatrix} \text{H}_3\text{N} \\ \text{H}_3\text{N} \end{smallmatrix} \text{Co en}_2 \right] \text{X}_3$ , was determined by their solubilities, the *cis*- being more readily soluble than the *trans*-isomerides (compare below). The configuration previously ascribed to them (Abstr., 1907, i, 290) is incorrect. Oxidation of the *isothiocyanatoamminediethylenediamine* salts,  $\left[ \begin{smallmatrix} \text{SCN} \\ \text{H}_3\text{N} \end{smallmatrix} \text{Co en}_2 \right] \text{X}_2$ , with hydrogen peroxide gives rise to the diammine salts, whereby the structure of the former salts is ascertained. The configuration of the *nitroamminediethylenediamine* salts,  $\left[ \begin{smallmatrix} \text{O}_2\text{N} \\ \text{H}_3\text{N} \end{smallmatrix} \text{Co en}_2 \right] \text{X}_2$ , follows from their formation from the isomeric *aquo-ammine* salts, or from their transformation into the chloro-ammine salts. On oxidation of the *isothiocyanatonitrodiethylenediamine* salts,  $\left[ \begin{smallmatrix} \text{SCN} \\ \text{O}_2\text{N} \end{smallmatrix} \text{Co en}_2 \right] \text{X}$ , with hydrogen peroxide, nitroammine-salts are formed, whereby the configuration of the former salts can be ascertained. Of the *dinitro-diethylenediamine* salts,  $[(\text{NO}_2)_2 \text{Co en}_2] \text{X}$ , the croceo-salts are the *trans*-, whilst the flavo-salts are the *cis*-isomerides. This is ascertained by their formation from the stereoisomeric diaquo-salts by the action of nitrous acid, the dinitrito-salts first formed transforming into the dinitro-salts. The configuration of the *chloronitro*-salts,  $\left[ \begin{smallmatrix} \text{Cl} \\ \text{O}_2\text{N} \end{smallmatrix} \text{Co en}_2 \right] \text{X}$ , is ascertained by their transformation into the dinitro-salts by interaction with sodium nitrite.

*Influence of the Constitution of the Complex Radicle,  $\left[ \text{Co} \begin{smallmatrix} \text{A}^4 \\ \text{B}_2 \end{smallmatrix} \right]$ , on the Existence of Stereoisomeric Cobalt Ammonias.*—The *cis*-compounds of the ammonia series are less readily produced than those of the diethylenediamine series, and transform much more readily into the *trans*-isomerides. *cis*-Dichloro-compounds of the trimethylenediamine series cannot be prepared, all methods of preparation giving the green *trans*-isomerides. The nature of the halogen has an effect, in that, although *cis*- and *trans*-isomerides have been prepared in the dichloro- and dibromo-diethylenediamine series, no *cis*-dibromo-compounds have been obtained in the ammonia series; in neither series could iodo-

compounds be obtained. The influence of the bivalent group Z in the salts  $[Z \text{ Co en}_2]X$ , is shown by the fact that, although sulphito-, carbonato-, oxalato-, and malonato-salts have been prepared, no compounds derived from succinic, malic, and tartaric acids have been obtained. The formation of a seven-ring does not, therefore, take place, which is in accordance with the results obtained with the alkylamines (compare Abstr., 1907, ii, 161).

*Ionisation Isomerides.*—A full list of such compounds is given; for example, the *cis*- and *trans*-isomerides of the chloronitrothiocyanate, nitroisothiocyanato-chloride, and chloroisothiocyanato-nitrite in the diethylenediamine series.

*Relation between the Solubility of the Cobalt Ammonias and their Constitution and Configuration.*—The *cis*-isomerides are generally more soluble than the *trans*-isomerides. There are exceptions, as, for example, with the dinitrodiethylenediaminecobaltic iodides. It is probable, also, that the solubility of the salt increases with the number of ionogenic radicles.

*Relation between the Colour of the Cobalt Ammonias and their Constitution and Configuration.*—The chief influence on the colour is exerted by the radicles directly connected with the cobalt atom, and is the only one considered here. No colourless cobalt compounds are known. The influence of the element directly attached to the cobalt atom is shown by the series, C, N, S, O, Cl, Br, I, the elements being arranged in the order of their bathochromic action. This series can be extended as follows, when the various radicles are taken into account: CN, CO; NO<sub>2</sub>, en, NH<sub>3</sub>, NCS; SO<sub>3</sub>; OH<sub>2</sub>, O·NO, O·Acyl, OH; Cl, Br, I; thus the least-coloured compounds of cobalt are the pale yellow cyanocobaltammonias,  $[\text{Co}(\text{CN})_6]\text{R}_3$ . Amines, for example, ethylenediamine, propylenediamine, hydroxylamine, and pyridine, have the same effect as ammonia. It is noteworthy that substitution in the *trans*-position has a much greater bathochromic effect than substitution in the *cis*-position.

*Differences in the Reactions of Stereoisomeric Cobalt Ammonias.*—Radicles which are in the *cis*-position with respect to each other are not so firmly combined as those in the *trans*-position, and enter into reaction much more readily; for example, by the action of hydrochloric acid on *cis*-dinitrotetramminecobaltic salts, both nitro-groups are replaced by chlorine, with the formation of the *trans*-dichloro-salts, whereas when the *trans*-dinitro-salts are heated with hydrochloric acid, only one nitro-group is replaced, the *trans*-chloronitro-salts being formed. Differences of this kind have caused many difficulties in the determinations of the configuration of the stereoisomerides. These difficulties are especially marked in the case of the isothiocyanato-salts, a full discussion of which compounds is given. Differences also occur in additive reactions; for example, the *trans*-chloroaminediethylenediamine salts readily give the diammine salts when dissolved in liquid ammonia:  $\left[ \begin{smallmatrix} (1) & \text{Cl} \\ (6) & \text{H}_3\text{N} \end{smallmatrix} \text{ Co en}_2 \right] \text{Cl}_2 + \text{NH}_3 = \left[ \begin{smallmatrix} \text{H}_3\text{N} \\ \text{H}_3\text{N} \end{smallmatrix} \text{ Co en}_2 \right] \text{Cl}_3$ , whereas the *cis*-compounds are unacted on, even after keeping for hours dissolved in liquid ammonia.

*Intramolecular Reactions with the Cobalt Ammonias.*—The various

cases are summarised in which there occurs: (a) Intramolecular reactions with expulsion of ammonia or water; for example, the chlorides, bromides, and sulphates of chloro-aquo- and bromo-aquo-diethylenediaminecobaltic salts are stable, whilst the nitrites, on keeping,

change in accordance with the equation:  $\left[ \begin{smallmatrix} \text{Cl} \\ \text{H}_2\text{O} \end{smallmatrix} \text{Co en}_2 \right] (\text{NO}_2)_2 \rightarrow$

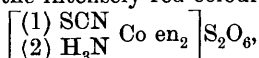
$\left[ \begin{smallmatrix} \text{Cl} \\ \text{O}_2\text{N} \end{smallmatrix} \text{Co en}_2 \right] \text{NO}_2 + \text{H}_2\text{O}$ . (b) Intramolecular reactions in which inter-

change of the acid-residues takes place; for example, when a drop of water is added to the pure, green *trans*-dichlorodiethylenediaminecobaltic nitrite,  $[\text{Cl}_2 \text{Co en}_2] \text{NO}_2$ , it immediately changes into the

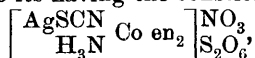
yellowish-red chloronitrodiethylenediamine chloride,  $\left[ \begin{smallmatrix} \text{Cl} \\ \text{O}_2\text{N} \end{smallmatrix} \text{Co en}_2 \right] \text{Cl}$ .

(c) Transformation of stereoisomerides into each other. Direct transformations have hitherto been observed in comparatively few cases, and even then it is probable that intermediate products are formed which have not so far been isolated.

*Additive Compounds of the Cobalt Ammonias.*—A full discussion is given of cases such as the following: By the addition of silver nitrate to a solution of the intensely-red coloured salt,



golden-yellow prisms of the composition  $\left[ \begin{smallmatrix} \text{SCN} \\ \text{H}_3\text{N} \end{smallmatrix} \text{Co en}_2 \right] \text{S}_2\text{O}_6, \text{AgNO}_3$  are obtained. The change in colour observed, and the various reactions of this compound, point to its having the constitution



that is, it is a silver thiocyanatoamminediethylenediaminecobaltic salt. The study of such compounds is of great service in elucidating the mechanism of the various reactions of the cobalt ammonias.

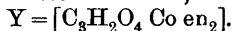
*Spatial Change of Position during Reactions of the Stereoisomeric Cobalt Ammonias.*—(Compare Abstr., 1911, i, 424.)

[With JOS. RAPIPORT.]—*Carbonatodiethylenediaminecobaltic* salts,  $\text{YX}$ , where  $\text{Y} = [\text{CO}_3 \text{Co en}_2]$ , are prepared from any dichloro- or dibromo-salt by the action of sodium or potassium carbonate. The mixture with water is boiled until the solution becomes an intense blue colour, when the reaction is complete. The *chloride*,  $\text{YCl} \cdot \text{H}_2\text{O}$ , is thus obtained from 1:6-dichlorodiethylenediaminecobaltic chloride by interaction with sodium carbonate. The hot filtrate from undissolved salt deposits, on cooling, dark red, flat, columnar crystals, which become anhydrous at 70–80°. It may also be obtained from a concentrated solution of the bromide by shaking with silver chloride. The *bromide*,  $\text{YBr} \cdot \text{H}_2\text{O}$ , is obtained from the chloride by precipitation with potassium bromide. On recrystallisation, it deposits partly as hydrated and partly as anhydrous salt. The hydrated salt forms large, dark red, hexagonal, efflorescent columns, the anhydrous salt being brownish-red in colour. One gram of the salt dissolves in 30 c.c. of water at 50°. The *iodide*,  $\text{YI}$ , is obtained similarly to the bromide, and forms shining, dark red, flat prisms, which are soluble in water to the extent of 1 gram in 70 c.c. of water at 80°. The *nitrate*,  $\text{YNO}_3 \cdot \text{H}_2\text{O}$ ,

results from the interaction of the bromide and silver nitrate; it crystallises in dark bluish-red, shining, flat needles. Twenty c.c. of water dissolve 1 gram at 60°. The *thiocyanate*, YSCN, the *dithionate*,  $Y_2S_2O_6 \cdot 2H_2O$ , and the *sulphate*,  $Y_2SO_4 \cdot 5H_2O$ , were also obtained by reactions involving double decomposition. They crystallise respectively in red, hexagonal prisms or needles, long, dark red prisms, and reddish-black, flat prisms. The sulphate loses  $5H_2O$  at 100°.

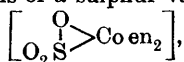
[With R. HARTMUTH.]—Oxalatodiethylenediaminecobaltic salts,  $[C_2O_4 Co en_2]X$ , have been known for some time (compare Abstr., 1899, ii, 660), and an attempt has now been made to introduce ammonia into the radicle to find out if a spatial transformation takes place. As a matter of fact, ammonia does enter into the inner sphere, but *cis-diamminediethylenediaminecobaltic* salts,  $Y_2(C_2O_4)X_4$ , are alone formed, where  $Y = [Co \begin{smallmatrix} (NH_3)_{1/2} \\ en_2 \end{smallmatrix}]$ . Four grams of the oxalatodiethylenediamine salt are heated with 15 c.c. of saturated ammonia solution for two hours in a bomb-tube at 110°; the contents of the tube are taken up with water, the solution concentrated, and potassium iodide added. The sparingly soluble oxalatodiethylenediaminecobaltic iodide is first precipitated, and from the mother liquor brown, monoclinic, columnar crystals of the *iodide oxalate*,  $Y_2(C_2O_4)I_4$ , are obtained. By interaction with silver chloride, irregular, light yellow, crystalline aggregates of the *chloride oxalate*,  $Y_2(C_2O_4)Cl_4$ , are obtained. In contradistinction to the aqueous ammonia, liquid ammonia has no action on the oxalato-chloride.

*Malonatodiethylenediaminecobaltic* salts,  $YX$ , where



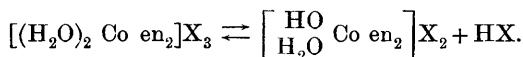
—The *hydrogen malonate*,  $YC_3H_2O_4$ , is obtained from carbonatodiethylenediaminecobaltic bromide by first preparing the hydroxide by shaking the solution with freshly precipitated silver oxide. Malonic acid (2 mols.) is added to the filtrate from the silver bromide, and on concentrating, carmine-red crystals of the desired salt are obtained. By double decomposition with potassium nitrate and ammonium thiocyanate respectively, red, shining leaflets of the *nitrate*,  $YNO_3$ , and *thiocyanate*, YSCN, are obtained. Attempts to prepare corresponding salts by using succinic, malic, or tartaric acids were unsuccessful.

[With MARIE POKROWSKA.]—*Sulphitodiethylenediaminecobaltic* salts,  $YX$ , where  $Y = [SO_3 Co en_2]$ .—The *chloride*,  $YCl \cdot \frac{1}{2}H_2O$ , is obtained by boiling down a solution of sodium sulphite (10 grams) with *trans*-dichlorodiethylenediaminecobaltic chloride (10 grams, free from hydrochloric acid) in 50 c.c. of water to half its bulk. After filtering, dark brown crystals of indefinite shape are deposited. The same results are obtained if the *cis*-dichloro-chloride is used in the preparation. The sulphito-group is co-ordinately connected with the cobalt in the *cis*-position, since on heating with concentrated hydrochloric acid, *cis*-dichlorodiethylenediaminecobaltic chloride is produced. Moreover, the brown colour of the salt shows that the  $SO_3$ -radicle is linked up with the cobalt by means of a sulphur valency, thus:



since if it were linked through two oxygen atoms it would be red in colour. On triturating the semihydrate with hydrochloric acid, a reddish-brown solution is formed, from which orange-brown, shining scales of the *trihydrate*,  $\text{YCl}_3 \cdot 3\text{H}_2\text{O}$ , can be obtained. The solution gives characteristic precipitates with potassium iodide, acetic acid, and sodium nitrite, and with chloroplatinic acid. On trituration with fuming hydrobromic acid and subsequent gentle warming, green crystals of *trans*-dibromodiethylenediaminecobaltic bromide are obtained. Both hydrates can be dehydrated at  $105^\circ$ . By double decomposition with potassium thiocyanate, brownish-yellow, shining needles or scales of the *thiocyanate*,  $\text{YSCN}_3 \cdot 2\text{H}_2\text{O}$ , are obtained. The *platinichloride*,  $\text{Y}_2\text{PtCl}_6 \cdot 4\text{H}_2\text{O}$ , forms brown, star-shaped crystals; the *aurichloride*,  $\text{YAuCl}_4 \cdot 3\text{H}_2\text{O}$ , crystallises in thin, yellowish-brown, shining scales.

[With K. R. LANGE].—*Diaquodiethylenediaminecobaltic* salts,  $\text{YX}_3$ , where  $\text{Y} = \left[ \begin{smallmatrix} \text{H}_2\text{O} \\ \text{H}_2\text{O} \end{smallmatrix} \text{Co en}_2 \right]$ .—The salts of the *cis*-series are all much more soluble than the *trans*-isomerides. The latter are remarkable in that by precipitation of their aqueous solutions with potassium iodide, the *trans*-hydroxo-aquo-iodide is formed and not the diaquo-iodide, which shows that in aqueous solutions the diaquo-salts are hydrolysed in accordance with the equation :



A number of salts have been prepared in addition to those previously described (compare Abstr., 1907, i, 188). The *cis-nitrate*,  $\text{Y}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ , was obtained from *cis*-diaquodiethylenediaminecobaltic bromide by the action of concentrated nitric acid at a low temperature. It forms red, glistening plates, and can be dehydrated over calcium chloride. The *cis-sulphate*,  $\text{Y}_2(\text{SO}_4)_3$ , was prepared from the bromide by interaction with silver sulphate, and crystallises in red, glistening needles. Other *cis*-salts could not be obtained.

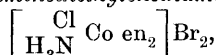
New methods of preparation of the *cis*-bromide are as follows : (1) 10 grams of carbonatodiethylenediaminecobaltic bromide are mixed with 18 c.c. of cold water, and 5 c.c. of concentrated nitric acid added drop by drop. The solution is neutralised with potassium hydroxide, half as much again of the hydroxide added, and then precipitated with sodium bromide (23 grams). (2) The hydroxo-aquobromide is triturated with a little concentrated hydrobromic acid, and then washed with alcohol and ether. The dry product is dissolved in cold water containing a little hydrobromic acid, saturated (at  $0^\circ$ ) hydrobromic acid added, and the solution allowed to crystallise in a freezing mixture.

The *trans-nitrate*,  $\text{Y}(\text{NO}_3)_3$ , was prepared from the *trans*-bromide by a method similar to that used for the *cis*-salt. It could also be obtained by interaction with silver nitrate. It forms brownish-red needles. The *trans-sulphate*,  $\text{Y}_2(\text{SO}_4)_3$ , was obtained from the bromide by interaction with sulphuric acid as brownish-red leaflets. The *trans-dithionate*,  $\text{Y}_2(\text{S}_2\text{O}_6)_3$ , and the *trans-thiocyanate*,  $\text{Y}(\text{SCN})_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ , crystallise respectively as slender, brownish-red needles and as dark brown plates. The iodide could not be obtained, for the reason already given.

An account is given of the transformation of the diaquodiethylenediaminecobaltic halogenides into dihalogenodiethylenediaminecobaltic salts on keeping for some time or on heating at 105—115°.

A number of *hydroxo-aquodiethylenediaminecobaltic* salts,  $YX_2$ , where  $Y = \left[ \begin{smallmatrix} \text{HO} \\ \text{H}_2\text{O} \end{smallmatrix} \text{Co en}_2 \right]$ , have been previously described (Abstr., 1907, i, 189). They have been further studied because the different stereoisomerides may be obtained from the same starting material under conditions of reaction which are only slightly different from each other; thus, in the former paper the *cis*-bromide was prepared from *cis*-dichloro-chloride (violeo-chloride), but it is now shown that when the latter compound is dissolved in concentrated aqueous ammonia and the solution triturated with solid sodium bromide, the *trans*-bromide,  $YBr_2$ , is formed. The *trans*-thiocyanate is reddish-brown in colour.

When dichlorovioleo-chloride (5 grams) is dissolved in concentrated ammonia (25 c.c.) by heating on a water-bath, the solution then kept in a vacuum over phosphoric oxide until the odour of ammonia has disappeared, and then precipitated with sodium bromide, a bluish-red precipitate of *cis*-chloroamminediethylenediaminecobaltic bromide,



is formed. The production of this compound is not due to the intermediate formation of the diaquo-bromide, since this salt when dissolved in concentrated ammonia gives rise to the hydroxo-aquo-bromide only.

The *trans*-bromide may also be prepared by carefully heating the *trans*-nitrate with dilute ammonia (1:1) until crystals begin to form on the side of the dish.

[With R. BOSSHARD.]—The formation of carbonatodiethylenediaminecobaltic salts from the stereoisomeric hydroxo-aquo-salts has been studied. In all cases one and the same series of carbonato-salts was formed, it being impossible to prepare stereoisomerides. The carbonato-salts were prepared by the action of carbon dioxide either on alkaline solutions or on aqueous solutions of the hydroxo-aquo-salts.

Dichlorotetramminecobaltic salts,  $YX$ , where  $Y = [\text{Cl}_2 \text{Co}(\text{NH}_3)_4]$ .—The constitution of the silver and bismuth salts described previously (Abstr., 1897, ii, 264) must be altered to  $\left[ \begin{smallmatrix} \text{AgCl} \\ \text{Cl} \end{smallmatrix} \text{Co}(\text{NH}_3)_4 \right] \text{Cl}_2$  and

$\left[ \begin{smallmatrix} \text{BiCl} \\ \text{Cl} \end{smallmatrix} \text{Co}(\text{NH}_3)_4 \right] \text{Cl}_2$ . A new method of preparation of the *cis*-chloride

is given. Carbonatotetramminecobalt chloride is shaken up with a saturated (at 0°) solution of hydrogen chloride in absolute alcohol until the evolution of carbon dioxide ceases. The greyish-blue reaction product, which is a mixture of the *cis*- and *trans*-dichloro-salts, after being washed free from acid with alcohol and dried, is extracted with a small quantity of ice-cold water, the *cis*-isomeride going into solution. The filtrate is immediately precipitated with sodium dithionate in order to obtain the violeo-dithionate, from which the chloride and other salts can be obtained in the manner previously described (Abstr., 1908, ii, 42). There is always a considerable loss of violeo-

salt, owing to its ready transformation, in aqueous solution, into chloroaquo-salt. The preparation by means of aqueous hydrochloric acid cooled with liquid air was by no means so satisfactory.

*Dichlorodiethylenediaminecobaltic* salts,  $YX$ , where  $Y = [Cl_2 Co en_2]X$ .—A new method of preparation of the normal *trans*-chloride is to precipitate an aqueous solution of the acid chloride with solid lithium chloride. The *trans*-nitrite,  $YNO_2$ , is obtained as small, green crystals by precipitation of an aqueous solution of the chloride, acidified with acetic acid, with sodium nitrite. When sulphuric acid is used as the precipitant, green crystals of the *trans*-hydrogen sulphate,  $YHSO_4$ , are obtained. The addition of silver nitrate to a solution of the chloride cooled with a freezing mixture gives a precipitate consisting of greenish-white, glistening leaflets, having the composition  $\left[ \begin{smallmatrix} AgCl & Co en_2 \\ Cl & \end{smallmatrix} \right]_2 \begin{smallmatrix} SO_4 \\ (NO_3)_2 \end{smallmatrix} \cdot H_2O$ .

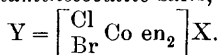
New methods of preparation of *cis*-dichlorodiethylenediaminecobaltic salts from carbonatodiethylenediaminecobalt chloride are given; they are similar to those already described for the corresponding tetrammine salts, except that the product of reaction is washed with cold water to free it from impurities, than which the *cis*-dichloro-salt is less soluble. A characteristic *cis*-sulphate,  $Y_2SO_4 \cdot 2H_2O$ , is described; it crystallises in small, reddish-violet needles.

[With L. GERB, S. LORIE, and JOS. RAPIPORT.]—*Dibromodiethylene-diaminecobaltic* salts,  $YBr$ , where  $Y = [Br_2 Co en_2]$ .—Only the *trans*-isomerides have hitherto been prepared (by Jörgensen), for which new methods of preparation are now given, as follows: (a) a solution of cobalt bromide in 10% ethylenediamine is oxidised by leading air through it, and then evaporated to dryness. The residue is then repeatedly treated with hydrobromic acid and evaporated until a uniform green salt remains, which consists of the acid bromide. On treatment with a little water, the *trans*-bromide is obtained. (b) Carbonatodiethylenediaminecobalt bromide is heated on the water-bath with a solution of hydrobromic acid ( $D = 1.49$ ) until the solution is green. On cooling, the acid bromide separates, from which the normal bromide is best obtained by heating at  $110^\circ$  until it no longer gives an acid solution. The *trans*-thiocyanate,  $YSCN$ , is precipitated as a canary-green, crystalline salt by the addition of potassium thiocyanate to a solution of the *trans*-bromide.

The methods for the preparation of the *cis*-bromide,  $YBr$ , are as follows: (1) a solution of the *trans*-bromide is evaporated on the water-bath several times to a syrupy consistency. On keeping in a vacuum desiccator, black crystals are then obtained, which give a greyish-violet powder; they consist chiefly of the *cis*-isomeride mixed with a little of the *trans*-isomeride. The latter can be extracted with a small quantity of water, leaving the *cis*-form, which can be purified by solution in water and precipitation with sodium bromide. (2) By fission of tetraethylenediaminedioldicobaltic bromide with concentrated hydrobromic acid into diaquo-bromide and the required dibromo-bromide. The diaquo-salt is removed from the mixture by solution in absolute alcohol. (3) From carbonatodiethylenediaminecobaltic bromide by treatment with an alcoholic or aqueous solution of hydrogen bromide

by a method similar to that described for the corresponding dichloro-salts. The *cis-bromide*,  $\text{YBr}$ , forms scaly crystals, possessing a colour and glance similar to that of graphite. By double decomposition with the appropriate salts of the alkali metals, the following compounds were prepared. The *cis-iodide*,  $\text{YI}$ , is similar in appearance to the bromide; the *cis-nitrate*,  $\text{YNO}_3$ , forms small, greyish-violet crystals, as also does the *cis-thiocyanate*,  $\text{YSCN} \cdot \text{H}_2\text{O}$ ; the crystals of the *cis-dithionate*,  $\text{Y}_2\text{S}_2\text{O}_6$ , are somewhat lighter in colour than those of the other salts.

*Chlorobromodiethylenediaminecobaltic* salts,  $\text{YX}$ , where



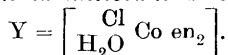
—Both the *cis*- and *trans*-isomerides have been prepared; the former are readily obtained pure, the latter only with difficulty, since they are generally mixed with *trans*-dibromo-salts. Two methods of preparation are given: (1) Two grams of chloroaquodiethylenediaminecobaltic bromide are covered with 2 c.c. of concentrated hydrobromic acid, and the mixture heated until complete solution takes place. On cooling, a mixture of the green and violet salt is obtained, which is washed with alcohol and ether, dried, and then treated with a small quantity of water to dissolve out the green salt. The violet salt (*cis*-isomeride) is collected, washed with water and alcohol, and dried. The green filtrate gives precipitates with metallic salts, which give analytical results corresponding with a mixture of dibromo- and chlorobromo-salts. (2) Chloroaquodiethylenediaminecobaltic bromide is heated for two hours at  $110^\circ$ , whereby a mixture of the *cis*- and *trans*-chlorobromo-bromides is produced. This is separated as in (1), the *trans*-nitrate being precipitated from the green filtrate by ammonium nitrate.

The *trans-nitrate*,  $\text{YNO}_3$ , forms small, light green, glistening leaflets. The *trans-dithionate*,  $\text{Y}_2\text{S}_2\text{O}_6$ , and *trans-thiocyanate*,  $\text{YSCN}$ , are prepared from the green filtrate mentioned above by double decomposition with the appropriate alkali salts; they form respectively glistening, green, flat crystals, and a light green precipitate. The *cis-bromide*,  $\text{YBr} \cdot \text{H}_2\text{O}$ , is a greyish-violet, microcrystalline salt; the *cis-nitrate*,  $\text{YNO}_3$ , forms dark violet needles, and the *cis-dithionate*,  $\text{Y}_2\text{S}_2\text{O}_6$ , small, violet leaflets.

When the *cis*-bromide is gently warmed with concentrated hydrobromic acid until a solution is formed, it is changed into *trans*-dibromodiethylenediaminecobaltic bromide, which is deposited on cooling in canary-green crystals.

*Halogenoaquodiethylenediaminecobaltic* salts,  $\left[ \begin{array}{c} \text{X} \\ \text{H}_2\text{O} \end{array} \text{Co en}_2 \right] \text{X}_2$ .—Only the *cis*-isomerides have so far been obtained; the cold aqueous solutions are fairly stable, but, on heating, complicated changes take place. By the action of concentrated aqueous ammonia on the chloroaquo- and bromoaquo-bromides, hydroxochloro- and hydroxobromobromides are obtained.

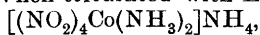
*cis-Chloroaquodiethylenediaminecobaltic* salts,  $\text{YX}_2$ , where



—The *sulphate*,  $\text{YSO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , is prepared by heating 20 grams of *trans*-dichlorodiethylenediaminecobalt chloride with 20 c.c. of water until a deep blue solution is obtained. After cooling, and keeping for one hour, ammonium sulphate (10 grams) is added; on keeping for a further twelve hours, bluish-red crystals of the sulphate are deposited, mixed with some green crystals which can be removed by shaking with a little cold water. The sulphate dissolves in concentrated ammonia, and the solution gives a bluish-red precipitate of chloro-amminediethylenediaminecobalt bromide with concentrated hydrobromic acid. The *chloride*,  $\text{YCl}_2$ , and the *bromide*,  $\text{YBr}_2 \cdot \text{H}_2\text{O}$ , are obtained from the sulphate by interaction with the respective halogen acids. The former is microcrystalline, and the latter forms small, crystalline leaflets; both are reddish-violet in colour. The *bromide-nitrate*,  $\text{YBrNO}_3$ , prepared from the bromide and lithium nitrate, is reddish-brown in colour. The *nitrite*,  $\text{Y}(\text{NO}_2)_2$ , from the chloride and sodium nitrite gives dark violet micro-crystals. It is unstable, changing to *cis*-chloronitrodiethylenediaminecobalt nitrite.

[With R. SCHMIDT.]—*cis*-Bromoquodiethylenediaminecobalt salts,  $\text{YX}_2$ , where  $\text{Y} = \left[ \begin{smallmatrix} \text{Br} \\ \text{H}_2\text{O} \end{smallmatrix} \text{Co en}_2 \right]$ .—The following methods are given for the preparation of the *bromide*,  $\text{YBr}_2 \cdot \text{H}_2\text{O}$ . (1) A solution of neutral 1 : 6-dichlorodiethylenediaminecobalt chloride containing nitric acid is heated with a concentrated solution of silver nitrate until it assumes a Bordeaux-red colour. After collecting the silver bromide, the filtrate is saturated with sodium bromide, first filtering off any more silver bromide which may be formed. After a few hours the bromide has deposited as a violet, microcrystalline powder. (2) A concentrated solution of the *trans*-dibromo-bromide is heated at  $40^\circ$  until it becomes violet in colour; after cooling, it is saturated with sodium bromide. Any green crystals of praseo-bromide which are precipitated with the bromoaquo-bromide are removed by fractional solution in ice-cold water, the praseo-bromide being the lesser soluble salt. (3) A solution of *trans*-dibromonitrate is treated similarly to the dibromo-bromide, except that it is heated over the bare flame. (4) The carbonato-chloride or bromide is treated with concentrated hydrobromic acid ( $D = 1.4$ ). The bromoaquo-bromide is separated from the less soluble *cis*-dibromo-bromide, which is formed at the same time, by fractional solution. (5) *cis*-Diaquo-bromide is heated at  $40^\circ$  with just enough water to give complete solution until a violet-coloured solution is obtained; the bromoaquo-salt is then precipitated with sodium bromide.

The bromide forms dark violet, leaf-like crystals. By double decomposition with sodium nitrate and sodium nitrite respectively, it gives the *nitrate*,  $\text{Y}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , and *nitrite*,  $\text{Y}(\text{NO}_2)_2$ , as bluish-violet, crystalline powders. When triturated with Erdmann's salt,



it gives a yellowish-green, tetranitrodiamminecobalt compound.

*Hydroxohalogeno-salts*,  $\left[ \begin{smallmatrix} \text{HO} \\ \text{X} \end{smallmatrix} \text{Co A}_4 \right] \text{X}$ .—*Hydroxochlorotetramminecobalt dithionate*,  $\left[ \begin{smallmatrix} \text{HO} \\ \text{Cl} \end{smallmatrix} \text{Co}(\text{NH}_3)_4 \right]_2 \text{S}_2\text{O}_6$ , is precipitated as a violet-blue

salt when solid chloroaquatetramminecobaltic chloride is dissolved in a saturated solution of sodium dithionate in concentrated ammonia, ammonium dithionate remaining in solution. The colour corresponds with that of the *cis*-dichlorotetrammine salts. The corresponding *hydroxochlorodiethylenediaminecobaltic bromide*,  $\left[ \begin{smallmatrix} \text{HO} \\ \text{Cl} \end{smallmatrix} \text{Co en}_2 \right] \text{Br}$ , is obtained as a brownish-violet, crystalline paste when chloroaquodiethylenediaminecobaltic bromide is treated with concentrated ammonia; when heated with concentrated hydrogen chloride, this salt gives a mixture containing a little 1:6-dichloro- with much 1:2-dichloro-diethylenediaminecobaltic chloride. *cis-Hydroxobromodiethylenediaminecobaltic bromide*,  $\left[ \begin{smallmatrix} \text{HO} \\ \text{Br} \end{smallmatrix} \text{Co en}_2 \right] \text{Br}$ , is similarly obtained as a brownish-violet salt from the bromoaquo-bromide and ammonia. When warmed with a little water, addition takes place with the formation of the *cis*-hydroxaquo-bromide; similarly, when triturated with concentrated hydrobromic acid, the *cis*-diaquo-bromide is obtained.

*Chloroisothiocyanatodiethylenediaminecobaltic* salts,  $\text{YX}$ , where  $\text{Y} = \left[ \begin{smallmatrix} \text{Cl} \\ \text{SCN} \end{smallmatrix} \text{Co en}_2 \right]$ .—A few of the *trans*-isomerides, which were, however, impure, have been described previously (Abstr., 1900, i, 86). The *trans-thiocyanate*,  $\text{YSCN}$ , is obtained by precipitating a solution of 1:6-dichlorodiethylenediaminecobaltic chloride with potassium thiocyanate. The precipitate consists of a mixture of about two-thirds of the *trans*- and one-third of the *cis*-isomeride. By appropriate treatment the pure *trans*-isomeride is obtained as sparingly soluble, violet leaflets. When triturated with hydrobromic acid, it gives glistening, bluish-violet crystals of the *trans-bromide*,  $\text{YBr} \cdot 2\text{H}_2\text{O}$ . This salt may also be prepared from praseo-chloride (Abstr., 1907, i, 291). With sodium dithionate, it gives bluish-violet, glistening crystals of the *trans-dithionate*,  $\text{Y}_2\text{S}_2\text{O}_6$ , and with perchloric acid, violet leaflets of the *trans-perchlorate*,  $\text{YClO}_4$ . The perchlorate may also be obtained directly from the *trans*-dichlorothiocyanate and perchloric acid.

The *trans*-isomerides dissolve readily in liquid ammonia, giving reddish-yellow solutions which deposit mixtures of the stereoisomeric *isothiocyanatoammine* salts. If the *trans*-perchlorate is boiled with sodium nitrite in concentrated aqueous solution until a reddish-brown colour is obtained, the solution cooled, and ammonium thiocyanate added, an isomorphous mixture of the 1:6-chloroisothiocyanato- and 1:6-nitroisothiocyanato-thiocyanates is precipitated. If the solution is boiled until brown in colour, small quantities of the *cis*-nitroisothiocyanato-salt crystallise on cooling. On heating a solution of *trans*-chloroisothiocyanato-bromide with potassium thiocyanate and cooling, needles of the *trans*-diisothiocyanato-thiocyanate separate, and from the mother liquor small quantities of the *cis*-isomeride can be obtained; oxidation of the *trans*-salt with hydrogen peroxide gives the *trans*-diammine salt.

On boiling a concentrated solution of the *trans*-chloroisothiocyanato-bromide (1 mol.) with silver nitrate (3 mols), filtering from silver bromide, and cooling, light violet, slender needles of an *additive com-*

-pound,  $\left[ \begin{smallmatrix} \text{Cl} \\ \text{A}_2\text{SCN} \end{smallmatrix} \text{Co en}_2 \right] (\text{NO}_3)_2$ , are obtained. On boiling the aqueous solution of this salt, silver chloride is slowly precipitated.

*cis-Chloroisoithiocyanatodiethylenediaminecobaltic chloride*,  $\text{YCl}$ , is obtained in the purification of the *trans*-thiocyanate in the form of bluish-red needles. It is purified by transformation into the perchlorate and precipitation of the solution of this salt with concentrated hydrochloric acid. By double decomposition of a solution of the perchlorate with the appropriate salts of the alkali metals, the following compounds were obtained: *cis-Dithionate*,  $\text{Y}_2\text{S}_2\text{O}_6 \cdot \text{H}_2\text{O}$ , brownish-red needles; *cis-nitrate*,  $\text{YNO}_3$ , dark bluish-red needles; *cis-sulphate*,  $\text{Y}_2\text{SO}_4$ , violet-red powder. The *cis-bromide*,  $\text{YBr} \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , was obtained from the chloride by interaction with hydrobromic acid. A method of preparation of the *cis*-chloride from *cis*-isoithiocyanatonitro-chloride by interaction with hydrochloric acid is also given.

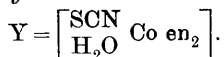
The action of hydrogen peroxide, liquid ammonia, potassium thiocyanate, sodium nitrite, and silver nitrate on the *cis*-salts is fully described.

*Bromoisothiocyanatodiethylenediaminecobaltic salts*,  $\text{YX}$ , where  $\text{Y} = \left[ \begin{smallmatrix} \text{Br} \\ \text{SCN} \end{smallmatrix} \text{Co en}_2 \right]$ .—Both series of isomerides are known, but the *cis*-salts are difficult to isolate, since in aqueous solution they are readily transformed into aquo-salts. The *trans*-isomerides on oxidation with hydrogen peroxide under certain conditions give 1:6-bromoamine salts, and under other conditions 1:6-dibromo-salts. Hydrogen peroxide completely oxidises the thiocyanate residue of the *cis*-isomerides, but if the aqueous solution is kept some time before hydrogen peroxide is added, a salt of the aquo-series is formed, which then gives rise to the bromoamine salt. With ammonia both isomerides give a mixture of *cis*- and *trans*-isoithiocyanatoamine-diethylenediaminecobaltic salts.

The *trans-thiocyanate*,  $\text{YSCN}$ , is prepared from 1:6-dibromodiethylenediaminecobaltic bromide by precipitation with potassium thiocyanate. The green precipitate and mother liquor are heated until a deep red solution is obtained. On cooling, and further addition of potassium thiocyanate, green, glistening needles of the required salt are obtained. Trituration with concentrated hydrobromic acid gives dark blue, prismatic crystals of the *trans*-bromide,  $\text{YBr} \cdot 2\text{H}_2\text{O}$ , and precipitation with perchloric acid, the *trans-perchlorate*,  $\text{YClO}_4$ , as dark blue, almost black, slender needles. The *trans-dithionate*,  $\text{Y}_2\text{S}_2\text{O}_6$ , forms violet-blue leaflets.

Three methods of preparation of the *cis-bromide*,  $\text{YBr}$ , are fully described, namely, from 1:6-dibromodiethylenediaminecobaltic bromide, 1:2-aquoisoithiocyanatodiethylenediaminecobaltic dithionate, and 1:2-nitroisoithiocyanatodiethylenediaminecobaltic sulphate. It forms garnet-red, glistening, prismatic crystals, and is used as a source of preparation of the other salts by methods involving double decomposition. The *cis-nitrate*,  $\text{YNO}_3$ , is violet-brown in colour, the *cis-dithionate*,  $\text{Y}_2\text{S}_2\text{O}_6$ , brownish-red, whilst the *cis-sulphate*,  $\text{Y}_2\text{SO}_4$ , gives reddish-lilac, silky, thin leaflets.

isoThiocyanatoaquadithylenediaminecobaltic salts,  $YX_2$ , where



—Both series of isomerides have been obtained, whereas with all other acidoquo-salts it has been possible to prepare one series only, either the *cis*- or *trans*-. The salts of the *cis*-series are yellowish-red to crimson in colour, whilst those of the *trans*-series are violet; the former are obtained from the stereoisomeric chloroisothiocyanato-salts by the action of concentrated ammonia, and the latter from the same salts by the action of potassium hydroxide.

The *cis*-dithionate,  $YS_2O_6 \cdot H_2O$ , is prepared by warming 1 : 6-chloro-isothiocyanatodithylenediaminecobaltic bromide with concentrated ammonia until a red solution is formed. The cooled solution is then poured into absolute alcohol, the precipitate dried on a porous plate, dissolved in cold water, and glacial acetic acid added to the solution until a precipitate begins to form. On further keeping, orange-coloured needles of the dithionate separate. With potassium thiocyanate the solution gives a crimson precipitate of the *cis*-thiocyanate,  $Y(\text{SCN})_2$ . With hydrogen peroxide, the dithionate gives a mixture of the *cis*- and *trans*-chloroammine salts; with concentrated hydrochloric acid, *cis*-chloroisothiocyanato-salts; with nitrous acid, *cis*-nitroisothiocyanatodithylenediaminecobaltic dithionate,  $\left[ \begin{array}{c} \text{O}_2\text{N} \\ \text{SCN} \end{array} \text{Co en}_2 \right]_2 \text{S}_2\text{O}_6$ , in the form of slender, yellow needles; with potassium thiocyanate, *cis*-diisothiocyanato-salts. With silver nitrate and perchloric acid, an orange-coloured additive product,  $\left[ \begin{array}{c} \text{AgSCN} \\ \text{H}_2\text{O} \end{array} \text{Co en}_2 \right] (\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ , is obtained.

The *trans*-bromide,  $Y\text{Br}_2 \cdot 2\text{H}_2\text{O}$ , is prepared as follows: 1 : 6-chloro-isothiocyanatothiocyanate dissolves in potassium hydroxide to a red solution; on cooling, brownish-red leaflets of 1 : 6-hydroxoisothiocyanato-thiocyanate,  $\left[ \begin{array}{c} \text{HO} \\ \text{SCN} \end{array} \text{Co en}_2 \right] \text{SCN} \cdot \text{H}_2\text{O}$ , separate. These are dissolved in a little water, excess of concentrated hydrobromic acid added, and the solution kept over sulphuric acid in a desiccator. After a few days, dark red crystals of the required bromide separate. From this salt, by the method of double decomposition, the *trans*-thiocyanate,  $Y(\text{SCN})_2 \cdot \text{H}_2\text{O}$ , is obtained as a violet precipitate, the *trans*-nitrate,  $Y(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , as bluish-red needles, and the *trans*-nitrite,  $Y(\text{NO}_2)_2$ , as dark violet-red crystals. On the addition of excess of silver nitrate to a well-cooled solution of the nitrate, bright red needles of an additive product,  $\left[ \begin{array}{c} \text{H}_2\text{O} \\ \text{Ag}_2\text{SCN} \end{array} \text{Co en}_2 \right] (\text{NO}_3)_4 \cdot \text{H}_2\text{O}$ , are deposited.

On oxidation with nitric acid or hydrogen peroxide, and subsequent evaporation with concentrated hydrochloric acid, the *trans*-aquoiso-thiocyanato-salts give only *trans*-chloroammine salts.

When solid sodium nitrite is added to a concentrated solution of 1 : 6-isothiocyanatoaquo-nitrate acidified with a few drops of acetic acid, a bright red precipitate of 1 : 6-nitritoisothiocyanatodithylenediaminecobaltic nitrite,  $Y\text{NO}_2 \cdot \text{H}_2\text{O}$ , where  $Y = \left[ \begin{array}{c} \text{ONO} \\ \text{SCN} \end{array} \text{Co en}_2 \right]$ , is

produced; with potassium thiocyanate the solution gives red needles of the 1:6-thiocyanate, YSCN.

*Chloroamminediethylenediaminecobaltic* salts,  $YX_2$ , where  $Y = \left[ \begin{smallmatrix} \text{Cl} \\ \text{H}_3\text{N} \end{smallmatrix} \text{Co en}_2 \right]$ .—The isomerides of this series are best distinguished by means of the dithionates; the *cis*-dithionate forms thick crystals, whilst the *trans*-dithionate crystallises in long, glistening needles. Both series of salts are bluish-red in colour. The *trans*-salts react very quickly with liquid ammonia, forming diammine salts, whereas the *cis*-isomerides are scarcely acted on. Jörgensen has already prepared a number of the *cis*-isomerides.

The best method of preparation for the *cis*-chloride,  $YCl_2$ , is the trituration of 1:6-dichlorodiethylenediaminecobaltic chloride with concentrated ammonia. The green salt first dissolves, and then a red paste of the required chloride separates. The addition of solid sodium perchlorate to a solution of the chloride precipitates long, red prisms of the *cis*-chloride-perchlorate,  $YCl(ClO_4)$ ; on recrystallisation from concentrated hydrochloric acid it is transformed into the chloride. The *cis*-nitrite,  $Y(NO_2)_2$ , forms brick-red crystals. The actions of sodium and silver nitrites, of potassium thiocyanate, and of liquid ammonia on the *cis*-chloride are fully described, as also the changes which aqueous solutions of the *cis*-nitrite undergo on warming.

To prepare the *trans*-chloride,  $YCl_2 \cdot H_2O$ , 1:6-chloro*isothiocyanato*-diethylenediaminecobaltic thiocyanate is oxidised with hydrogen peroxide in aqueous solution acidified with sulphuric acid. Precipitation with hydrochloric acid then gives a chloride-sulphate, which is recrystallised from hydrochloric acid several times, and the aqueous solution then precipitated with barium chloride to remove the sulphuric acid. It forms bright ruby-red prisms. It may also be prepared from 1:6-nitroammine salts by heating with concentrated hydrochloric acid, and from 1:6-dichloro-salts by the action of a methyl-alcohol solution of ammonia. The *trans*-chloride-perchlorate,  $YCl(ClO_4)$ , is prepared from 1:6-chloro*isothiocyanato*diethylenediaminecobaltic perchlorate by a method similar to that used for the chloride; it forms bright red, glistening leaflets or flat needles. The *trans*-chloride hydrogen sulphate,  $YCl(HSO_4)$ , is obtained by repeated evaporation on the water-bath of 1:6-nitroamminedithionate with hydrochloric acid; it crystallises in thick, ruby-red plates. The *trans*-dithionate,  $YS_2O_6 \cdot H_2O$ , crystallises as bright red, slender needles when sodium dithionate is added to a solution of the chloride-perchlorate. The *dichromate*, *nitrate*, and *nitrite* have also been obtained. The actions of sodium and silver nitrites, of potassium thiocyanate, and of liquid ammonia on the *trans*-chloride-perchlorate are fully described, as also the changes which aqueous solutions of the *trans*-nitrite undergo on keeping or on warming.

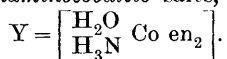
*Bromoamminediethylenediaminecobaltic* salts,  $YX_2$ , where  $Y = \left[ \begin{smallmatrix} \text{Br} \\ \text{H}_3\text{N} \end{smallmatrix} \text{Co en}_2 \right]$ .—Both series of isomerides have been prepared, the *cis*-isomerides being the more easily obtained. The determination of their configuration depends on the formation of the *trans*-isomerides from *trans*-bromo*isothiocyanato*-salts by oxidation with hydrogen

peroxide. Both series are very similar in colour. The *cis*-dithionate forms short, compact crystals, whilst the *trans*-isomeride gives long, slender needles; also, the former salt readily dissolves in concentrated hydrobromic acid, with the formation of the bromide, whereas the latter is unaltered.

[With W. E. Boës.]—The *cis*-bromide,  $\text{YBr}_2 \cdot 2\text{H}_2\text{O}$ , is obtained when moist 1 : 6-dibromodiethylenediaminecobaltic bromide is treated at a low temperature with ammonia (1 : 1), drop by drop, until the green colour changes to a dark violet. At higher temperatures, the diammine-salt is produced, owing to the addition of a further molecule of ammonia. When recrystallised from water, it forms bundles of reddish-violet, glistening needles; when precipitated from the aqueous solution by the addition of concentrated hydrobromic acid, the anhydrous salt,  $\text{YBr}_2$ , is obtained as dark brownish-red prisms or needles. It may also be prepared (1) by the action of ammonium bromide on tetraethylenediaminediaquotetrodicobalticobaltous sulphate, and (2) by the action of hydrobromic acid on 1 : 2-nitroamminediethylenediaminecobaltic salts or on 1 : 2-aquoamminediethylenediaminecobaltic salts. By appropriate double decomposition the following salts were obtained: *cis*-bromide-nitrate,  $\text{YBr}(\text{NO}_3)$ , as reddish-violet crystals; the *cis*-dithionate,  $\text{YS}_2\text{O}_6$ , as reddish-violet, thin leaflets; the *cis*-platinochloride,  $\text{YPtCl}_4$ , as reddish-brown leaflets. The *cis*-nitrate,  $\text{Y}(\text{NO}_3)_2$ , was obtained from the bromide by trituration with concentrated nitric acid as dark reddish-violet, long, rectangular columns.

The *trans*-dithionate,  $\text{YS}_2\text{O}_6$ , is obtained from 1 : 6-bromoisothiocyanatodiethylenediaminecobaltic bromide by oxidation at  $50^\circ$  with hydrogen peroxide in aqueous solution acidified with acetic acid, and subsequent precipitation with sodium dithionate. It forms bluish, rose-coloured, slender needles. With ammonium iodide the solution gives reddish-brown, glistening, flat needles of the *trans*-iodide,  $\text{YI}_2 \cdot \text{H}_2\text{O}$ . The *trans*-bromide,  $\text{YBr}_2 \cdot \text{H}_2\text{O}$ , was prepared from 1 : 6-aquoamminediethylenediaminecobaltic bromide by evaporation with concentrated hydrobromic acid on the water-bath. It forms large, dark reddish-violet prisms, and serves as the source of the *trans*-nitrate,  $\text{Y}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ , and the *trans*-perchlorate,  $\text{Y}(\text{ClO}_4)_2$ , the latter crystallising in violet needles.

Aquoamminediethylenediaminecobaltic salts,  $\text{YX}_3$ , where



—Both series of isomerides have been prepared. They are obtained by the action of potassium hydroxide or of freshly precipitated silver oxide on the stereoisomeric chloroamine- and bromoamine-diethylenediaminecobaltic salts. In every case, partial transformation takes place, so that a mixture of the isomerides is produced. The product of action of the alkali is an hydroxoamine salt, the aquoamine salt being produced when the solution is acidified. Potassium hydroxide produces a greater relative transformation than silver oxide; more *trans*-isomeride seems to be produced at low than at ordinary temperatures. The mixture of the isomerides is separated by taking advantage of the fact that the *trans*-aquoamine-bromide is much less soluble in dilute

hydrobromic acid than the *cis*-isomeride. The isomerides can be distinguished from each other (1) by transformation into the chloroamminedithionate (*q.v.*) by warming with hydrochloric acid, and subsequent precipitation with sodium dithionate; (2) by warming the aqueous solution to which sodium nitrite and a little acetic acid has been added to 60—70°. A yellow solution is produced, which, on the addition of sodium dithionate, gives an insoluble precipitate if the *cis*-isomeride is present, or a precipitate which can be recrystallised from water if the *trans*-isomeride is present.

The *trans*-bromide,  $\text{YBr}_3 \cdot \text{H}_2\text{O}$ , forms pale brick-red needles, and is used as the source of other salts, methods of double decomposition being employed. The *trans*-iodide,  $\text{YI}_3 \cdot \text{H}_2\text{O}$ , forms brownish-red, flat, prismatic crystals; the *trans*-nitrate,  $\text{Y}(\text{NO}_3)_3$ , crystallises in fire-red, glistening prisms; the *trans*-platinichloride,  $\text{Y}_2(\text{PtCl}_6)_3 \cdot 2\text{H}_2\text{O}$ , gives small, dark, brownish-red crystals, and the *trans*-platinochloride,  $\text{Y}_2(\text{PtCl}_4)_3 \cdot 2\text{H}_2\text{O}$ , forms slender, light brown crystals.

The *cis*-bromide,  $\text{YBr}_3 \cdot \text{H}_2\text{O}$ , forms clumps of small, red crystals.

The diisothiocyanatodiethylenediaminecobaltic salts,  $\text{YX}$ , where  $\text{Y} = [(\text{SCN})_2\text{Co en}]_2$ , have already been described (compare Bräunlich, Abstr., 1900, i, 86). Their true configuration has now been determined as follows. By violent oxidation with concentrated nitric acid and subsequent evaporation with hydrochloric acid, the *trans*-isomerides give mainly *trans*-chloroammine salts, together with some *trans*-diammine salts; oxidation with hydrogen peroxide gives only the latter salts. Under the same treatment the *cis*-isomerides give respectively *trans*-dichloro-salts, together with a little *cis*-chloroammine-salt, and *cis*-chloroammine salt. On oxidation with chlorine the *trans*-isomerides give *trans*-diammine salts, and the *cis*-isomerides, *trans*-dichloro-salts.

[With C. RIX.]—A new method of preparing the *cis*-salts is as follows: 1:2-nitrosoisothiocyanatodiethylenediaminecobaltic thiocyanate is evaporated with hydrochloric acid, whereby pure *cis*-diisothiocyanatodiethylenediaminecobaltic chloride,  $\text{YCl}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ , is obtained.

The solubilities at 25° of the various salts in grams per 50 c.c. of water containing acetic acid are as follows: chloride, 0.2766; bromide, 0.1996; iodide (at 24°), 0.465; nitrate, 0.1968; thiocyanate, 0.1860.

Stereoisomeric diamminediethylenediaminecobaltic salts,  $\text{YX}_3$ , where  $\text{Y} = [(\text{NH}_3)_2\text{Co en}]_2$ , have already been described (Abstr., 1907, i, 290), but the wrong configuration has been assigned to them; those which were formerly characterised as *cis*-compounds are now found to be the *trans*-isomerides, and vice-versa. The evidence for this is based on their relation with the diisothiocyanato- and isothiocyanato-ammine-salts, which has already been indicated, and on the resolution of the *cis*-compounds into the optically active isomerides. The *trans*-salts are sparingly soluble, whilst the *cis*-salts are readily soluble. A new method of preparation is described, by the oxidation of the isothiocyanatoamminediethylenediaminecobaltic salts with hydrogen peroxide in the presence of halogen acid.

[With R. SAMANEK.]—Mixtures of the two series of salts have also been obtained by the action of liquid ammonia on the following compounds: 1:6-dichloro-, 1:6-dibromo-, and 1:2-dibromo-diethylene-

diaminecobaltic salts; 1:6-chloroammine-, 1:6- and 1:2-bromoammine-diethylenediaminecobaltic salts. The separation of the isomerides can be brought about by taking advantage of the fact that the bromide of the *trans*-series is only sparingly soluble in hydrobromic acid, whereas the *cis*-bromide is readily soluble; or, better still, by precipitation of concentrated solutions of the salts with sodium dithionate, whereby the *trans*-dithionate is obtained, it being practically insoluble in water; from the mother liquor the *cis*-periodide is precipitated by the addition of a solution of iodine in hydriodic acid, and by trituration of this salt with sodium thiosulphate the *cis*-iodide is obtained.

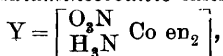
In all reactions leading to the formation of diammine salts, the *cis*-isomerides are formed in preponderating amount. If the action of ammonia on the 1:6-dichloro-salts is not sufficiently energetic, some 1:2-chloroammine salt is formed.

iso*Thiocyanatoamminediethylenediaminecobaltic* salts,  $YX_2$ , where  $Y = \left[ \begin{smallmatrix} \text{SCN} \\ \text{H}_3\text{N} \end{smallmatrix} \text{Co en}_2 \right]$ .—The two series of isomerides have been obtained, and are very important, because of their genetic relations with other series, in the determination of configurations, etc. A mixture of both isomerides is always obtained in their preparation, no matter whether 1:2-chloro-, 1:2-bromo-, or 1:6-chloro-, 1:6-bromo-*isothiocyanato*-diethylenediaminecobaltic salts are used to obtain them by interaction with liquid ammonia. The relative proportion of the isomerides produced is not independent of the nature of the ionogenic radicle in the salt used.

The *cis*- and *trans-thiocyanates*,  $Y(\text{SCN})_2$ , are obtained by dissolving 1:6-chloro*isothiocyanato*diethylenediaminecobaltic thiocyanate in liquid ammonia and allowing the solution to evaporate at the ordinary temperature. The residue is dissolved in water containing acetic acid, and, on keeping, the *trans*-thiocyanate is deposited as slender, glistening, reddish-orange needles; the *cis*-thiocyanate is precipitated from the mother liquors by the addition of much potassium thiocyanate in the form of reddish-brown, crystalline crusts. By appropriate double decomposition the following salts were obtained: *cis-dithionate*,  $YS_2O_6$ , brilliant, orange-red leaflets; *cis-iodide*,  $YI_2$ , short, columnar, reddish-brown crystals; *trans-iodide*,  $YI_2 \cdot H_2O$ , small, brick-red prisms. The *trans-bromide-dithionate*,  $Y_2Br_2(S_2O_6)_2 \cdot 2H_2O$ , was prepared by trituration of the thiocyanate with hydrobromic acid and subsequent precipitation with sodium dithionate; it forms brownish-red, prismatic crystals. With silver nitrate the *cis*-dithionate gives glistening, yellow crystals of an *additive product*,  $\left[ \begin{smallmatrix} \text{H}_3\text{N} \\ \text{AgSCN} \end{smallmatrix} \text{Co en}_2 \right] \begin{smallmatrix} \text{S}_2\text{O}_6 \\ \text{NO}_3 \end{smallmatrix}$ , whilst the *trans*-perchlorate, prepared from the thiocyanate and perchloric acid, gives yellow needles of the *additive product*,  $\left[ \begin{smallmatrix} \text{H}_3\text{N} \\ \text{Ag}_2\text{SCN} \end{smallmatrix} \text{Co en}_2 \right] (\text{NO}_3)_4$ .

A detailed account is given of the action of oxidising agents and of potassium thiocyanate on the *cis*- and *trans*-isomerides.

*Nitratoamminediethylenediaminecobaltic* salts,  $YX_2$ , where



are obtained by the evaporation of the stereoisomeric aquoammine-diethylenediaminecobaltic nitrates with concentrated nitric acid. In the preparation of the *trans*-isomeride from the 1:6-aquoammine salt, some *cis*-isomeride is formed at the same time, but the two are readily separated by taking advantage of the fact that the *cis*-dithionate is almost insoluble in water. Their configuration is determined by evaporation with concentrated hydrochloric acid, which gives the corresponding chloroammine salts. Liquid ammonia gives a mixture of the stereoisomeric diammine salts.

The *cis*-nitrate,  $\text{Y}(\text{NO}_3)_2$ , forms small, glistening, orange-red crystals; the *cis*-dithionate,  $\text{YS}_2\text{O}_6 \cdot \text{H}_2\text{O}$ , is an orange-coloured powder. The *trans*-dithionate,  $\text{YS}_2\text{O}_6$ , crystallises in orange-coloured needles.

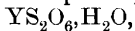
[With W. E. Böes].—Nitroamminediethylenediaminecobaltic salts,  $\text{YX}_2$ , where  $\text{Y} = \left[ \begin{smallmatrix} \text{O}_2\text{N} \\ \text{H}_3\text{N} \end{smallmatrix} \text{Co en}_2 \right]$ .—Both series of isomerides have been prepared, and are distinguished from each other by the fact that the *cis*-salts are much more soluble than the *trans*-salts, this difference being especially marked in the dithionates. The configuration is best decided by evaporation of the salt to dryness with hydrochloric acid, solution of the residue in water, and precipitation with sodium dithionate of the chloroamminediethylenediaminecobaltic dithionate, the *cis*- and *trans*-isomerides of which are very characteristic.

The *cis*-bromide,  $\text{YBr}_2$ , is obtained by adding an excess of a saturated solution of sodium nitrite to a saturated (at  $25^\circ$ ) solution of 1:2-aquoamminediethylenediaminecobaltic bromide, acidifying with acetic acid, and warming at  $40^\circ$  until the solution becomes orange-yellow in colour. After keeping for twenty-four hours a precipitate consisting of a mixture of the bromide and nitrite is deposited; it is dissolved in water, and the solution saturated at  $35^\circ$  with potassium bromide. On cooling, large, dark yellow plates of the bromide are obtained. The following salts were obtained from the bromide, for the most part by the usual methods of double decomposition. The *cis*-chloride,  $\text{YCl}_2$ , forms orange-yellow prisms or else a microcrystalline precipitate; the *cis*-iodide,  $\text{YI}_2$ , crystallises in reddish-brown needles; the *cis*-nitrate,  $\text{Y}(\text{NO}_3)_2$ , in flat, tabular, or needle-shaped crystals. The *cis*-dithionate,  $\text{YS}_2\text{O}_6$ , forms small, golden-yellow leaflets, whilst the *cis*-sulphate,  $\text{YSO}_4$ , crystallises in long, radiating, light yellow, prismatic needles. The *cis*-bromide-nitrate,  $\text{YBr}(\text{NO}_3)$ , is prepared by the gradual addition of concentrated nitric acid to a well-cooled solution of the nitrate; it forms large, glistening, reddish-brown prisms.

The following methods of preparation of the *cis*-isomerides are also described: (1) By the action of silver nitrite on 1:2-chloroammine-diethylenediaminecobaltic chloride. (2) By the action of ammonia on 1:6-dinitrodiethylenediaminecobaltic salts. (3) By oxidation of 1:2-nitroisothiocyanatodiethylenediaminecobaltic salts.

The *trans*-nitrate,  $\text{Y}(\text{NO}_3)_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ , is prepared by dissolving 1:6-nitronitratodiethylenediaminecobaltic nitrate in liquid ammonia, and allowing the solution to evaporate spontaneously. The residue is recrystallised from water, whereby a mixture of large, dark brown plates and small, light yellow crystals is obtained, which are

mechanically separated. The latter crystals consist of 1 : 6 dinitro-nitrate, whilst the former are the required *trans*-nitrate, and, after further recrystallisation, are obtained as flat, rhombic tablets. By appropriate double decomposition, the nitrate yielded the following salts: the *trans*-iodide,  $\text{YI}_2 \cdot \text{H}_2\text{O}$ , as brown, glistening, prismatic crystals; the *trans*-bromide,  $\text{YBr}_2$ , as thick, short, columnar or tabular, dark brown crystals; the *trans*-thiocyanate,  $\text{Y}(\text{SCN})_2$ , as thick, glistening, brownish-yellow plates; the *trans*-dithionate,



as long, glistening, fluted prisms. This latter salt was also obtained from a solution of the *trans*-chloride, prepared by the interaction of 1 : 6-chloronitrodiethylenediaminecobaltic chloride and liquid ammonia.

The solubilities of the various *trans*-salts, expressed in grams of salt per 10 c.c. of water at  $27^\circ$ , are: nitrate, 2.827; thiocyanate, 1.458; bromide (at  $26^\circ$ ), 0.6867; iodide, 0.7707.

*Nitroisothiocyanatodiethylenediaminecobaltic* salts,  $\text{YX}$ , where  $\text{Y} = \left[ \begin{smallmatrix} \text{O}_2\text{N} \\ \text{SCN} \end{smallmatrix} \text{Co en}_2 \right]$ .—The salts of the *trans*-series are more easily soluble than the *cis*-isomerides, the sulphates showing the greatest difference in solubility. There is also a marked difference in the colour of the salts, the *cis*-compounds being brownish-yellow, whilst the *trans*-compounds are dark brown.

The following reactions are different in the two series. Hydrogen peroxide partly oxidises the *cis*-salts to *cis*-nitroammine-salts, and partly oxidises the thiocyanate group completely away; the *trans*-salts, under similar conditions, give only *trans*-nitroquo-salts, the thiocyanate group being split off completely. On heating with concentrated hydrochloric acid, the *cis*-isomerides give the *cis*-chloroisothiocyanato-salts, whereas the *trans*-isomerides are not affected by the same treatment. On oxidation with nitric acid and subsequent evaporation with hydrochloric acid, the *cis*-salts give 1 : 6-dichloro-salts, whilst the *trans*-salts give 1 : 6-chloronitro-salts.

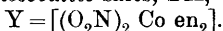
[With C. RIX].—The *cis*-chloride,  $\text{YCl} \cdot \text{H}_2\text{O}$ , is obtained by intramolecular transformation from 1 : 2-chloronitrodiethylenediaminecobaltic thiocyanate, a solution of which in water containing acetic acid is evaporated to half its volume. The red colour changes to brown, and on cooling brownish-yellow needles of the *cis*-chloride deposit containing  $2\text{H}_2\text{O}$ , but  $1\text{H}_2\text{O}$  is lost in a desiccator over calcium chloride. The chloride serves for the preparation of the other salts, for the most part by the method of double decomposition. The *cis*-bromide,  $\text{YBr}$ , forms light brown, nodular crystals; the *cis*-iodide,  $\text{YI}$ , crystallises in brown prisms; the *cis*-sulphate,  $\text{Y}_2\text{SO}_4$ , forms yellow, glistening scales; the *cis*-nitrate,  $\text{YNO}_3$ , forms brown, thick crystals; and the *cis*-thiocyanate,  $\text{YSCN}$ , crystallises in brown leaflets. The *cis*-sulphate may also be obtained by heating a solution of *cis*-chloroisothiocyanatodiethylenediaminecobaltic chloride with sodium nitrite and subsequent precipitation with ammonium sulphate. The *cis*-thiocyanate is also prepared by heating a solution of the *cis*-chloronitro-chloride with potassium thiocyanate.

[With N. GOSLINGS].—The *trans*-thiocyanate,  $\text{YSCN}$ , is obtained as

brown, prismatic crystals when potassium thiocyanate is added to a solution of 1 : 6-chloronitrodiethylenediaminecobaltic nitrate. Methods are also described for its preparation by the action of potassium thiocyanate on nitratonitrodiethylenediaminecobaltic thiocyanate and on 1 : 6-nitroamminediethylenediaminecobaltic nitrate. The *trans-chloride*,  $\text{YCl} \cdot \text{H}_2\text{O}$ , is obtained as reddish-brown, tabular crystals by dissolving the thiocyanate in concentrated hydrochloric acid and precipitation with alcohol; the other salts are prepared from it by appropriate double decomposition. The *trans-bromide*,  $\text{YBr} \cdot \text{H}_2\text{O}$ , forms brown, tabular crystals; the *trans-iodide*,  $\text{YI}$ , crystallises in glistening, brown, irregular leaflets; the *trans-nitrate*,  $\text{YNO}_3 \cdot \text{H}_2\text{O}$ , forms brown plates, as also does the *trans-nitrite*,  $\text{YNO}_2 \cdot \text{H}_2\text{O}$ . With silver nitrate the *trans-nitrate* gives long, yellow needles of an *additive compound*,  $\left[ \text{AgSCN} \begin{smallmatrix} \text{O}_2\text{N} \\ \text{Co en}_2 \end{smallmatrix} \right] (\text{NO}_3)_2$ .

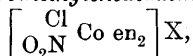
*Dinitrotetraminecobaltic* salts,  $\text{YX}$ , where  $\text{Y} = [(\text{NO}_2)_2\text{Co}(\text{NH}_3)_4]$ .—[With L. COHN].—By the addition of rubidium nitrate to a solution of the *cis-nitrate* (flavonitrate), a *rubidium double nitrate*,  $\text{YNO}_3 \cdot \text{RbNO}_3$ , is obtained as brown, rhombic, tabular crystals. It is analogous with the potassium double nitrate already prepared by Jürgensen.

*Dinitrodiethylenediaminecobaltic* salts,  $\text{YX}$ , where



—A number of the stereoisomerides have been described previously as dinitrito-salts (Abstr., 1901, i, 511); the true dinitrito-salts were prepared later (Abstr., 1907, i, 291). It has been found that the *cis-nitrate* is transformed into the *trans-nitrate* when its aqueous solution is heated. The *cis-thiocyanate*,  $\text{YSCN}$ , is obtained from the *cis-nitrate* by precipitation with potassium thiocyanate; it forms glistening, yellowish-brown, tabular crystals. The *trans-thiocyanate*,  $\text{YSCN}$ , forms orange-yellow, glistening, thick crystals. The *trans-hydrogen sulphate*,  $\text{YHSO}_4$ , has been prepared from the iodide by interaction with silver oxide and subsequent neutralisation with sulphuric acid; it forms glistening, yellowish-red needles.

Stereoisomeric *chloronitrodiethylenediaminecobaltic* salts,



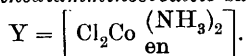
have already been described (Abstr., 1901, i, 512). It has since been found that the *trans-salts* can be exposed to the action of concentrated hydrochloric acid for a long time without effect, whilst the *cis-salts* rapidly give 1 : 2- and 1 : 6-dichloro-salts.

*trans-Nitronitratodiethylenediaminecobaltic* salts,  $\text{YX}$ , where  $\text{Y} = \left[ \begin{smallmatrix} \text{O}_2\text{N} \\ \text{O}_3\text{N} \end{smallmatrix} \text{Co en}_2 \right]$ .—Only the *nitrate*,  $\text{YNO}_3$ , has been obtained. It is prepared by the oxidation of 1 : 2-dinitrodiethylenediaminecobaltic nitrate with concentrated nitric acid, and forms glistening, chamois-coloured crystals. By precipitation of the aqueous solution with concentrated nitric acid, an *acid nitrate*,  $\text{YNO}_3 \cdot \text{HNO}_3$ , is obtained.

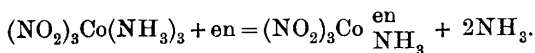
*trans-Nitroaquodiethylenediaminecobaltic* salts,  $\text{YX}_2$ , where  $\text{Y} = \left[ \begin{smallmatrix} \text{O}_2\text{N} \\ \text{H}_2\text{O} \end{smallmatrix} \text{Co en}_2 \right]$ .—The *sulphate*,  $\text{YSO}_4$ , is obtained as follows: 2·8 grams of solid ammonium sulphate are added to a solution of 4 grams

of 1 : 6-nitronitrato-diethylenediaminecobaltic nitrate in 10 c.c. of water, and then alcohol added until no further precipitate forms. It crystallises in orange-coloured needles. No other salts could be obtained, owing to their great solubility.

*Dichloroethylenediaminediamminecobaltic* salts, YX, where

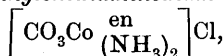


—Both series of stereoisomerides have been obtained. The method of preparation is briefly as follows: By warming trinitrotri-amininecobalt with ethylenediamine, trinitroethylenediamineamminecobalt is obtained



By heating with concentrated hydrochloric acid, the latter salt is transformed into dichloroaquoethylenediamineamminecobaltic chloride,  $\left[ \begin{smallmatrix} \text{Cl}_2 & \text{en} \\ \text{H}_2\text{O} & \text{Co} & \text{NH}_3 \end{smallmatrix} \right] \text{Cl}$ , of which 1 gram is then dissolved in 25% ammonia ( $3\frac{1}{2}$  c.c.). After five minutes, 3.5 c.c. of concentrated hydrochloric acid are added to the solution, which is then heated until it becomes greenish-blue in colour. On cooling, green crystals of the *trans*-chloride,  $\text{YCl} \cdot \frac{1}{2}\text{H}_2\text{O}$ , are deposited, from which, by the method of double decomposition, the following salts were obtained, generally as green precipitates: *trans-nitrate*,  $\text{YNO}_3$ ; *trans-iodide*,  $\text{YI}$ ; *trans-bromide*,  $\text{YBr}$ ; *trans-thiocyanate*,  $\text{YSCN}$ ; *trans-hydrogen sulphate*,  $\text{YHSO}_4 \cdot \text{H}_2\text{O}$ ; *trans-dithionate*,  $\text{Y}_2\text{S}_2\text{O}_6$ . The iodide is sensitive to light.

The *cis*-isomerides were prepared from the *trans*-compounds as follows: By heating a solution of the *trans*-chloride with potassium carbonate until the colour had changed to red, and then cooling, garnet-red crystals of *carbonatoethylenediaminediamminecobaltic chloride*,

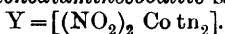


were obtained. By treating this compound with concentrated hydrochloric acid in the cold, a solution of the required *cis*-chloride was obtained, from which, on the addition of ammonium bromide, the *cis*-bromide,  $\text{YBr}$ , was deposited as a bluish-violet precipitate. The *cis*-dithionate,  $\text{Y}_2\text{S}_2\text{O}_6$ , is a violet precipitate obtained from a solution of the bromide by the addition of sodium dithionate.

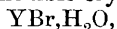
[With G. LINDENBERG.]—*Diacidoditrimethylenediaminecobaltic* salts,  $[\text{X}_2\text{Co}(\text{tn})_2]\text{X}$ .—Only the 1 : 6-dinitro- and 1 : 6-dichloro-salts have so far been prepared. The 1 : 6-dichloro-salts are distinguished from the corresponding diethylenediamine salts by their ready hydration (formation of aquo-salts) in aqueous solution. The neutral, green solution of a dichloroditrimethylenediamine salt rapidly becomes violet in colour; the addition of concentrated hydrochloric acid restores the green colour.

Carbonato-salts have been prepared from the 1 : 6-dichloro-salts, but could not be made to furnish the stereoisomeric 1 : 2-dichloro-salts.

*trans-Dinitroditrimethylenediaminecobaltic* salts, YX, where



—The *nitrite*,  $\text{YNO}_2$ , is obtained by heating potassium cobaltinitrite with trimethylenediamine in aqueous solution. It forms large, thick, yellowish-brown, pleochroic, rhombic crystals. The *bromide*,



and the *iodide*,  $\text{YI} \cdot 2\text{H}_2\text{O}$ , are obtained from the nitrite by interaction with potassium bromide and iodide respectively, the former as brownish-yellow, monoclinic crystals, and the latter as yellow to yellowish-green, pleochroic, rhombic prisms. The *chloride*,  $\text{YCl} \cdot \text{H}_2\text{O}$ , and *nitrate*,  $\text{YNO}_3$ , are best obtained from the iodide by interaction with silver chloride and nitrate respectively; the former gives light to dark brown, pleochroic, monoclinic crystals, and the latter rhombic plates.

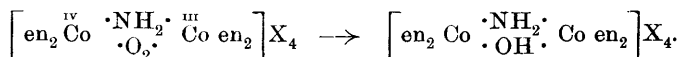
1 : 6-Dichloroditrimethylenediaminecobaltic chloride,  $[\text{Cl}_2 \text{Co tn}_2]\text{Cl}$ , is obtained by heating the dinitronitrite with hydrochloric acid; a green solution is obtained, which, on cooling, deposits green, prismatic, columnar crystals. The solution is turned red by sodium hydroxide and ammonia, and gives characteristic precipitates with the bromide, iodide, thiocyanate, permanganate, ferrocyanide, ferricyanide, or nitrate of potassium, and with sodium thiosulphate. Hydrogen sulphide precipitates cobalt sulphide. Potassium platinichloride gives green crystals of the *platinichloride*,  $[\text{Cl}_2 \text{Co tn}_2]_2 \text{PtCl}_6$ .

Carbonatoditrimethylenediaminecobaltic chloride,  $[\text{CO}_3 \text{Co tn}_2]\text{Cl} \cdot \text{H}_2\text{O}$ , was obtained by heating a solution of the 1 : 6-dichloro-chloride with sodium carbonate until it became bluish-red in colour. The addition of alcohol precipitated a white salt, and the red solution remaining deposited the required chloride in red, needle-shaped crystals. By interaction with hydrogen chloride, no matter under what conditions, the green 1 : 6-dichloro-chloride was always obtained. T. S. P.

### Optically-active Compounds of Cobalt and Chromium.

ALFRED WERNER (*Arch. Sci. Phys. Nat.*, 1911, [iv], 32, 457—467).—A general account is given of results which have, for the most part, been already published (*Abstr.*, 1911, i, 613, 838, 960; this vol., i, 10). In addition, the author mentions that optically-active compounds of the *tetraethylenediamine-μ-aminoperoxodicobalt* and *tetraethylenediamine-μ-amino-ol-dicobalt* series have been obtained. The rotations of the compounds of the first series are very large, the nitrate of the first series having a specific rotation of  $840^\circ$ , which corresponds with a molecular rotation of about  $6000^\circ$ .

From a consideration of the results hitherto obtained it follows that the sign of the rotation is not connected with the configuration of the diethylenediaminecobaltic radicle. This is well shown by the fact that *l*-tetraethylenediamine-μ-aminoperoxodicobalt salts furnish *d*-tetraethylenediamine-μ-amino-ol-dicobalt salts on reduction :



Also, *l*-chloroisothiocyanatodiethylenediaminecobaltic salts and *d*-chloronitrodiethylenediaminecobaltic salts both give rise to *d*-nitroisothiocyanatodiethylenediaminecobaltic salts by interaction with sodium nitrite and potassium thiocyanate respectively.

An examination of the compounds hitherto prepared shows that it is not always the isomeride of the same sign of rotation which gives the least soluble salt with *d*-bromocamphorsulphonic acid.

T. S. P.

**Preparation of Acid Chlorides from Two or More Molecules of Carbamide Chloride by Elimination of Hydrogen Chloride.** VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 238961).—When carbamide chloride is heated in the absence of moisture either with or without a solvent, two or more molecules condense with evolution of hydrogen chloride.

*Allophanic chloride*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{COCl}$ , a fuming, colourless, readily decomposable powder, which reacts energetically with water according to the equation:  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{COCl} + \text{H}_2\text{O} = \text{CO}(\text{NH}_2)_2 + \text{CO}_2 + \text{HCl}$ , was thus obtained at  $30^\circ$ , whilst at about  $100^\circ$  three molecules combined, yielding *biuretcarboxyl chloride*,  $\text{C}_2\text{H}_4\text{N}_3\text{O}_2 \cdot \text{COCl}$ , a colourless, non-fuming powder, decomposed by water with elimination of hydrogen chloride and carbon dioxide:  $\text{C}_2\text{H}_4\text{O}_2\text{N}_3 \cdot \text{COCl} + \text{H}_2\text{O} = \text{HCl} + \text{CO}_2 + \text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ .

F. M. G. M.

**Hypochlorous [Acid and] Amides.** ÉTIENNE BOISMENU (*Compt. rend.*, 1912, 154, 1482—1484. Compare Abstr., 1911, i, 957).—The action of an aqueous solution of hypochlorous acid on amides at  $0^\circ$  gives rise to monochloro- or dichloro-amides, according to the proportion of amide and of water employed. The dichloro-derivatives are yellow liquids, the stability of which diminishes as the molecular weight increases. On treatment with amides, they yield monochloro-derivatives.

*Acetyldichloroamide*,  $\text{CH}_3 \cdot \text{CO} \cdot \text{NCl}_2$ , has an odour of chlorine, and is insoluble in water. It decomposes above  $6^\circ$ , depositing crystals of acetylchloroamide. *Propionyldichloroamide* and *formyldichloroamide* have also been prepared. The latter is very explosive, and must be kept in well cooled vessels (compare Mauguin, Abstr., 1909, i, 892).

W. O. W.

**Cobalt Thiocyanates, and the Cause of the Colour Changes in Cobalt Salts.** ARTHUR HANTZSCH and YUJI SHIBATA (*Zeitsch. anorg. Chem.*, 1912, 73, 309—324).—Cobaltous thiocyanate is largely bimolecular in urethane solution at  $49^\circ$ , but almost completely unimolecular in alcoholic solution at  $78^\circ$ . The existence of complex ions in the alcoholic solution is shown by the method used by Donnan and Bassett (*Trans.*, 1902, 81, 944). The absorption spectra show the blue cobalt band, and a broad band in the ultra-violet with its maximum at  $1/\lambda$  3400 and minimum at  $1/\lambda$  3850. The absorption is slightly increased at  $55^\circ$  and  $80^\circ$ . Beer's law is departed from at considerable dilutions.

The colour of the blue solution is attributed to the presence of the complex salt,  $\text{Co}(\text{SCN})_4\text{Co}$ , in confirmation of which it is noted that the compound,  $\text{Co}(\text{SCN}_4)\text{Me}_2$ , is blue. The salt,  $\text{Co}(\text{SCN})_4\text{K}_2$ , is blue, but its spectrum in absolute alcohol is practically identical with that of cobalt thiocyanate, indicating dissociation into its components. Amyl alcohol gives an almost identical solution, whilst moist ether

contains the salt in an almost undissociated condition. The action of alcohols in promoting dissociation is attributed to the formation of the known alcoholates of cobalt thiocyanate. The decomposition is still more pronounced in aqueous solution, but is lessened by the addition of potassium thiocyanate.

The blue colour of cobalt thiocyanate is changed to pink by the addition of mercuric chloride or zinc chloride. The colour of the salt,  $\text{Co(SCN)}_2 \cdot \text{HgCl}_2$ , is not altered by further addition of mercuric chloride. This salt has not been isolated, but when the alcoholic solution is evaporated with a further quantity of mercuric chloride, pink crystals of a compound,  $2\text{Co(SCN)}_2 \cdot 3\text{HgCl}_2$ , are obtained. The change of colour in cobalt chloride solution is also due to the formation of a compound,  $[\text{CoCl}_4(\text{HgCl}_2)_2]\text{Co}$ , and not, as assumed by Donnan and Bassett, to  $(\text{HgCl}_4)\text{Co}$ .

The molecular weight of cobalt thiocyanate in aqueous solution shows that it only dissociates into two ions, except in very dilute solutions, whilst the chloride and bromide yield three ions, even in concentrated solutions. It is therefore considered to exist in solution as the compound  $[\text{Co}(\text{SCN})_5(\text{H}_2\text{O})_5]\text{SCN}$ . The whole of the colour changes may be explained as changes of the co-ordinative unsaturated complex,  $\text{CoX}_4$ , into the saturated complex,  $\text{CoX}_6$ . C. H. D.

**Systems Formed by Antimony Chloride and Bromide with Monosubstituted Benzene Hydrocarbons.** BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1275—1302. Compare Abstr., 1911, i, 273).—The author has subjected to thermal analysis the systems formed by antimony chloride and bromide with toluene, ethylbenzene, propylbenzene (see Abstr., 1911, i, 532), and *isoamyl*-benzene. The results are given in the form both of curves and of tables.

Rosenheim and Stellmann (Abstr., 1902, i, 68) state that antimony trichloride forms with toluene a compound having a composition analogous to that of the benzene compound, namely,  $3\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{Me}$ ; but this compound is really  $2\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{Me}$ , the solid phase corresponding with  $3\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{Me}$  being antimony trichloride itself.

The melting points of the thirteen compounds formed by the eight systems examined are as follows :

	$2\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{R}$ .	$\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{R}$ .	$2\text{SbBr}_3 \cdot \text{C}_6\text{H}_5\text{R}$ .	$\text{SbBr}_3 \cdot \text{C}_6\text{H}_5\text{R}$ .
$\text{SbX}_3 \cdot \text{C}_6\text{H}_5\text{Me}$ .....	42·5°	15—16° (decomp.)	38—39° (decomp.)	9° (decomp.)
$\text{SbX}_3 \cdot \text{C}_6\text{H}_5\text{Et}$ .....	37·0	39·0°	—	33 „
$\text{SbX}_3 \cdot \text{C}_6\text{H}_5\text{Pr}$ .....	9—10 (decomp.)	1·5	—	1 „
$\text{SbX}_3 \cdot \text{C}_6\text{H}_5 \cdot \text{C}_2\text{H}_{11}$ ...	7·5° (decomp.)	—20·5	—	—15 „

It will be seen that increase of the magnitude of the benzene substituent is accompanied by decrease in the stability of the compounds formed with antimony trichloride and tribromide.

The transition (*p*) and eutectic (*e*) points, and the corresponding

compositions (mols. of hydrocarbon per mol. of antimony chloride), are given in the following table :

	$\frac{2\text{SbCl}_3, \text{C}_6\text{H}_5\text{R}}{\text{SbCl}_3, \text{C}_6\text{H}_5\text{R}}$		$\frac{2\text{SbCl}_3, \text{C}_6\text{H}_5\text{R}-\text{SbCl}_3}{\text{SbCl}_3, \text{C}_6\text{H}_5\text{R}-\text{SbCl}_3}$		$\frac{\text{SbCl}_3, \text{C}_6\text{H}_5\text{R}-\text{SbCl}_3}{\text{SbCl}_3, \text{C}_6\text{H}_5\text{R}-\text{SbCl}_3}$	
	Temp.	Composition.	Temp.	Composition.	Temp.	Composition.
$\text{SbCl}_3-\text{C}_6\text{H}_5\text{Me}$ ..	11°	1·8 (p)	40·0°	0·46 (e)	—	—
$\text{SbCl}_3-\text{C}_6\text{H}_5\text{Et}$ .....	35	0·62 (e)	36·8	0·47 (e)	33°	0·52 (e)
$\text{SbCl}_3-\text{C}_6\text{H}_5\text{Pr}$ .....	—	—	8·5	0·88 (p)	1	0·98 (e)
$\text{SbCl}_3-\text{C}_6\text{H}_5\cdot\text{C}_5\text{H}_{11}$ ..	-33	3·1 (p)	-21·0	1·3 (p)	-5	1·2 (p)

The transition points for  $\text{SbBr}_3, \text{C}_6\text{H}_5\text{R}-\text{SbBr}_3$  are as follows :

	Temp.	Composition.
$\text{SbBr}_3-\text{C}_6\text{H}_5\text{Me}$ .....	—	—
$\text{SbBr}_3-\text{C}_6\text{H}_5\text{Et}$ .....	29°	1·17
$\text{SbBr}_3-\text{C}_6\text{H}_5\text{Pr}$ .....	-5	3·1
$\text{SbBr}_3-\text{C}_6\text{H}_5\cdot\text{C}_5\text{H}_{11}$ .....	-17	5·07

This continual fall in the transition temperature again indicates diminution of stability of these compounds as the magnitude of the hydrocarbon increases.

T. H. P.

**Systems Formed by Antimony Trichloride and Tribromide with Disubstituted Benzene Hydrocarbons.** BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1303—1328). —The systems here described contain *o*-, *m*-, or *p*-xylene or *p*-cymene. The results of the thermal analyses are given as curves and tables.

The replacement of a second hydrogen atom of benzene by an alkyl radicle (compare preceding abstract) produces no change in the character of the system, the temperature diagrams being similar to those given by the systems containing monosubstituted benzenes. Also, here too, antimony chloride gives compounds of the two types  $2\text{SbCl}_3, \text{C}_6\text{H}_4\text{R}_2$  and  $\text{SbCl}_3, \text{C}_6\text{H}_4\text{R}_2$ , whilst the bromide, as a rule, yields only one compound,  $\text{SbBr}_3, \text{C}_6\text{H}_4\text{R}_2$ . The compounds are of approximately the same stability as those formed with toluene or ethylbenzene. The results obtained with the three xylenes show that isomerism exerts a marked influence on the physical properties of these compounds.

The melting points of the hydrocarbons and of the various compounds they form are given below, the numbers for methylbenzene being inserted for purposes of comparison :

	Hydro-carbon.	$2\text{SbX}_3, \text{C}_6\text{H}_4\text{R}_2$ .	Diff.	$\text{SbX}_3, \text{C}_6\text{H}_4\text{R}_2$ .	Diff.
$\text{SbCl}_3-p\text{-C}_6\text{H}_4\text{Me}_2$ .....	14°	70°	56°	56°	42°
$\text{SbCl}_3-m\text{-C}_6\text{H}_4\text{Me}_2$ .....	-57	38	95	7·5	64·5
				(decomp.)	
$\text{SbCl}_3-o\text{-C}_6\text{H}_4\text{Me}_2$ .....	-29	33·5	62·5	19·5°	48·5
$\text{SbCl}_3-\text{C}_6\text{H}_5\text{Et}$ .....	-93	37	130	39	132
$\text{SbCl}_3-p\text{-C}_6\text{H}_4\text{MePr}^\beta$ ..	-75	40	115	5—6	80
				(decomp.)	
$\text{SbBr}_3-p\text{-C}_6\text{H}_4\text{Me}_2$ .....	14	67·5	53·5	—	—
$\text{SbBr}_3-m\text{-C}_6\text{H}_4\text{Me}_2$ ..	-57	—	—	13·5	70·5
$\text{SbBr}_3-o\text{-C}_6\text{H}_4\text{Me}_2$ .....	-29	—	—	24	53
$\text{SbBr}_3-\text{C}_6\text{H}_5\text{Et}$ .....	-93	—	—	33	126
				(decomp.)	
$\text{SbBr}_3-p\text{-C}_6\text{H}_4\text{MePr}^\beta$ ..	-75	—	—	10	85
				(decomp.)	

T. H. P.

**Relations of Trisubstituted Benzene Hydrocarbons to Antimony Trichloride and Tribromide.** BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1329—1341).—The systems formed by antimony trichloride and tribromide with 1 : 3 : 5- and 1 : 2 : 4-trimethylbenzenes (mesitylene and  $\psi$ -cumene) have been examined.

Mesitylene forms compounds of the two types  $2\text{SbX}_3 \cdot \text{C}_6\text{H}_3\text{Me}_3$  and  $\text{SbX}_3 \cdot \text{C}_6\text{H}_3\text{Me}_3$  with both antimony chloride and bromide, and the same is the case with  $\psi$ -cumene. The only other benzene hydrocarbon with which this has been found to occur is toluene.

The melting points of these compounds are as follows :

	$2\text{SbX}_3 \cdot \text{C}_6\text{H}_3\text{Me}_3$ .	$\text{SbX}_3 \cdot \text{C}_6\text{H}_3\text{Me}_3$ .
$\text{SbCl}_3$ -1 : 3 : 5- $\text{C}_6\text{H}_3\text{Me}_3$ .....	75.5°	43° (decomp.)
$\text{SbCl}_3$ -1 : 2 : 4- $\text{C}_6\text{H}_3\text{Me}_3$ .....	56.0	-4 to -5° „
$\text{SbBr}_3$ -1 : 3 : 5- $\text{C}_6\text{H}_3\text{Me}_3$ .....	69.5	38—39 „
$\text{SbBr}_3$ -1 : 2 : 4- $\text{C}_6\text{H}_3\text{Me}_3$ .....	36.0 (decomp.)	13 „

The eutectic points and the corresponding compositions are as follows :

System ...	(1) $\text{C}_6\text{H}_3\text{Me}_3$ - $\text{SbX}_3 \cdot \text{C}_6\text{H}_3\text{Me}_3$ .			(2) $2\text{SbX}_3 \cdot \text{C}_6\text{H}_3\text{Me}_3$ - $\text{SbX}_3$ .		
	Temp.	Com- position.	M. p. of hydro- carbon.	Temp.	Com- position.	M. p. of $\text{SbX}_3$ .
$\text{SbCl}_3$ -1 : 3 : 5- $\text{C}_6\text{H}_3\text{Me}_3$	-55.6°	126.2	-54.4°	58.5°	0.15	73°
$\text{SbCl}_3$ -1 : 2 : 4- $\text{C}_6\text{H}_3\text{Me}_3$	-60.0	8.25	-57.4	51.0	0.27	73
$\text{SbBr}_3$ -1 : 3 : 5- $\text{C}_6\text{H}_3\text{Me}_3$	-55.2	147.0	-54.4	69.0	0.42	94
$\text{SbBr}_3$ -1 : 2 : 4- $\text{C}_6\text{H}_3\text{Me}_3$	-58.8	28.4	-57.4	—	—	—

(The composition is given in mols. of hydrocarbon per mol. of  $\text{SbX}_3$ .)

The transition points,  $\text{SbX}_3 \cdot \text{C}_6\text{H}_3\text{Me}_3$ - $2\text{SbX}_3 \cdot \text{C}_6\text{H}_3\text{Me}_3$ , are as follows :

	Temp.	Composition.
$\text{SbCl}_3$ -1 : 3 : 5- $\text{C}_6\text{H}_3\text{Me}_3$ .....	38°	1.8
$\text{SbCl}_3$ -1 : 2 : 4- $\text{C}_6\text{H}_3\text{Me}_3$ .....	-5	1.83
$\text{SbBr}_3$ -1 : 3 : 5- $\text{C}_6\text{H}_3\text{Me}_3$ .....	29	3.45
$\text{SbBr}_3$ -1 : 2 : 4- $\text{C}_6\text{H}_3\text{Me}_3$ .....	7	1.72

Increase of the number of hydrogen atoms of benzene replaced by alkyl radicles does not diminish, but rather increases, the capability of these hydrocarbons to form compounds with antimony trichloride and tribromide.

T. H. P.

**Electrolytic Reduction of Nitrobenzene.** RALPH CUTHBERT SNOWDON (*J. Physical Chem.*, 1911, 15, 797—844).—The author endeavoured to develop an electrolytic method of reducing nitrobenzene which should not require the use of a porous cup or a platinum anode.

Nitrobenzene was vigorously stirred with ferrous chloride solution at 100° in a long cell provided with iron electrodes. The amount of anode iron dissolved was largely in excess of the electrolytic equivalent, and dissolution of iron also occurred at the cathode in increasing proportion as the current density was lowered. With high current densities (10 amp./dm<sup>2</sup>), cathode corrosion was very small, and the

yield attained 95% of aniline on the total iron dissolved. Although sheet iron in ferrous chloride solution will not reduce nitrobenzene on boiling, it was found that under the emulsifying influence of rapid stirring the iron electrodes dissolved equally, without electrolytic aid, and gave a 78% yield of aniline calculated on the iron dissolved, so that the commercial reduction of nitrobenzene by massive iron might be rendered possible by suitable agitation to bring the substances into intimate contact. The presence of a dissolved ferrous salt is essential in the electrolytic as in the chemical reduction. Ferrous chloride is apparently without action on nitrobenzene, so that its catalytic activity must be attributed to a depolarising influence on the iron. In this respect ferrous chloride and acetate are more efficient than the sulphate and benzoate.

Nitrobenzene is reduced at 100° by alkaline sodium sulphide, freshly precipitated ferrous hydroxide, and sodium arsenite, but not by alkaline potassium ferrocyanide.

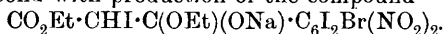
Sodium arsenite gives 60—90% of azoxybenzene, 5—14% of aniline, and a trace of azobenzene. This is contrary to electrolytic experience where azobenzene is produced above and azoxybenzene below 90°. Alkaline sodium sulphide and ferrous hydroxide give aniline and small amounts of azobenzene. The yield appears to vary with the order in which the three components, nitrobenzene, sodium hydroxide, and reducing agent, are mixed. R. J. C.

**Aromatic Nitro-derivatives.** ROBERT CIUSA (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 523—524. Compare *Abstr.*, 1911, i, 931).—The observation of Werner (*Abstr.*, 1910, i, 20) that trinitromesitylene gives yellow solutions in some organic solvents, although it is not dissociated in formic acid solution, indicates that there is no connexion between the dissociability of the aromatic nitro-derivatives and their power to form additive products. The author now finds that tetranitromethane also is not dissociated in formic acid solution, although it can form additive products. R. V. S.

**Isomorphous Mixtures: the Systems Chloronitrobenzenes—Bromonitrobenzenes.** ROBERT KREMANN (*Zeitsch. Kryst. Min.*, 1911, 50, 86; from *Jahrb. k.k. geol. Reichs.*, 1908, 58, 659—672).—The time-cooling curves and the freezing curves of the three systems (ortho, meta, para) show that the crystallisation interval for mixtures of the ortho-series is very small; that of the meta-series is also small, but it is larger in the para-series. The fusion curves of the two last systems belong to Roozeboom's type V. L. J. S.

**1-Bromo-2:4:6-tri-iodo-3:5-dinitrobenzene and Some of its Derivatives.** C. LORING JACKSON and HAROLD E. BIGELOW (*Amer. Chem. J.*, 1911, 46, 549—574).—It has been shown by Jackson and Robinson (*Abstr.*, 1890, 377) that 1:3:5-tribromo-4:6-dinitrobenzene is converted by ethyl sodiomalonate into ethyl 3-bromo-4:6-dinitrophenylmalonate. It has now been found that when 1-bromo-2:4:6-tri-iodo-3:5-dinitrobenzene is treated with ethyl sodiomalonate at the ordinary temperature, 1-bromo-2:6-di-iodo-3:5-dinitrobenzene and ethyl ethanetetra-carboxylate are produced, whilst if the mixture is

heated, ethyl 2-bromo-3-iodo-4:6-dinitrophenylmalonate is obtained. This shows that the explanation given previously (Jackson and Moore, Abstr., 1890, 497; Jackson, Abstr., 1890, 983) is not correct, but that it must be assumed that ethyl sodiomalonate reacts in the enolic form, and that the iodine atom and the  $\cdot\text{C}_6\text{BrI}_2(\text{NO}_2)_2$  group are added at the double bond with production of the compound

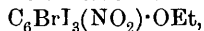


On acidification, the hydrogen of the  $\cdot\text{OH}$  group might combine with the substituted phenyl group with formation of the compounds  $\text{C}_6\text{HBrI}_2(\text{NO}_2)_2$  and  $\text{CHI}(\text{CO}_2\text{Et})_2$ ; the latter would then react with the excess of ethyl sodiomalonate to produce ethyl ethanetetra-carboxylate.

1-Bromo-2:4:6-tri-iodobenzene,  $\text{C}_6\text{H}_2\text{BrI}_3$ , m. p.  $146^\circ$ , obtained by treating a mixture of 2:4:6-tri-iodoaniline, glacial acetic acid, and hydrobromic acid with sodium nitrite, crystallises in pale yellow needles, and when heated with fuming nitric acid is converted into 1-bromo-2:4:6-tri-iodo-3:5-dinitrobenzene,  $\text{C}_6\text{BrI}_3(\text{NO}_2)_2$ , m. p.  $292^\circ$ , which forms white needles. When tri-iodoaniline containing dark-coloured impurities was employed, the crude 1-bromo-2:4:6-tri-iodobenzene yielded, on nitration, some 1:3-dibromo-2:4:6-tri-iodo-5-nitrobenzene,  $\text{C}_6\text{Br}_2\text{I}_3\cdot\text{NO}_2$ , m. p. about  $256^\circ$  (decomp.), which crystallises in hexagonal prisms.

1-Bromo-2:6-di-iodo-3:5-dinitrobenzene,  $\text{C}_6\text{HBrI}_2(\text{NO}_2)_2$ , m. p.  $187^\circ$ , crystallises in straw-coloured needles. Ethyl 2-bromo-3-iodo-4:6-dinitrophenylmalonate,  $\text{C}_6\text{HBrI}(\text{NO}_2)_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , m. p.  $107^\circ$ , forms stout, lemon-yellow crystals. A small quantity of another compound, m. p. about  $250^\circ$  (decomp.), was also isolated from the product of the reaction between ethyl sodiomalonate and 1-bromo-2:4:6-tri-iodo-3:5-dinitrobenzene.

By the action of sodium ethoxide on 1-bromo-2:4:6-tri-iodo-3:5-dinitrobenzene, 3-bromo-2:4:6-tri-iodo-5-nitrophenetole,



m. p.  $148^\circ$ , is obtained, which crystallises in light pink needles, and is reduced by zinc and acetic acid to *m*-aminophenol. 3-Bromo-2:4:6-tri-iodo-5-nitroanisole,  $\text{C}_6\text{BrI}_3(\text{NO}_2)\cdot\text{OMe}$ , m. p.  $163^\circ$ , forms pale yellow needles.

When 2-bromo-1:3:5-tri-iodo-4:6-dinitrobenzene is heated with zinc and acetic acid, 5-bromo-*m*-phenylenediamine is produced, but on reduction with ferrous hydroxide it is converted into 1-bromo-2:4:6-tri-iodo-*m*-phenylenediamine,  $\text{C}_6\text{BrI}_3(\text{NH}_2)_2$ , m. p.  $187^\circ$ , which forms stout, greyish-white needles, and yields a hydrochloride, decomposing at  $100^\circ$ .

Reduction experiments have been carried out with several other iodo-compounds. Zinc and acetic acid remove iodine from 1:3:5-tri-iodo-4:6-dinitrobenzene. 2:4:6-Tri-iodoaniline is not affected by tin and hydrochloric acid, and only very slightly by zinc and acetic acid. 1-Bromo-2:4:6-tri-iodobenzene is reduced by zinc and acetic acid with formation of *p*-iodobromobenzene. These experiments show that iodine is more easily replaced by hydrogen than is bromine.

Sodium ethoxide does not react with 2:4:6-tri-iodobenzene, and only very slightly with 1-bromo-2:4:6-tri-iodobenzene. E. G.

**Preparation of Alkylamines by Catalysis.** PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1911, 153, 1204—1208. Compare Abstr., 1909, i, 292; 1911, ii, 627).—An extension of the general reaction already described to the preparation of new amines.

*iso*Propyl alcohol is transformed into *isopropylamine* when its vapour mixed with ammonia is passed over thorium dioxide at 250°; the yield is 20%. At higher temperatures propylene is formed together with *diisopropylamine*. The reaction proceeds with difficulty in the case of *diphenylcarbinol*. At 280° the corresponding amine is obtained, but the chief product is tetraphenylethylene; this substance is easily obtained at 300° in absence of ammonia.

*cyclo*Hexanol and also its 2-, 3-, and 4-methyl derivatives yield the primary and secondary amines at 290—320°. 4-Methylcyclohexylamino-4-methylcyclohexane, (C<sub>6</sub>H<sub>10</sub>Me)<sub>2</sub>NH, b. p. 275° (decomp.), forms a *phenylcarbamide*, m. p. 181°.

The following secondary amines were prepared by passing a mixture of *cyclohexylamine* and an alcohol over thorium dioxide at 320°. *Ethylaminocyclohexane*, C<sub>6</sub>H<sub>11</sub>·NHEt, *Propylaminocyclohexane*, b. p. 185°; the *phenylcarbamide* has m. p. 113°. *iso*Butylaminocyclohexane, b. p. 193°; the *phenylcarbamide* has m. p. 90°. *iso*Amylaminocyclohexane, b. p. 205°; the *phenylcarbamide* has m. p. 129°. *Benzylaminocyclohexane*, b. p. 195°/80 mm., the *phenylcarbamide* has m. p. 121°.

*cyclo*Hexylamino-2-methylcyclohexane, b. p. 260° with slight decomposition; the *hydrochloride* has m. p. 182°, and the *phenylcarbamide*, m. p. 140°; the 3-methyl derivative, b. p. 270° (decomp.), forms a *hydrochloride*, m. p. 197°, and a *phenylcarbamide*, m. p. 191°, whilst the 4-methyl derivative, b. p. 270°, gives a *phenylcarbamide*, m. p. 108°. The yield of the latter was 20%; the lowest yield was obtained in the case of *methylaminocyclohexane*. W. O. W.

**Behaviour of Nitrosomonoarylcabamides towards Primary Amines and Phenols.** J. HAAGER (*Monatsh.*, 1911, 32, 1089—1102).—Nitrosomonoarylcabamides condense in alcoholic solution with primary aromatic bases to diazoamino-compounds, which contain the aromatic nuclei of both components, and to arylcabamides which contain the nuclei of the bases. Accordingly, the rest of the carbamic acid, and not the nitroso-group, is eliminated from the nitrosocabamides. The change is the same when the mixture of the components is heated.

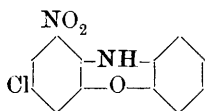
Nitrosoarylcabamides react also with alkaline, and with alcoholic, solutions of phenols and their derivatives, with the formation of, hydroxyazo-compounds and alkaline salts of cyanic acid, which have been formed by the elimination of -CO·NH<sub>2</sub> from the nitrosocabamides.

Nitrosophenylcabamide reacts with aniline to form diazoamino-benzene and phenylcabamide; with *p*-toluidine, benzenediazoamino-toluene, m. p. 85°, and *p*-tolylcabamide are obtained. Nitroso-*p*-tolylcabamide and aniline yield the same compounds.

Nitrosocabamide with phenol yields benzeneazophenol; with resorcinol it gives benzeneazoresorcinol, m. p. 161°. *p*-Nitrosotolylcabamide and resorcinol give rise to *p*-tolueneazoresorcinol, m. p. 183—184°. E. F. A.

**The Action of Phosphorus Thiochloride on Alkaline Solutions of Phenols.** WILHELM AUTENRIETH (*Ber.*, 1911, 44, 3754—3755).—The author draws attention to the fact that several of the substances prepared previously by himself (*Abstr.*, 1898, i, 419) have since been described afresh with different nomenclature (Ephraim, *Abstr.*, 1911, i, 284; this vol., i, 26). D. F. T.

**Dinitrophenols.** FRITZ ULLMANN and SHRIRANG M. SANÉ (*Ber.*, 1911, 44, 3730—3737. Compare *Abstr.*, 1908, i, 525; 1909, i, 21, 23).—On warming 4-chloro-2:6-dinitrophenol with toluenesulphonyl chloride and diethylaniline, 1:4-dichloro-2:6-dinitrobenzene is obtained; it forms colourless leaflets, m. p. 105° (corr.). If, however, the diethylaniline is replaced by sodium carbonate solution, the product is 4-chloro-2:6-dinitrophenyl *p*-toluenesulphonate; this crystallises in colourless needles, m. p. 127° (corr.); the action of ammonia on a boiling xylene solution of this ester yields 4-chloro-2:6-dinitroaniline (compare Körner, *Abstr.*, 1876, i, 230); similarly, the action of aniline on an alcoholic solution of the ester produces orange-yellow needles of 4-chloro-2:6-dinitrodiphenylamine, m. p. 130°, the same substance being obtained also from aniline and 1:4-dichloro-2:6-dinitrobenzene. The



last-named substance also reacts with dimethylamine, yielding 4-chloro-2:6-dinitrodimethylaniline as orange-yellow crystals, m. p. 111° (probably identical with that already described by Pinnow, *Abstr.*, 1899, i, 203). By the action of the above-mentioned dichlorodinitrobenzene or chlorodinitrophenyl *p*-toluenesulphonate on *o*-aminophenol there is obtained 3-chloro-5-nitrophenoxazine (annexed formula) in violet needles, m. p. about 192°.

1:2-Dichloro-3:5-dinitrobenzene is obtained from 6-chloro-2:4-dinitrophenol in a similar manner to the 1:4-dichloro-isomeride above; it forms hexagonal, pale yellow tablets, m. p. 56°; in boiling alcoholic solution with ammonia it yields yellow needles of 2-chloro-4:6-dinitroaniline (m. p. 157°), and with aniline, brick-red crystals of 2-chloro-4:6-dinitrodiphenylamine. Heated in alcoholic solution with *o*-aminophenol, it yields 3:5-dinitrophenoxazine (compare Turpin, *Trans.*, 1891, 59, 722).

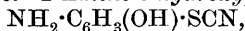
2-Chloro-3:5-dinitrotoluene, m. p. 63° (corr.), is obtained by the action of toluenesulphonyl chloride and diethylaniline on 3:5-dinitro-*o*-cresol; the lower m. p. previously obtained for this substance (Nietzki and Rehe, *Abstr.*, 1893, i, 15) was due to impurity. In the above process, 3:5-dinitro-*o*-tolyl *p*-toluenesulphonate (colourless needles, m. p. 167°), is obtained as a by-product. If the above chlorodinitrotoluene is allowed to react with *o*-aminophenol, 2:4-dinitro-6-methyl-2'-hydroxydiphenylamine is obtained, which crystallises in reddish-brown tablets, m. p. 177° (corr.), and by treatment with dilute soda passes into 3-nitro-5-methylphenoxazine (brown needles, m. p. 205° with decomp.).

The methyl esters of 3:5-dinitro-2-hydroxybenzoic acid and of 3:5-dinitro-4-hydroxybenzoic acid on treatment with toluenesulphonyl chloride and diethylaniline give the methyl esters of 2-chloro-3:5-

dinitrobenzoic acid (compare Purgotti, Abstr., 1902, i, 777) and 4-chloro-3:5-dinitrobenzoic acid (compare Ullmann, Abstr., 1909, i, 475) respectively. D. F. T.

**The Action of Metals on Fused Picric Acid.** J. SAPOSHNIKOFF (*Zeitsch. ges. Schiess. Sprengstoffwesen*, 1911, 6, 183—185).—Kast's work is discussed (Abstr., 1911, i, 852). The author heated one gram of various metals (in shavings or powder) with two grams of picric acid at 125°; the amount of dissolved metal was estimated and found, with the exception of tin, to be in proportion to the equivalent weights of the metal. The respective weights dissolved by the picric acid were: tin, 0.00; aluminium, 0.0488; iron, 0.153; copper, 0.1754; nickel, 0.1862; zinc, 0.2046, and lead, 0.2798 gram. F. M. G. M.

**Electrolytic Reduction of Nitrated Phenyl Thiocyanates.** FRITZ FICHTER and THEODOR BECK (*Ber.*, 1911, 44, 3636—3648).—Müller has shown that the reduction of *o*-nitrophenyl, *p*-nitrophenyl, and 2:4-dinitrophenyl thiocyanates by alcoholic ammonium sulphide causes elimination of the thiocyano-group and the formation of nitrated diphenyl disulphides, whilst their reduction by stannous chloride yields thiazole derivatives (*Zeit. Farb. Ind.*, 1906, 5, 357). The authors now show that different products are obtained by the electrolytic reduction of these thiocyanates at lead or copper cathodes; the thiocyano-group is only attacked when lead cathodes are used. The reduction of phenyl thiocyanate in 2*N*-alcoholic sulphuric acid at a rotating lead cathode and with a current density of 0.02 ampere per sq. cm. (the anodic compartment contains a lead plate in 2*N*-sulphuric acid) yields hydrogen cyanide and 57.5% of phenyl mercaptan. Under similar conditions the reduction of *o*-nitrophenyl thiocyanate yields 1-aminobenzthiazole, which is probably produced by the secondary interaction of the *o*-aminophenyl mercaptan and hydrogen cyanide initially formed. With a copper cathode and a current density of 0.019 ampere per sq. cm., *o*-nitrophenylthiocyanate is reduced to the *sulphate* of 2-amino-5-hydroxyphenyl thiocyanate,  $C_7H_6ON_2S, H_2SO_4, H_2O$ , probably through the intermediate formation of a hydroxylamine derivative. 2-Amino-5-hydroxyphenyl thiocyanate,



m. p. 121°, yields an *N*-acetyl derivative, m. p. 206° (decomp.) (the methyl ether of which has m. p. 81°), a *diacetyl* derivative, m. p. 183°, and, after diazotisation, couples with  $\beta$ -naphthol to form an azo-compound, m. p. 130°.

*p*-Nitrophenyl thiocyanate is reduced to *p*-aminophenyl thiocyanate at a lead or copper cathode, but in the latter case the intermediate product, *p*-thiocyanoazoxybenzene,  $ON_2(C_6H_4 \cdot SCN)_2$ , m. p. 170—171°, reddish-yellow leaflets, can be isolated.

The electrolytic reduction of 2:4-dinitrophenyl thiocyanate, on account of its slight solubility and the consequent large volume of solution, must be effected with large stationary cathodes of lead or copper foil; also the solution (in alcoholic sulphuric acid) must be hot, and a large current density, 0.033—0.038 ampere per sq. cm., must be

employed. With a lead cathode, the product is 1:4-diamino-5-hydroxybenzthiazole sulphate,  $\text{NH}_2 \cdot \text{C}_6\text{H}_2(\text{OH}) \begin{smallmatrix} \text{S} \\ \text{N} \end{smallmatrix} \text{C} \cdot \text{NH}_2, \text{H}_2\text{SO}_4$ , the formation of which is readily explicable in view of the course of the reduction of the *o*- and *p*-nitrophenyl thiocyanates. In favour of this constitution is the fact that the sulphate yields a diacetylaminoderivative, m. p. 268°, which is soluble in sodium hydroxide, and forms 1-amino-4-acetyl-amino-5-methoxybenzthiazole, m. p. 257—258°, with methyl sulphate and sodium hydroxide. When reduced at a copper cathode and with a current density of 0.05—0.06 ampere per sq. cm., 2:4-dinitrophenyl thiocyanate yields, at first the sulphate of 4-nitro-2-amino-5-hydroxyphenyl thiocyanate,  $3\text{C}_7\text{H}_5\text{O}_3\text{N}_3\text{S} \cdot \text{H}_2\text{SO}_4$  (diacetyl derivative,  $\text{C}_{11}\text{H}_9\text{O}_5\text{N}_3\text{S}$ , yellow, microcrystalline powder), and finally the sulphate of 2:4-diamino-5-hydroxyphenyl thiocyanate,  $\text{C}_7\text{H}_7\text{ON}_3\text{S} \cdot \text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  (NN-diacetyl derivative, m. p. 217°; triacetyl derivative, m. p. 156°).  
C. S.

**New Halogen Compounds of the Normal Butane Series.**  
JULIUS VON BRAUN and H. DEUTSCH (*Ber.*, 1911, 44, 3699—3706. Compare Braun, *Abstr.*, 1911, i, 610).—Phenoxybutylene,  $\text{C}_4\text{H}_7 \cdot \text{OPh}$ , obtained on decomposition of phenoxybutyltrimethylammonium hydroxide,  $\text{OPh} \cdot [\text{CH}_2]_4 \cdot \text{NMe}_3 \cdot \text{OH}$ , yields with bromine phenyl- $\gamma\delta$ -dibromobutyl ether,  $\text{OPh} \cdot \text{C}_4\text{H}_7\text{Br}_2$ , which is converted by hydrogen bromide into  $\alpha\beta$ -tribromobutane,  $\text{CH}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CHBr} \cdot \text{CH}_2\text{Br}$ . Magnesium removes two atoms of bromine, forming magnesium butylene bromide,  $\text{MgBr} \cdot [\text{CH}_2]_2 \cdot \text{CH} \cdot \text{CH}_2$ , and this is readily converted into  $\Delta\gamma$ -pentenoic acid,  $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , confirming the structural formula assigned to the preceding compounds.

Phenoxybutylene unites with hydrogen bromide to form phenyl  $\gamma$ -bromobutyl ether,  $\text{OPh} \cdot [\text{CH}_2]_2 \cdot \text{CHMeBr}$ .

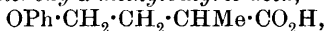
Phenoxybutylene is an oil, b. p. 208—210°/760 mm., 94—95°/16 mm.

Phenyl  $\gamma\delta$ -dibromobutyl ether is a colourless, odourless oil, b. p. 191—194°/13 mm.

$\alpha\beta$ -Tribromobutane is a colourless liquid of pleasant odour, b. p. 115—117°/10 mm.

The magnesium compound interacts with a variety of substances, so introducing the homoallyl complex,  $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2$ ; thus with benzaldehyde, phenylbutenylcarbinol,  $\text{OH} \cdot \text{CHPh} \cdot [\text{CH}_2]_2 \cdot \text{CH} \cdot \text{CH}_2$ , is obtained as a viscid, colourless liquid of ethereal odour, b. p. 125°/11 mm.

Phenyl- $\gamma$ -bromobutyl ether is a colourless, odourless oil, b. p. 130—131°/9 mm. After prolonged boiling with potassium cyanide, the nitrile is obtained as a colourless, odourless oil, b. p. 156—157°/10 mm., and this, when boiled for ten hours with alcoholic potassium hydroxide, gives  $\gamma$ -phenoxy- $\alpha$ -methylbutyric acid,



which separates in lustrous, colourless crystals, m. p. 79°. The silver salt is a colourless, caseous precipitate.  
E. F. A.

**Simple Method of Formation of Hydroxyhydrindones.** KARL AUWERS (*Ber.*, 1911, **44**, 3692—3699. Compare *Abstr.*, 1910, i, 629).—On heating *p*-tolyl  $\alpha$ -bromopropionate with aluminium chloride, 7-hydroxy-4-methyl-1-hydrindone,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CO}\end{smallmatrix}\rangle\text{CH}_2$ , is obtained instead of *o*-bromopropionyl-*p*-cresol as expected. The structure of the hydrindone is established by the facts that it yields a semicarbazone and phenylhydrazone both soluble in alkali, and containing therefore a phenolic hydroxyl. The nucleus can be benzoylated and methylated, and this methyl derivative still forms a semicarbazone.

In a similar manner, the homologous isomeric methyl derivatives have been obtained from the *p*-tolyl  $\alpha$ -bromobutyrate and  $\alpha$ -bromo*iso*-butyrate. It is characteristic of these oxyhydrindones that their aqueous or alcoholic solutions are coloured deep blue by ferric chloride.

It is probable in the above reaction that *p*-cresol vinyl ketone,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{CH}:\text{CH}_2$ , is formed as an intermediate product. The yield of hydroxyhydrindones is only about 50% of the possible; coumaranone derivatives are also formed.

*p*-Tolyl  $\alpha$ -bromopropionate forms colourless, lustrous needles, m. p.  $33^\circ$ , b. p.  $145\text{--}150^\circ/18\text{ mm.}$

7-Hydroxy-4-methyl-1-hydrindone separates in flat, colourless, lustrous needles, m. p.  $110\text{--}111^\circ$ . The semicarbazone crystallises in colourless needles, m. p. above  $280^\circ$ ; the phenylhydrazone forms lustrous, almost colourless, fatty needles, m. p.  $183^\circ$ . The benzylidene compound crystallises in faintly yellow-coloured needles, m. p.  $129^\circ$ . The benzoate is characterised by short, colourless, lustrous, fatty needles, m. p.  $124\text{--}125^\circ$ , and the methyl ether by stellate aggregates of slender, colourless, lustrous needles, m. p.  $112\text{--}113^\circ$ . This methyl ether forms a semicarbazone, colourless needles, m. p.  $220\text{--}224^\circ$ , and a benzylidene derivative, colourless, lustrous needles, m. p.  $185\text{--}186^\circ$ .

*p*-Tolyl  $\alpha$ -bromoisobutyrate forms slender, colourless needles, m. p.  $39\text{--}40^\circ$ , b. p.  $152^\circ/18\text{ mm.}$

7-Hydroxy-2 : 4-dimethyl-1-hydrindone,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CO}\end{smallmatrix}\rangle\text{CHMe}$ , crystallises in colourless needles, m. p.  $53^\circ$ ; the benzoyl derivative yields lustrous, colourless needles, m. p.  $113\text{--}114^\circ$ ; the semicarbazone gives colourless, glass-like crystals, which gradually become citron-yellow on exposure; they become brown at  $220^\circ$ , m. p.  $230\text{--}232^\circ$ .

This hydrindone does not form a benzylidene compound.

7-Hydroxy-3 : 4-dimethyl-1-hydrindone,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Me}\langle\begin{smallmatrix}\text{CHMe} \\ \text{CO}\end{smallmatrix}\rangle\text{CH}_2$ , separates in stunted, colourless, lustrous crystals, m. p.  $53\text{--}54^\circ$ . The semicarbazone forms stunted crystals, m. p.  $217^\circ$ ; the benzylidene compound gives glass-like, yellow, flat needles, m. p.  $114^\circ$ .

*p*-Tolyl  $\alpha$ -bromobutyrate is an oil, b. p.  $160\text{--}163^\circ/20\text{ mm.}$

E. F. A.

**Retene.** II. ALFRED HEIDUSCHKA and H. GRIMM (*Arch. Pharm.*, 1912, **250**, 33—45. Compare *Abstr.*, 1910, i, 397).—Retenequinone reacts with organomagnesium haloids to form dihydroxydialkyl-

dihydroretenes, and these were isolated in a crystalline condition in the case of the phenyl, benzyl, *p*-tolyl, naphthyl, and methyl derivatives, but could not be obtained pure in the case of *o*-tolyl, *m*-xylyl, bromocamphor, ethyl, or *i*-amyl derivatives. Experiments on the reduction and dehydration of dihydroxydiphenyldihydrorotene are also recorded.

*Dihydroxydiphenyldihydrorotene*,  $C_{30}H_{28}O_2$ , m. p.  $172^\circ$ , obtained by condensing magnesium phenyl bromide with retenequinone in ether, forms colourless crystals, and is coloured red by sulphuric acid, yellow by fuming nitric acid. Heated with acetyl chloride, it yields

the corresponding *anhydride*,  $C_{16}H_{16}\begin{matrix} \text{CPh} \\ | \\ \text{CPh} \end{matrix} > O$ , m. p.  $143\text{--}144^\circ$ , crys-

tallising in clusters of needles, and giving when heated with potassium hydroxide in alcohol, in closed vessels, an *acid*, which probably corresponds with the product described by Acree (Abstr., 1905, i, 216) as obtained from diphenylphenanthrone; its ethereal solution is coloured blue by ammoniacal copper oxide, and then yields a *copper* derivative,  $(C_{30}H_{27}O_2)_2Cu$ , m. p.  $142^\circ$ , which at  $125\text{--}140^\circ$  slowly loses ammonia and turns green.

When heated with zinc dust, dihydroxydiphenyldihydrorotene yields *diphenylretene*, m. p.  $200^\circ$ , crystallising in colourless needles from alcohol or acetone. Reduction with hydriodic acid and phosphorus gives rise to *diphenylhexahydrorotene* (which forms colourless crystals, sinters at  $82^\circ$ , and melts completely at  $118^\circ$ ), and eventually to Liebermann and Spiegel's retenedodecahydride.

On bromination in carbon disulphide, dihydroxydiphenyldihydrorotene gives a pale yellow, finely granular powder, which on distillation with zinc yielded diphenylretene. Chlorination produced a similar product, containing 39.5% chlorine.

*Dihydroxydi-p-tolyldihydrorotene*, m. p.  $203^\circ$ , obtained in a manner analogous to that described for the phenyl derivative, forms glancing, colourless leaflets. The *anhydride*, m. p.  $152\text{--}154^\circ$ , occurs in colourless, transparent, small tablets. The products of bromination and chlorination resemble those of the lower homologue. *Dihydroxydibenzoyldihydrorotene*, m. p.  $200\text{--}201^\circ$ , forms stellate clusters of small, glancing needles. *Dihydroxydinaphthylidihydrorotene*, m. p.  $217\text{--}218^\circ$ , was isolated with some difficulty by treating the crude product with warm toluene; it yields an *anhydride*, m. p.  $188^\circ$ , which forms small glancing crystals from acetone or alcohol. *Dihydroxydimethyldihydrorotene*, m. p.  $166\text{--}167^\circ$ , was eventually obtained in poor yield as small, colourless crystals, giving a violet-brown coloration with sulphuric acid.

On chlorination in carbon tetrachloride with iodine as carrier, retene furnishes a viscid product, which on precipitation from alcohol with water forms an amorphous, colourless *substance*,  $C_{18}H_{14}Cl_9$  [?], m. p.  $98\text{--}100^\circ$ . T. A. H.

**Influence of Sulphur and Sulphur-containing Groups on the Order of Substitution of Hydrogen Atoms in Benzene by Bromine.** EDOUARD BOURGEOIS and A. ABRAHAM (*Rec. trav. chim.*, 1911, 30, 407—425. Compare Abstr., 1904, i, 28).—Substances

containing either of the groups  $-\text{SH}$ ,  $>\text{S}:\text{O}$ ,  $-\text{SO}_2\text{H}$ , are completely transformed by bromine. The authors have studied the action of bromine on aromatic sulphides and disulphides, sulphones and sulphononic acids. With bromine, the sulphides give rise to dibromides of the type  $\text{SRR}'\cdot\text{Br}_2$ , which show no tendency to split up into the sulphide and free bromine, but readily become transformed into substitution products.

*Phenylmethylylsulphonium dibromide*,  $\text{SMePhBr}_2$ , is obtained as a red, crystalline substance, m. p.  $87-88^\circ$ , when bromine acts on phenyl methyl sulphide in carbon tetrachloride solution below  $0^\circ$ . Above this temperature it gives off hydrogen bromide, and is transformed into *p*-bromophenyl methyl sulphide, m. p.  $37-37.5^\circ$ . This, when oxidised by potassium permanganate in acetic acid solution, yields the corresponding sulphone, m. p.  $102.5-103^\circ$ , which with phosphorus pentachloride gives *p*-chlorobromobenzene. The sulphide can also be obtained by the action of methyl iodide on the sodium salt of *p*-bromothiophenol.

*Diphenylsulphonium dibromide*,  $\text{SPh}_2\text{Br}_2$ , is obtained by a similar reaction to the above as a red, crystalline precipitate, which still more readily passes into the corresponding *p*-bromophenyl sulphide.

Phenyl disulphide when dissolved in bromine yields *p*-dibromophenyl disulphide (compare Hübner and Alsberg, *Annalen*, 1870, 156, 328).

Phenyl methyl sulphone is not attacked by bromine unless a catalyst, such as ferric chloride, is employed, in which case there is produced *p*-bromophenylmethylylsulphone, identical with that obtained by the oxidation of the corresponding sulphide with potassium permanganate (*loc. cit.*).

In all the above cases, the bromine atom enters the para-position to the sulphur-containing group, whilst, in the case of the sulphononic acids, the group  $-\text{SO}_3\text{H}$  directs the bromine to the meta-position.

W. G.

**Oxonium Compounds.** GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1244—1257).—According to Nef's theory, the first stage of the interaction of an alkyl halide with alcoholic alkali hydroxide consists of the dissociation of the alkyl halide into halogen hydracid, which is neutralised by the alkali, and the methylene residue  $\text{R}\cdot\text{CH}_2\cdot$ , which either combines with the alcohol, forming a simple ether, or undergoes isomeric change into an olefine. The fact that *tert*.-butyl iodide, which is incapable of methylene dissociation, gives no ether when treated with alcoholic alkali hydroxide, is regarded as confirmation of Nef's theory. The author finds that this evidence is fallacious, since tertiary alkyl halides, such as *tert*.-amyl bromide, do give ethers under the above conditions, although the yield is very small; also *tert*.-butyl iodide yields an appreciable amount of ether if treated with the alcoholic alkali in a sealed tube. Another observation which is not in agreement with Nef's theory is that triphenylmethyl chloride reacts with alcohols, giving ethers in theoretical yields.

The most obvious method of explaining these reactions is to assume that the alkyl halogen compound,  $\text{RX}$ , dissociates into alkyl

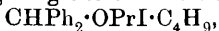
and halogen, which then combine with the alcohol, forming an oxonium compound,  $R'H:O:RX$ . The latter may then decompose in two ways, giving (1)  $R'O:R + HX$  or (2)  $R'H:O:HX +$  an olefine. These reactions would hence be closely analogous to those between alkyl halides and amines (see this vol., i, 116).

Owing to the doubt which exists concerning the intermediate formation of oxonium compounds in such reactions as the above and in the Grignard reaction, the author has studied the following reactions.

(1) The action of propyl iodide on triphenylmethyl ethyl ether in presence of magnesium. Here the first stage of the reaction consists in the formation of the oxonium compound,  $CPh_3 \cdot OEt \cdot PrI$ , which then decomposes, giving triphenylmethyl iodide and ethyl propyl ether.

(2) With the same ether as in (1), *isobutyl* iodide in presence of magnesium combines to form an oxonium derivative, which is subsequently resolved into triphenylmethyl iodide and ethyl *isobutyl* ether.

(3) Diphenylmethyl propyl ether and *isobutyl* iodide react in presence of magnesium, giving the oxonium compound,



which decomposes in three ways, giving (a)  $CHPh_2I + C_4H_9 \cdot OPr$ ; (b)  $C_4H_9I + CHPh_2 \cdot OPr$ ; and (c)  $C_3H_7I + CHPh_2 \cdot O \cdot C_4H_9(?)$ .

*Diphenylmethyl propyl ether*,  $CHPh_2 \cdot OPr$ , prepared by the interaction of diphenylbromomethane and propyl alcohol in presence of potassium hydroxide, is a colourless, mobile liquid, b p.  $161^\circ/11$  mm.

T. H. P.

**Some Chlorine Derivatives of Cholesterol.** STEPHAN MINOVICI and BELLA HAUSKNECHT (*Biochem. Zeitsch.*, 1912, 38, 46—52).—When cholesterol in alcoholic solution is treated with chlorine gas, two substances are formed; one,  $C_{40}H_{72}O_3Cl_2$  or  $C_{42}H_{72}O_3Cl_2$ , is soluble in alcohol and contains water of crystallisation, m. p.  $125^\circ$ , and when anhydrous, m. p.  $130^\circ$ ; the other,  $C_{56}H_{104}O_5Cl_2$ , m. p.  $195^\circ$  (precipitated from ethereal solution by alcohol), is insoluble in alcohol. The formation of the former substance can be explained on the assumption that two molecules of cholesterol combine to form an ether, from which by the chlorinating and oxidising action of the chlorine, two vinyl and two *isobutyl* groups are eliminated and replaced by hydroxyl and chlorine. By the action of hydrogen chloride and hydrogen peroxide, a third chlorine derivative,  $C_{26}H_{47}OCl$ , was obtained; it forms slender needles containing water of crystallisation, m. p.  $123^\circ$ .

S. B. S.

**Preparation of Arylpolymethylenchloro-compounds.** EMANUEL MERCK (D.R.-P. 238959).—When benzo- $\epsilon$ -chloroamylamide,  $C_6H_5 \cdot CO \cdot NH \cdot [CH_2]_5Cl$  is heated with aluminium chloride in benzene solution and the mixture subsequently treated with steam, it yields *benzo- $\epsilon$ -phenylamylamide*,  $C_6H_5 \cdot CO \cdot NH \cdot [CH_2]_5 \cdot Ph$ , a yellow oil, b. p.  $273—275^\circ/15$  mm., which on hydrolysis furnishes  $\epsilon$ -phenylamyl-

*amine*,  $\text{NH}_2 \cdot [\text{CH}_2]_5 \text{Ph}$ , b. p.  $131^\circ/15 \text{ mm.}$ , *picrate*, m. p.  $152-153^\circ$ , and *platinichloride*, m. p.  $220^\circ$ .

$\epsilon$ -*Chloroamylbenzene*, obtained by heating the foregoing benzophenylamylamide with phosphorus pentachloride, has an unpleasant odour and b. p.  $134^\circ/18 \text{ mm.}$

*Benzo- $\delta$ -phenylbutylamide*, glistening needles, m. p.  $83.5^\circ$ , is analogously prepared from benzochlorobutylamide with phosphorus pentachloride; it furnishes  $\delta$ -chlorobutylbenzene,  $\text{C}_6\text{H}_5 \cdot [\text{CH}_2]_4 \text{Cl}$ , b. p.  $122-123^\circ/17 \text{ mm.}$   
F. M. G. M.

**Preparation of Derivatives of *o*-Thiolbenzoic Acid.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 237773).—When dichloroethylene (1 mol.) reacts with an alcoholic solution of a thiolbenzoic acid (2 mols.), it yields acetyl**bisthiolbenzoic acids** (*bismethinethiolbenzoic acids*) of the general formula  $\text{CO}_2\text{R} \cdot \text{R} \cdot \text{S} \cdot \text{CH} : \text{CH} : \text{S} \cdot \text{R} \cdot \text{CO}_2\text{R}'$ , where R is a benzene or naphthalene residue, and R' a metal, aryl, or alkyl group. The preparation of acetylene**bisthiolbenzoic acid** is described.

F. M. G. M.

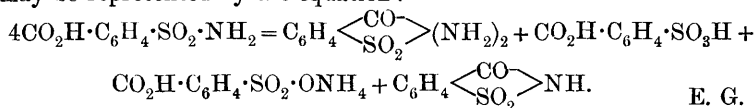
**Products Formed by the Action of Heat on *p*-Sulphamidobenzoic Acid.** W. B. STODDARD (*Amer. Chem. J.*, 1912, 47, 1—20).—Remsen and Muckenfuss (Abstr., 1896, i, 481) found that when *p*-sulphamidobenzoic acid is heated at  $220^\circ$  for eight hours, there are formed *p*-sulphobenzoic acid, ammonium hydrogen *p*-sulphobenzoate, an “infusible diamide of *p*-sulphobenzoic acid,” and “*iso-p*-sulphamidobenzoic acid.”

When the “infusible diamide” is heated with phosphorus pentachloride at  $194-197^\circ$ , *p*-chlorobenzonitrile is produced. An attempt was made to remove one of the nitrogen atoms, whilst leaving the other, by heating the compound with hydrochloric acid, but without success. It was also found that the desired result could not be attained by diazotisation or by heating with sodium carbonate solution. When a current of steam was passed through a mixture of the diamide and magnesium hydroxide, ammonia was liberated, and a *magnesium* salt was obtained of an acid, isomeric with *p*-sulphamidobenzoic acid, but entirely different from “*iso-p*-sulphamidobenzoic acid.” The corresponding *potassium* salt reacts readily with phosphorus pentachloride, but the infusible diamide is not thereby regenerated. These facts indicate that the nitrogen atoms of the infusible diamide are both attached to carbon, and that the acid isomeric with *p*-sulphamidobenzoic acid is probably *p*-carbamidobenzenesulphonic acid.

When Remsen and Muckenfuss’ “*iso-p*-sulphamidobenzoic acid” is heated in a sealed tube with concentrated hydrochloric acid at  $100^\circ$ , the infusible diamide is produced. If the acid is heated in a sealed tube with water at  $220^\circ$ , a small quantity of a substance is produced which crystallises in thin plates. Analyses of the barium and sodium salts of “*iso-p*-sulphamidobenzoic acid” have shown that this acid is not isomeric with *p*-sulphamidobenzoic acid, but has the composition of an anhydride of the latter,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{SO}_2 \end{smallmatrix} \text{NH}$ . Determinations have

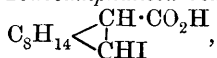
been made of the electrical conductivity of solutions of both these acids.

It is suggested that the action of heat on *p*-sulphamidobenzoic acid may be represented by the equation :



E. G.

Bornylene from  $\beta$ -Iodohydrobornylenecarboxylic [ $\beta$ -Iodocamphanecarboxylic] Acid : Dibromobornylenecarboxylic [ $\alpha\beta$ -Dibromocamphanecarboxylic] Acid and Dihydrobornylenecarboxylic [*ortho*-Camphanecarboxylic] Acid. JULIUS BREDT and W. HILBING (*J. pr. Chem.*, 1911, [ii], 84, 778—786. Compare Abstr., 1910, i, 498).— $\beta$ -Iodocamphanecarboxylic acid,



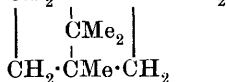
prepared by the action of hydrogen iodide on a glacial acetic acid solution of bornylenecarboxylic acid, crystallises in needles, m. p. 129—130°. It dissolves in hot aqueous sodium carbonate, yielding a crystalline *sodium* salt, together with the hydroxy-acid,  $\text{C}_{11}\text{H}_{18}\text{O}_3$ , previously described (*loc. cit.*). When heated with strong aqueous sodium hydroxide, the sodium salt yields bornylene, which has  $[\alpha]_D^{20} = 23\cdot68^\circ$  in toluene, and  $[\alpha]_D^{19} = 23\cdot94^\circ$  in benzene. A glacial acetic acid solution of bornylene, when heated at 70° with sulphuric acid, yields a bornyl acetate, b. p. 103—104°/14 mm., which, on hydrolysis, furnishes a borneol of m. p. 175—178°.

$\alpha\beta$ -Dibromocamphanecarboxylic acid,  $\text{C}_8\text{H}_{14}\left\langle\begin{smallmatrix}\text{CBr}\cdot\text{CO}_2\text{H} \\ \text{CHBr}\end{smallmatrix}\right\rangle$ , obtained

by the addition of bromine to bornylenecarboxylic acid in carbon tetrachloride solution, and purified by means of the *sodium* salt, crystallises in needles, m. p. 159—160°.

*ortho*-Camphanecarboxylic acid (*loc. cit.*), prepared by reducing  $\beta$ -iodocamphanecarboxylic acid, yields a *chloride*, b. p. 114—115°/14 mm., and an *amide*, m. p. 166—167°, which is con-

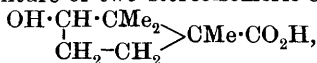
verted by the Hofmann reaction into an *amine* of the annexed formula. Improvements in the preparation of bornylenecarboxylic acid are also described.



*Ethyl bornylenecarboxylate*, obtained as a by-product in crystallising the anhydride from alcohol, has b. p. 121—122°/16 mm.

F. B.

Electrolytic Reduction of Camphononic Acid to *cis-trans*-Camphononic Acid : Camphonololactone. JULIUS BREDT [and, in part, with WILHELM LUND and AUGUST AMANN] (*J. pr. Chem.*, 1911, [ii], 84, 786—799).—When subjected to electrolytic reduction, camphononic acid yields a mixture of two stereoisomeric camphononic acids,



which may be separated by distillation, whereby the *cis*-camphonolic acid is converted into the corresponding lactone, whilst the *cis-trans*-isomeride distils unchanged.

$\text{CH}_2 \cdot \text{CH} - \text{O}$   
 $\quad \quad |$   
 $\quad \quad \text{CMe}_2$   
 $\text{CH}_2 \cdot \text{CMe} \cdot \text{CO}$  *cis-Camphonolactone* (annexed formula) has m. p. 160—161°, b. p. 239·2°,  $[\alpha]_D^{17} - 16\cdot2^\circ$  in alcohol.

*cis-Camphonolic acid* is obtained by the addition of the calculated amount of cold dilute hydrochloric acid to its *barium* salt, which is prepared by the action of barium hydroxide on the preceding lactone. It has  $[\alpha]_D^{20} - 33\cdot4^\circ$  in alcohol, and a varying m. p. according to the rapidity of heating; when rapidly heated, it has m. p. 197—198°.

The isomeric *cis-trans-camphonolic acid* has m. p. 249—250°.

*γ-Bromocamphononic acid*,  $\begin{matrix} \text{CHBr} \cdot \text{CMe}_2 \\ | \\ \text{CH}_2 - \text{CH}_2 \end{matrix} > \text{CMe} \cdot \text{CO}_2\text{H}$ , obtained by the action of saturated aqueous hydrobromic acid on the *cis*-lactone, has m. p. 146—147°, and when treated with aqueous sodium carbonate is reconverted into the lactone.

Both *cis-trans-camphononic acid* and *cis-camphonolactone* are oxidised by concentrated nitric acid to camphoronic acid.

Improvements in the method of preparing camphononic acid (Lapworth and Lenton, *Trans.*, 1901, 79, 1287) are also described.

F. B.

**Resolution of Mandelic Acid into its Active Components by means of Phenylethylamine.** LENNART SMITH (*J. pr. Chem.*, 1911, [ii], 84, 743—744).—The resolution of *r*-mandelic acid has been accomplished by crystallising the *l*-β-phenylethylamine salt from water, the salt of the *d*-acid being the less soluble. The pure *d*-acid is obtained from the mandelic acid, recovered from the mother liquor, by crystallisation with *d*-phenylethylamine.

F. B.

**Atrolactic [ $\alpha$ -Hydroxy- $\alpha$ -phenylpropionic] Acid.** LENNART SMITH (*J. pr. Chem.*, 1911, [ii], 84, 731—743).—The first part of this paper contains an account of a large number of experiments on the formation of acetophenonecyanohydrin, and the hydrolysis of the latter compound to atrolactic acid. This is followed by a description of the resolution of the acid into its optically active components, and of its behaviour towards hydrochloric acid.

In the preparation of atrolactic acid by Spiegel's method (*Abstr.*, 1881, 277; compare Staudinger and Ruzicka, *Abstr.*, 1911, i, 462), better yields are obtained by replacing the hydrochloric acid by glacial acetic acid.

Atrolactic [ $\alpha$ -hydroxy- $\alpha$ -phenylpropionic] acid crystallises with  $\frac{1}{2}\text{H}_2\text{O}$ , and the *potassium*, *sodium*, and *magnesium* salts with  $2\text{H}_2\text{O}$ ; the *strontium* salt,  $\text{Sr}(\text{C}_9\text{H}_9\text{O}_3)_2 \cdot 4\text{H}_2\text{O}$ , and *calcium* salt,  $\text{CaH}_2(\text{C}_9\text{H}_9\text{O}_3)_4$ , m. p. 216° (decomp.), are also described; the affinity constant  $K = 0\cdot0341$ .

The resolution of the acid into its optically active component is accomplished by crystallisation of its salt with *l*-β-phenylethylamine, the salt of the *d*-acid being the less soluble (compare McKenzie and Clough,

Trans., 1910, 97, 1016). The pure *l*-acid is obtained by crystallising the acid recovered from the mother liquors with *d*-phenylethylamine. The *l*-phenylethylamine salts of both the *d*- and the *l*-acids were analysed. The barium,  $\text{BaX}_{20}\frac{1}{2}\text{H}_2\text{O}$ , calcium,  $\text{CaX}_{20}3\frac{1}{2}\text{H}_2\text{O}$ , and potassium,  $\text{KX}_{20}2\text{H}_2\text{O}$ , salts of the active acids are also described ( $\text{X} = \text{C}_9\text{H}_9\text{O}_3$ ).

Hydratropic acid is readily obtained from atrolactic acid by heating it with concentrated hydrochloric acid for three-quarters of an hour on the water-bath, and reducing the product with sodium amalgam. When heated with concentrated hydrochloric acid for four hours at 130—135°, atrolactic acid yields  $\beta$ -chloro- $\alpha$ -phenylpropionic acid together with  $\alpha$ - and  $\beta$ -isotropic acids. By heating tropic acid at 170—180°, it is converted into atropic acid, which is accompanied by small quantities of  $\alpha$ - and  $\beta$ -isotropic acids.

From these experiments the conclusion is drawn that the action of hydrochloric acid on atrolactic acid yields successively atropic,  $\beta$ -chloro- $\alpha$ -phenylpropionic, and isotropic acids.

F. B.

**$\alpha$ -Phenyl- $\alpha$ -ethylglycollic Acid.** LENNART SMITH (*J. pr. Chem.* 1911, [ii], 84, 744—745). —  $\alpha$ -Phenyl- $\alpha$ -ethylglycollic [ $\alpha$ -hydroxy- $\alpha$ -phenylbutyric] acid is best prepared by the addition of glacial acetic acid to a mixture of potassium cyanide and propiophenone, and hydrolysis of the nitrile thus obtained by means of hydrogen chloride in ethereal solution, the resulting amide being finally hydrolysed by aqueous sodium hydroxide. It crystallises in needles, m. p. 132° (corr.) (compare Grignard, Abstr., 1903, i, 32), and is resolved into its optically active components by crystallisation of the *d*- $\beta$ -phenylethylamine salt. *l*- $\alpha$ -Hydroxy- $\alpha$ -phenylbutyric acid has, in aqueous solution,  $[\alpha]_D^{18} - 14^\circ$ .

F. B.

**Ethyl Anisoylacetates.** ANDRÉ WAHL and C. SILBERZWEIG (*Bull. Soc. chim.*, 1912, [iv], 11, 25—34. Compare Abstr., 1908, i, 647; 1910, i, 263). — Ethyl *m*- and *p*-methoxybenzoylacetates have been prepared by condensing ethyl acetate with ethyl *m*- and *p*-methoxybenzoates in presence of sodium. The corresponding *ortho*-compound has already been prepared by Tahara (Abstr., 1892, 844).

*Ethyl p-anisoylacetate*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , is a pale yellow liquid, b. p. 180—190°/10—12 mm., decomposing partly into *p*-anisoyldehydracetic acid. It yields a green copper salt,  $(\text{C}_{12}\text{H}_{13}\text{O}_4)_2\text{Cu}$ , m. p. 210°, and a nitroso-derivative, m. p. 113—114°.

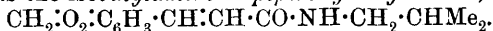
*Ethyl m-methoxybenzoylacetate* also decomposes very readily on distillation. It yields a green copper salt, m. p. 168—169°, and a nitroso-derivative, m. p. 94°.

W. G.

**Preparation of Halogenated 2-Anthraquinonylaminobenzoic Acids.** FRITZ ULLMANN (D.R.-P. 238106. Compare Abstr., 1906, i, 426, 953; 1910, i, 270). — 4-Bromo-2-anthraquinonylaminobenzoic acid,  $\text{C}_{14}\text{H}_7\text{O}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CO}_2\text{H}$ , a violet powder, which does not fuse at 300°, is obtained by heating 1-chloroanthraquinone (24.2 parts) with 4-bromoanthranilic acid (22 parts), potassium acetate (20 parts), copper acetate (1 part), and copper powder (1 part) at 160° in amyl-alcoholic solution.

F. M. G. M.

**Fagaramide, a New Nitrogenous Substance from the Root-bark of *Fagara xanthoxyloides*.** HERMANN THOMS and F. THÜMEN (*Ber.*, 1911, 44, 3717—3730).—The root-bark of *Fagara xanthoxyloides* contains a nitrogenous substance,  $C_{14}H_{17}O_3N$ , crystallising from alcohol in well-formed crystals, m. p. 119—120°. Thirty grams were obtained from 40 kilos. of the drug. The compound termed *fagaramide* is identified as the *isobutylamide* of *piperonylacrylic acid*,



On prolonged boiling with 50% alcoholic potassium hydroxide, it is decomposed into *isobutylamine* and *piperonylacrylic acid*.

Fagaramide is prepared synthetically by condensing *piperonylacrylic chloride* and *isobutylamine* in ethereal solution. In a similar manner, the isomerides are prepared, namely, the normal, secondary, and tertiary butylamides of *piperonylacrylic acid*. All four isomerides form characteristic, crystalline dibromo-derivatives.

Fagaramide reacts neutral, and does not form salts; it belongs to the same group as *piperine*.

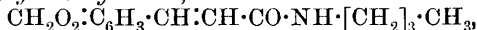
All four isomerides have the same physiological action, namely, narcotic on cold-blooded animals, but practically none on warm-blooded animals.

*Fagaramide* is obtained by extraction with benzene. The *dibromide*,  $C_{14}H_{17}O_3NBr_2$ , forms slender, colourless needles, m. p. 154—155°.

On oxidation of *fagaramide*, *piperonal* and *piperonylic acid*, m. p. 230° (not 227·5—228°), are obtained. *Piperonylacrylic acid* has m. p. 242° (not 238° or 232—234° as stated in the literature). *isoButylamine hydrochloride* has m. p. 177—178° (not 160°).

*Piperonylacrylic chloride*,  $CH_2O_2\cdot C_6H_5\cdot CH:CH\cdot COCl$ , is conveniently prepared by the action of thionyl chloride on the acid.

*Piperonylacryl-n-butylamide*,



forms very minute crystals, m. p. 85—86°. The *dibromide* separates in small, colourless needles, m. p. 134—135° (decomp.).

*Piperonylacryl-sec-butylamide*,



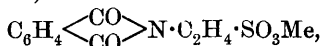
yields colourless needles, m. p. 161—162°; the *dibromide* has m. p. 164—165° (decomp.).

*Piperonylacryl-tert-butylamide*,  $CH_2O_2\cdot C_6H_5\cdot CH:CH\cdot CO\cdot NH\cdot CMe_3$ , forms strongly refractive, pale yellow prisms, which are colourless when powdered, m. p. 138—139°; the *dibromide* crystallises in slender, colourless needles, m. p. 182—183° (decomp.). E. F. A.

**Aminosulphones and Allied Compounds.** SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1911, 44, 3628—3636).—The analogous behaviour of ketones and sulphones in many reactions led the authors to hope that  $\gamma$ - and  $\delta$ -aminosulphones might yield heterocyclic bases, just as  $\gamma$ - and  $\delta$ -amino-ketones yield pyrrolines and tetrahydropyridines respectively. This expectation has not been fulfilled, but the work has led to the production of the following substances.

When warmed with phosphorus pentachloride, *phthalyltaurine* yields *phthalyltauryl chloride*,  $C_6H_4\langle\begin{smallmatrix} CO \\ CO \end{smallmatrix}\rangle N\cdot C_2H_4\cdot SO_2Cl$ , m. p. 160°.

This substance is very stable to hot water, does not react with benzene and aluminium chloride, but is converted into the *methyl ester*,



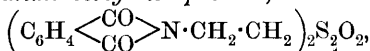
m. p. 103—104°, by methyl-alcoholic sodium methoxide.

*Phenyl β-phthalimidoethyl sulphone*,

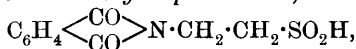


m. p. 185—185·5°, obtained from benzenesulphinic acid, alcoholic sodium ethoxide, and β-bromoethylphthalimide at 100°, yields, by hydrolysis by acetic acid and hydrochloric acids at 140°, *phenyl-β-aminoethylsulphone hydrochloride*,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{SO}_2\text{Ph} \cdot \text{HCl}$ , m. p. 155—155·5°, glistening needles. *Phenyl-γ-phthalimidopropylsulphone*, m. p. 126°, and *phenyl-γ-aminopropylsulphone hydrochloride*, m. p. 222°, are obtained by similar methods from γ-iodopropylphthalimide. Phenyl mercaptan and β-bromoethylphthalimide react with boiling alcoholic potassium hydroxide to form *phenyl β-phthalimidoethyl sulphide*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{N} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{SPh}$ , m. p. 59—60°, long needles, by the hydrolysis of which *phenyl β-aminoethyl sulphide hydrochloride*,  $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{SPh} \cdot \text{HCl}$ , m. p. 160—161°, is obtained.

β-Phthalimidoethyl mercaptan is converted by warm nitric acid, D 1·2, into β-phthalimidoethyl disulphoxide,



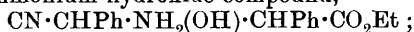
m. p. 155—156°, which reacts in benzene with aluminium chloride on the water-bath to form, after treating the product with hydrochloric acid, β-phthalimidoethylsulphinic acid,



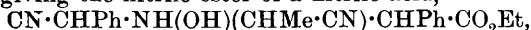
m. p. 149—149·5° (decomp.), glistening, white leaflets. This acid, which is also obtained by reducing the disulphoxide or phthalyltauryl chloride by zinc dust and 96% alcohol, is decomposed by boiling 20% hydrochloric acid, yielding phthalic acid, taurine, and β-phthalimidoethyl disulphoxide. C. S.

**Action of α-Hydroxyisobutyronitrile on the Nitrile Ester of Iminodi-phenylacetic Acid.** GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1235—1244).—It has been previously suggested (Abstr., 1909, i, 771, 772; 1910, i, 825) by the author that in the action of α-hydroxypropionitrile on the nitrile esters of propionyliminocycloheptanecarboxylic and iminodi-phenylacetic acids, an intermediate, unstable compound of the ammonium hydroxide type is formed, this then undergoing decomposition into other hydroxy-nitriles and nitrile esters of imino-acids. Such intermediate formation of ammonium hydroxide compounds is assumed also (1) in the formation of amines and amino-, imino-, and nitrilo-acids by the action of hydroxy-nitriles on either ammonia or its derivatives; (2) in the interaction of alkyl halides or halogen derivatives of acids with ammonia or its organic derivatives, and in a number of other reactions.

Most of the reactions represented in this way are explained equally well by Nef's "methylene-dissociation"; thus the interaction of the nitrile ester of iminodi-phenylacetic acid and  $\alpha$ -hydroxypropionitrile may be regarded as occurring in the following stages: (1) the hydroxynitrile dissociates into methylene derivative and water:  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CN} = \text{CH}_3\cdot\text{C}(\text{CN})\cdot + \text{H}_2\text{O}$ ; (2) water and the nitrile ester give the ammonium hydroxide compound,

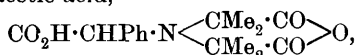


(3) the ethylenecyanogen combines with the ammonium hydroxide compound, giving the nitrile ester of a nitrilo-acid,



which then decomposes into derivatives of an imino-acid of lower molecular weight and mandelonitrile.

In order to arrive at a decision between these two explanations, the author has investigated the action of  $\alpha$ -hydroxyisobutyronitrile, which is incapable of methylene dissociation on the nitrile ester of iminodi-phenylacetic acid. The result confirms the author's view of these reactions, the product of the reaction being anhydronitrilodisobutyricphenylacetic acid,



which is formed as follows:  $\text{CN}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et} + \text{OH}\cdot\text{CMe}_2\cdot\text{CN} = \text{CN}\cdot\text{CHPh}\cdot\text{NH}(\text{OH})(\text{CMe}_2\cdot\text{CN})\cdot\text{CHPh}\cdot\text{CO}_2\text{Et} = \text{OH}\cdot\text{CHPh}\cdot\text{CN} + \text{CN}\cdot\text{CMe}_2\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$ ; the latter +  $\text{OH}\cdot\text{CMe}_2\cdot\text{CN} = \text{CN}\cdot\text{CMe}_2\cdot\text{NH}(\text{OH})(\text{CMe}_2\cdot\text{CN})\cdot\text{CHPh}\cdot\text{CO}_2\text{Et} = \text{H}_2\text{O} + \text{CN}\cdot\text{CMe}_2\cdot\text{N}(\text{CMe}_2\cdot\text{CN})\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$ . This nitrile ester then undergoes hydrolysis to the substituted triacetic acid, which is subsequently transformed into the corresponding anhydride.

*Anhydronitrilodisobutyricphenylacetic acid*,  $\text{C}_{16}\text{H}_{19}\text{O}_5\text{N}$  (see above), crystallises from aqueous alcohol in silky needles, m. p. 180—181° (slowly heated in sealed capillary). As would be expected from the fact that iminodicarboxylic acids are rendered neutral to phenolphthalein by one equivalent of alkali hydroxide, two equivalents of the latter are sufficient to neutralise this anhydride. T. H. P.

**Photochemical Behaviour of Nitroterephthalaldehyde.** HERMANN SUIDA (*J. pr. Chem.*, 1911, [ii], 84, 827—830).—The author finds that nitroterephthalaldehyde is very sensitive to light. A cold xylene solution of the aldehyde on exposure to direct sunlight rapidly becomes turbid, and deposits a yellow solid consisting of 2-nitroso-4-aldehydobenzoic acid,  $\text{CHO}\cdot\text{C}_6\text{H}_3(\text{NO})\cdot\text{CO}_2\text{H}$ . The acid slowly chars at 250—300°, but when placed in a bath at 300° instantly melts with decomposition. It dissolves in alkalis and alkaline carbonates, yielding yellowish-green solutions. Its solution in concentrated sulphuric acid develops with a trace of phenol an emerald-green coloration.

Details of a lecture experiment illustrating the photochemical transformation of the aldehyde are given. F. B.

**Angeli-Rimini Reaction of the Aldehydes.** ANGELO ANGELI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 445—449. Compare Balbiano, *Abstr.*, 1911, i, 987).—The author has prepared Wallach's ketone,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}(\text{OMe})_2$ , and Balbiano's product from anethole

glycol, and finds that they are identical, and do not give the Angeli-Rimini reaction when it is carried out as originally described. The reaction, however, is given by these substances when an excess of alkali is employed. This explains Balbiano's results. It is advisable to add the calculated quantity of alkali in small portions (compare Angeli and Castellana, *Abstr.*, 1909, i, 392), and in the qualitative test it is better to use the sodium salt of Piloty's acid. Deoxybenzoin, benzoin, benzil, and dibenzyl ketone behave similarly, giving the reaction only when an excess of alkali is employed. R. V. S.

***o*-Hydroxyacetophenone, 5-Chloro-*o*-hydroxyacetophenone, and Certain Chlorochalkones and Chloroflavones.** FRANZ KUNCKELL [with ALBERT FÜRSTENBERG] (*Ber.*, 1911, 44, 3654—3656. Compare *Abstr.*, 1901, i, 213).—The authors describe the preparation of *o*-hydroxyacetophenone from 5-acetyl-amino-2-hydroxyacetophenone, and of 5-*ω*-dichloro-2-hydroxyacetophenone (m. p. 64°) from *ω*-chloro-5-amino-2-hydroxyacetophenone. The corresponding *ω*-chloro-5-bromo-2-hydroxyacetophenone has m. p. 68°.

5-Chloro-2-hydroxyacetophenone condenses with benzaldehyde in the presence of sodium hydroxide to form 5-chloro-2-hydroxychalkone, m. p. 108°, which readily combines with bromine to form a dibromide of m. p. 185°. H. W.

**Chalkone and Hydrochalkones.** GUIDO BARGELLINI and LEDA BINI (*Gazzetta*, 1911, 41, ii, 435—445).—Hydrochalkones may be prepared conveniently by reducing chalkones with hydrogen in the presence of platinum-black. In this way, from an ethereal solution of 2-hydroxychalkone, 2-hydroxydihydrochalkone was obtained; the product is best purified by conversion into the semicarbazone,  $C_{16}H_{17}O_2N_3$ , which forms white needles, m. p. 174—175° (softening at 170°).

The reduction of 4-methoxychalkone with zinc dust and acetic acid yielded a substance (probably a diketonic condensation product),  $C_{32}H_{30}O_4$ , which crystallises in colourless needles, m. p. 224—225°. When 4-methoxychalkone in ethereal solution is reduced with hydrogen in presence of platinum-black, 4-methoxydihydrochalkone,  $C_{16}H_{16}O_2$ , is obtained; it crystallises in colourless needles, m. p. 59—60° (softening at 55°), and it gives a yellow coloration with concentrated sulphuric acid. The semicarbazone,  $C_{17}H_{19}O_2N_3$ , forms colourless needles, m. p. 118—120°.

3:4-Dimethyleneoxychalkone, when reduced with zinc and acetic acid, yields a substance,  $C_{32}H_{26}O_6$ , which crystallises in colourless needles, and is solid at 260°. When the reduction is effected with hydrogen in the presence of platinum-black, 3:4-dimethyleneoxydihydrochalkone,  $C_{16}H_{14}O_3$ , is produced; it crystallises in colourless needles, m. p. 39—40° (softening at 35°), and gives a red coloration with concentrated sulphuric acid. The semicarbazone,  $C_{17}H_{17}O_3N_3$ , forms colourless needles, m. p. 153—154°. R. V. S.

**Preparation of Benzoylaminoanthraquinones.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 238488).—When 1:5-dibenzoyldiaminoanthraquinones are oxidised with either

manganese dioxide, a persulphate or a perchlorate, a hydroxy-group is introduced into either position 4 or 8.

1 : 5-Dibenzoyldiaminoanthraquinone (10 parts) dissolved in 100 parts of sulphuric acid (10%  $\text{SO}_3$ ) was slowly treated at  $5-10^\circ$  with manganese dioxide (3.5 parts), maintained below  $15^\circ$  with continual stirring during two hours, and the 4-hydroxy-1 : 5-dibenzoyldiaminoanthraquinone subsequently isolated by known methods.

4-Chloro-8-hydroxy-1 : 5-dibenzoyldiaminoanthraquinone was prepared in a similar manner with potassium persulphate from 4-chloro-1 : 5-dibenzoyldiaminoanthraquinone, whilst 2-chloro-1 : 5-dibenzoyldiaminoanthraquinone furnished 2-chloro-4(8)-hydroxy-1 : 5-dibenzoyldiaminoanthraquinone.  
F. M. G. M.

**Preparation of Dianthraquinonyl- or Polyanthraquinonyl carbamides.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 238550, 238551, 238552, and 238553. Compare Abstr., 1911, i, 469, 655, 995).—The preparation of dianthraquinonylcarbamides has previously been described, and the reaction has now been extended to the case of heteronuclear  $\beta\beta'$ -diaminoanthraquinones.

These compounds, orange-yellow powders, are obtained by the action of  $\beta\beta'$ -anthraquinonylenedicarboxyl chlorides (obtained from 2 : 6- or 2 : 7-diaminoanthraquinones with excess of carbonyl chloride) on amino- or diamino-anthraquinones.

The second and third patents state that  $\beta\beta'$ -dianthraquinonyl-carbamide can be readily prepared by heating  $\beta$ -aminoanthraquinone at  $170^\circ$  with carbamide or ethyl urethane, either with or without solvent, until evolution of ammonia (and in the latter case, alcohol) ceases. The fourth patent deals with the employment of substituted aryl- or diaryl-carbamides, and describes *p*-tolyl-2-anthraquinonyl-carbamide, yellow crystals, obtained by the prolonged boiling of *p*-toluidine with 2 : 2'-dianthraquinonylcarbamide.  
F. M. G. M.

[Preparation of Anthracene Derivatives.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 238980).—It is now found that the compounds previously described (Abstr., 1907, i, 226) can be prepared from 1 : 1'-dianthraquinonyl-2 : 2'-dialdehyde by reduction with either an alkaline solution of sodium hyposulphite or with zinc in concentrated sulphuric acid solution.  
F. M. G. M.

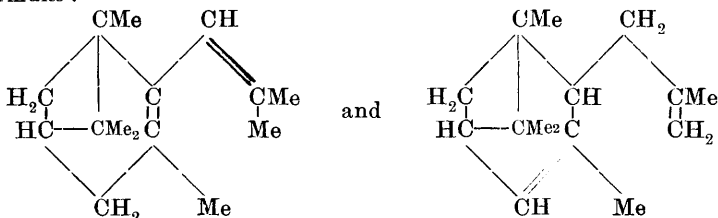
**Decomposition of Alkylidenehydrazines: Conversion of Ionone and  $\psi$ -Ionone into the Corresponding Hydrocarbons,  $\text{C}_{13}\text{H}_{22}$ .** NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1398—1402).—The decomposition of iononehydrazone in presence of potassium hydroxide is an exothermic reaction, and gives rise to *a-ionane*,  $\text{CHEt}:\text{CH}:\text{CH} < \begin{smallmatrix} \text{CMe}_2 \cdot \text{CH}_2 \\ \text{CMe} = \text{CH} \end{smallmatrix} > \text{CH}_2$ , which is a colourless liquid with a faint odour of turpentine, b. p.  $220-221^\circ/747$  mm.,  $D_{20}^{20}$  0.8530,  $n_D^{20}$  1.4784. It readily oxidises in the air, combines with 4 atoms of bromine, and in acetic anhydride solution gives a raspberry-red coloration with a drop of sulphuric acid. It shows the normal molecular refraction, whereas the similar hydrocarbon corresponding

with  $\beta$ -ionone should exhibit considerable exaltation, owing to the presence of conjugated double bonds.

$\psi$ -Ionane,  $\text{CHEt}:\text{CH}:\text{CH}_2:\text{CMe}:\text{CH}:\text{CH}_2:\text{CH}:\text{CMe}_2$  (?), obtained in a similar manner from  $\psi$ -ionone, is a colourless, faintly-smelling liquid, b. p. 224—225°/751 mm.,  $D_0^{20}$  0.8151,  $n_D$  1.4725; it rapidly turns yellow in contact with the air, unites with 6 atoms of bromine, and is converted into  $\alpha$ -ionane when its acetic acid solution is boiled with a small quantity of sulphuric acid. The formula given above is of doubtful accuracy, as the hydrocarbon does not exhibit optical exaltation. T. H. P.

**Crystalline Form and Optical Characters of Pinocampheol Methyl Xanthate.** N. I. SURGUNOFF (*Zeitsch. Kryst. Min.*, 1911, 50, 62—63; from *Bull. Soc. Nat. Moscow*, 1907, 543—551).—The crystals of pinocampheol methyl xanthate (Tschugaeff, *Abstr.*, 1908, i, 93) are orthorhombic with  $a:b:c = 1.3747:1:0.9787$ . L. J. S.

**Constituents of Essential Oils. The Constitution of the Active Caryophyllenes; Transformation of the Active Caryophyllenes into Monocyclic Derivatives.** FRIEDRICH W. SEMMLER and ERWIN W. MAYER (*Ber.*, 1911, 44, 3657—3679).—The authors have subjected caryophyllene to the action of ozone, and studied the decomposition products of the ozonide so formed. They consider that crude caryophyllene is composed chiefly of three caryophyllenes, namely, Deussen's inactive  $\alpha$ -caryophyllene and two active caryophyllenes, which they name *terp.*-caryophyllene and *lim.*-caryophyllene, and to which they assign the respective provisional formulæ:



Commercial caryophyllene, when dissolved in ethyl chloride and subjected to the action of ozone, yields a soluble *ozonide*,  $\text{C}_{15}\text{H}_{24}\text{O}_6$ , together with a small quantity of an insoluble *ozonide*, which probably contains seven or eight atoms of oxygen. When the soluble ozonide is heated in glacial acetic acid solution, it yields carbon dioxide and formaldehyde, together with a mixture of acidic and neutral products. From the acidic products a keto-acid,  $\text{C}_{11}\text{H}_{18}\text{O}_3$ , a diketo-acid,  $\text{C}_{14}\text{H}_{22}\text{O}_4$ , and an acid,  $\text{C}_8\text{H}_{14}\text{O}_2$ , were isolated.

The *keto*-acid,  $\text{C}_{11}\text{H}_{18}\text{O}_3$ , is a pale yellow, mobile oil of b. p. 183—187°/11.5 mm.,  $D_0^{20}$  1.040,  $\alpha_D^{20} + 44^\circ$ ,  $n_D^{20}$  1.4677. Its *silver* salt was analysed. The *methyl* ester has b. p. 139—142°/15.5 mm.,  $D_0^{20}$  0.9913,  $n_D^{20}$  1.4527,  $\alpha_D^{20} + 42^\circ$ . The *semicarbazone* has m. p. 183°. When oxidised with nitric acid, the keto-acid yields dimethylsuccinic acid and dibasic *caryophyllenic acid*,  $\text{C}_9\text{H}_{14}\text{O}_4$ . The latter forms a non-crystalline syrup of b. p. 215—218°/9 mm., 222—225°/13 mm. It is

remarkably stable towards nitric acid. The *silver* and *copper* salts were prepared. The *methyl* ester has b. p. 127—131°/11 mm.,  $D^{20}_D$  1·0456,  $n^{20}_D$  1·4462,  $\alpha^{20}_D$  + 44°. When boiled with acetic anhydride, caryophyllenic acid yields an *anhydride* of b. p. 152—158°/10 mm.,  $D^{20}_D$  1·1399,  $n^{20}_D$  1·4755,  $\alpha^{20}_D$  - 28°. Similar products were obtained when the keto-acid was oxidised by bromine in alkaline solution. Oxidation with permanganate also gave caryophyllenic acid, to which the formula  $\text{CH}_2 \begin{array}{c} \text{CMe}(\text{CO}_2\text{H}) \\ \text{CH}(\text{CO}_2\text{H}) \end{array} \text{CMe}_2$  is assigned.

The *diketo*-acid,  $\text{C}_{14}\text{H}_{22}\text{O}_4$ , is a viscous, yellow oil of b. p. 229—232°/11·5 mm.,  $D^{20}_D$  1·0830,  $n^{20}_D$  1·4804,  $\alpha^{20}_D$  + 41°. Its *silver* salt begins to darken at 130°, and has m. p. about 145°. Its *methyl* ester has b. p. 184—188°/12 mm.,  $D^{20}_D$  1·047,  $\alpha^{20}_D$  + 38°,  $n_D$  1·4680. With semicarbazide hydrochloride it gives no product of definite m. p. When oxidised with nitric acid, it yields succinic acid and caryophyllenic acid. On treatment with bromine in alkaline solution, it yields caryophyllenic acid, together with a mixture of acids of high boiling point.

The *acid*,  $\text{C}_8\text{H}_{14}\text{O}_2$ , has b. p. 120—128°/9 mm.,  $D^{20}_D$  0·9827,  $n_D$  1·4457,  $[\alpha]_D$  + 17°, and is monobasic. Its *methyl* ester has b. p. 64—68°/9 mm.,  $D^{20}_D$  0·922,  $[\alpha]^{20}_D$  + 20°,  $n_D$  1·4316. Its *amide* melts at 96°.

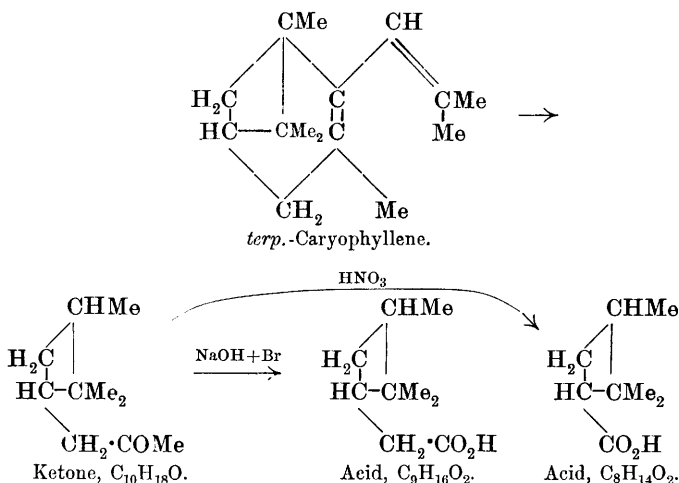
From the neutral portion (see above), a ketone,  $\text{C}_{10}\text{H}_{18}\text{O}$ , a probable *keto-aldehyde*,  $\text{C}_{11}\text{H}_{18}\text{O}_2$ , a diketone,  $\text{C}_{12}\text{H}_{20}\text{O}_2$ , and a deketo-aldehyde,  $\text{C}_{14}\text{H}_{22}\text{O}_3$ , were isolated.

The *ketone*,  $\text{C}_{10}\text{H}_{18}\text{O}$ , is a mobile, pale green liquid of b. p. 73—76°/11·5 mm. It has  $D^{20}_D$  0·8823,  $n^{20}_D$  1·4387,  $\alpha_D$  - 7°. Its *semicarbazone* has m. p. 176°. When reduced by sodium amalgam it yields an *alcohol*,  $\text{C}_{10}\text{H}_{20}\text{O}$ , b. p. 87—89°/11·5 mm.,  $D^{20}_D$  0·8707,  $n^{20}_D$  1·4507,  $[\alpha]^{20}_D$  - 6°. This, on treatment with phosphorus pentachloride, passes into the corresponding *chloride* (b. p. 70—73°/10 mm.,  $D^{20}_D$  0·882), which, when heated with quinoline, yields the *hydrocarbon*,  $\text{C}_{10}\text{H}_{18}$ . The latter has b. p. 50—54°/11·5 mm.,  $D^{20}_D$  0·812,  $n^{20}_D$  1·4410,  $\alpha^{20}_D$  - 6°. When oxidised by bromine in alkaline solution, the ketone yields carbon tetrabromide, together with a *monobasic acid*,  $\text{C}_9\text{H}_{16}\text{O}_2$ , b. p. 131—133°/13·5 mm.,  $D^{23}_D$  0·9773,  $n^{20}_D$  1·4500,  $\alpha^{20}_D$  - 7°, the *silver* salt of which had m. p. 219°, after darkening at about 160°. The *methyl* ester has b. p. 86—89°/15 mm.,  $D^{23}_D$  0·9208,  $n^{20}_D$  1·4360,  $\alpha^{20}_D$  - 5·5°. The *amide* has m. p. 114°. On oxidation with nitric acid, the ketone yields an *acid*,  $\text{C}_8\text{H}_{14}\text{O}_2$ , b. p. 119—122°/12 mm.,  $D^{20}_D$  0·972,  $n^{20}_D$  1·4457,  $\alpha^{20}_D$  + 7·5°. This yielded a *methyl* ester of b. p. 69—73°/15 mm.,  $D^{20}_D$  0·9359,  $n^{20}_D$  1·4307,  $\alpha^{20}_D$  + 22°, and an *amide*, m. p. 115—116°. The formation of these compounds is represented by the scheme on p. 122.

The *diketone*,  $\text{C}_{12}\text{H}_{20}\text{O}_2$ , after treatment with permanganate to destroy any aldehyde present, is a colourless, mobile oil, b. p. 137—142°/9 mm.,  $D^{20}_D$  0·9600,  $n^{20}_D$  1·4677,  $\alpha^{20}_D$  + 34°. The b. p. was unaltered by a second treatment with permanganate, whilst the following values were found for the remaining constants:  $D^{20}_D$  0·9598,  $n_D$  1·4622,  $\alpha_D$  + 39°. Its *semicarbazone* had m. p. 219°. On oxidation with nitric acid, the diketone yields dimethylsuccinic acid and caryophyllenic acid. Oxidation with bromine in alkaline solution leads to the same products.

The *diketo-aldehyde*,  $\text{C}_{14}\text{H}_{22}\text{O}_3$ , is a viscous, yellowish-green oil of

b. p. 181—184°/13 mm.,  $D^{20}_D$  1.0280,  $n^{20}_D$  1.4774,  $\alpha^{20}_D$  -25°. It does not yield a uniform semicarbazone. When oxidised with permanganate, it yields the acid  $C_{14}H_{22}O_4$  (see above). Nitric acid converts it into succinic acid and caryophyllenic acid.



Deussen's caryophyllene was converted into caryophyllene dihydrochloride, which, on treatment with methyl-alcoholic potassium hydroxide, yielded the previously-described "recovered" dextrorotatory caryophyllene (Abstr., 1911, i, 73). An attempt to transform this, through the nitrosite, into Deussen's laevorotatory caryophenylene was unsuccessful.

Reduction of the blue nitrosite (Deussen, Abstr., 1907, i, 945) led to the formation of a substance,  $C_{15}H_{27}N$ , which is probably an amine. It has b. p. 148—150°/13 mm.,  $D^{20}_D$  0.9297,  $\alpha^{20}_D$  +13°,  $n^{20}_D$  1.5030.

H. W.

**New Philippine Essential Oils.** BENJAMIN T. BROOKS (*Philippine J. Sci.*, 1911, 6, 333—351. Compare Abstr., 1911, i, 1000).—The essential oil from the flowers of *Michelia longifolia* contains linalool, eugenol methyl ether, and methylbutyric and acetic acids, and a very small percentage of thymol.

The leaves of *Toddalia asiatica* (L.) (*T. Aculeata Pers.*, Kurz) yield 0.08% of an essential oil, which gave the following constants:  $n^{30}_D$  1.4620,  $D^{30}_D$  0.9059. The oil is largely linalool, but also contains a white, crystalline, camphor-like compound, m. p. 96.5—97°, which is very unstable.

The leaves of *Clausena anisum olens* yield 1.20% of an essential oil with the following constants:  $n^{30}_D$  1.5235  $D^{30}_D$  0.963, ester number 3.6. It contains chavicol methyl ether to the extent of 93%.

About 0.2% of an essential oil with  $D^{30}_D$  0.850 is obtainable from the leaves of *Limnophila sp.*

Orange-peel oils were also examined, the *naranjita* variety giving a much greater yield than the *cajel*. The two oils resemble one

another very closely, the former having constants:  $n_D^{30}$  1.4700,  $[\alpha]_D^{30}$  90.85°, ester number 8.0; the latter,  $n_D^{30}$  1.4675,  $D_{30}^{30}$  0.8390, ester number 8.5.

The leaves of *Citrus decumana* yield 1.7% of an essential oil, with constants:  $n_D^{30}$  1.4644,  $D_{30}^{30}$  0.8700,  $[\alpha]_D^{30}$  22.90°, ester number 10. It contains dipentene and linalool and a trace of an aldehyde.

The oil from the leaves of *Citrus hystrix* has the following constants:  $n_D^{30}$  1.4650,  $D_{30}^{30}$  0.9150,  $[\alpha]_D^{30}$  -10.50°, ester number 50.2. W. G.

**The Essential Oil of Seseli bocconi.** LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 481—486).—The essential oil of this plant has been obtained by distilling it in steam. By fractional distillation of the oil a number of fractions were isolated, of which the more volatile consist of terpenes,  $\alpha$ -pinene and  $\beta$ -phellandrene having been identified. The oil also contains compounds with carbonyl groups (probably aldehydes), and ethers and alcohols are also present. R. V. S.

**Chemistry of Caoutchouc. III. Theory of Vulcanisation. II.** DAVID SPENCE [with J. H. SCOTT] (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 300—306. Compare Spence and Scott, *Abstr.*, 1911, i, 657).—Further experiments have been made on the extraction of sulphur from vulcanised caoutchouc by treatment for measured time intervals with equal successive quantities of boiling acetone. These show that equilibrium between the adsorbed sulphur and that in the acetone solution is rapidly attained, and this fact is regarded as favourable to the interpretation which has already been given to the exponential form of the extraction curves. From two series of observations made with the same mixture of para-caoutchouc and sulphur which had been subjected to the vulcanising process for different periods of time, it is found that the proportion of chemically combined sulphur increases with the period of vulcanisation, and that the initial portions of the extraction curves, corresponding with the removal of the free sulphur, are also different in the two cases. When a non-vulcanised mixture of caoutchouc and sulphur is similarly extracted with boiling acetone, the form of the extraction curve obtained is quite different. The removal of the sulphur from the unvulcanised mixture is, however, also a slow process by reason of the inclusion of the free sulphur in the jelly-like mass which the non-vulcanised caoutchouc forms in contact with the boiling acetone.

An extraction experiment with ebonite gave an extraction curve differing from those obtained with samples of vulcanised caoutchouc, but in this case, also, there appears to be a considerable amount of sulphur which is present in the chemically combined form.

H. M. D.

**Brazilian Copal.** STANISLAUS MACHENBAUM (*Arch. Pharm.*, 1912, 250, 6—12).—The copal was red to yellow in colour, and was in small pieces, showing a thin, weathered layer. It sintered at 127°, melted completely at 160°, and had the following percentage solubilities in

the solvents named: alcohol 76, acetone 80, alcohol and ether 92, light petroleum 20. The copal gave the following constants: acid numbers (a) direct 123.2, (b) indirect 128.5; saponification numbers (a) cold 136.2, (b) hot 144.2.

An ethereal extract of the resin was shaken with ammonium carbonate solution, which (1) extracted two acids, of which one, *brazilcopalic acid*,  $C_{24}H_{40}O_3$ , m. p. 170—175°, yielded a lead salt insoluble in alcohol, and (2) precipitated a mixture of two acids, of which one, m. p. 195—200°, gave a lead salt insoluble in alcohol. Sodium carbonate solution then extracted from the ethereal solution two acids, of which *brazilcopalolic acid*,  $C_{22}H_{38}O_2$ , m. p. 95—100°, gave an insoluble lead salt. The residual ethereal solution yielded nothing to potassium hydroxide solution, but on steam distillation furnished a volatile oil, boiling chiefly at 245—255°, and a residue of *α-brazilcopaloresen*, as a brownish-yellow, viscid mass.

The portion of the copal insoluble in ether was dissolved in a mixture of alcohol and ether, and extracted with potassium hydroxide solution, which removed a mixture of resin acids. These were dissolved in alcohol, precipitated as lead salts by lead acetate, regenerated, and separated into two portions by treatment with cold alcohol: the soluble portion is *α-brazilcopalinic acid*,  $C_{16}H_{30}O_2$ , m. p. 180—185°. The solution after extraction with potassium hydroxide contained *β-brazilcopaloresen* and a little volatile oil. All the substances described are amorphous. The acids give phytosterol-like reactions, and their acid numbers are recorded.

T. A. H.

**Columbia Copal.** STANISLAUS MACHENBAUM (*Arch. Pharm.*, 1912, 250, 13—19).—The copal was in large pieces, and had a slight turpentine-like odour. It sintered at 120°, melted completely at 155°, and had the following percentage solubilities: ether 56, alcohol 78, alcohol and ether 90, light petroleum 18. Its constants were as follows: acid numbers (a) direct 105, (b) indirect 106.1, saponification numbers (a) cold 106.8, (b) hot 110.6. An ethereal extract of the resin was extracted with (1) ammonium carbonate solution and (2) sodium carbonate solution. In each case a mixture of two resin acids was extracted, and was separated into its components by solution in alcohol and precipitation by lead acetate. The acid giving an insoluble lead salt alone was examined in each case, the other being viscid and intractable. As in the case of Brazilian copal (preceding abstract), ammonium carbonate precipitated two resin acids from the ethereal extract; of these, the one giving an insoluble lead salt had m. p. 170—175°. That extracted by ammonium carbonate is *columbiacopalic acid*,  $C_{22}H_{40}O_3$ , m. p. 145—150°. The acid subsequently removed by sodium carbonate is *columbiacopalolic acid*,  $C_{22}H_{40}O_2$ , m. p. 90°.

The residual ethereal extract contained volatile oil, boiling chiefly at 210—220°, and brown, viscid *α-columbiacopaloresen*. The portion of the crude copal insoluble in ether was dissolved in a mixture of alcohol and ether, and extracted with potassium hydroxide solution, which removed *α-columbiacopalinic acid*,  $C_{14}H_{24}O_2$ , m. p. 180—185°, soluble in cold alcohol, and *β-columbiacopalinic acid*,  $C_9H_{20}O_3$ , m. p.

190°, soluble in hot alcohol.  $\beta$ -*Columbiacopaloresen* remained in the solution.

All the products mentioned are amorphous. The acid numbers and phytosterol-like reactions of the resin acids are recorded.

T. A. H.

**So-called Chicle Gum.** J. E. QUINTUS BOSZ and N. H. COHEN (*Arch. Pharm.*, 1912, 250, 52—62).—Tschirch and Schereschewski's work on this material (Abstr., 1905, i, 685) has been repeated, and it is shown that their  $\alpha$ -chicalban is  $\alpha$ -amyrin acetate, their  $\beta$ -chicalban is a mixture of esters of lupeol and  $\beta$ -amyrin, their  $\gamma$ -chicalban contains as its principal constituent a substance,  $C_{56}H_{112}O$ ,  $C_{57}H_{114}O$ , or  $C_{58}H_{116}O$ , m. p. 68°, which on admixture with Hesse's  $\beta$ -cerotinone melts at 66—68°, and is possibly identical with that substance (Abstr., 1893, i, 57). Chicalfluavil is a mixture of all the substances mentioned above. On steam distillation, chicle "gum" yielded a minute quantity of an alkaline distillate with an odour of amines, and on hydrolysis by alkalis furnished acetic, hexoic, and cinnamic acids. The portion of the "gum" insoluble in acetone is brittle, and has none of the properties of caoutchouc, so that the properties of chicle "gum," which render it suitable for "chewing gum" manufacture, do not depend on the presence of caoutchouc-like substances.

T. A. H.

**Occurrence of Chitin.** EDMUND O. VON LIPPMANN (*Ber.*, 1911, 44, 3716—3717).—A colourless, thin, tough skin, forming a light grey, amorphous powder when dry, which collected on the surface of some waste liquors in a sugar factory which had been set aside for several months, is shown to be composed of chitin produced by bacterial action.

E. F. A.

**Lutein from Yolk of Egg.** RICHARD WILLSTÄTTER and HEINRICH H. ESCHER (*Zeitsch. physiol. Chem.*, 1912, 76, 214—225).—The chemically indifferent yellow pigments of plants and animals are divided into the hydrocarbons of the carotene group,  $C_{40}H_{56}$ , soluble in light petroleum, and the oxygen compounds of the xanthophyll group,  $C_{40}H_{56}O_2$ , soluble in alcohol (Willstätter and Mieg, Abstr., 1907, i, 865). Lycopene, the colouring matter of tomatoes, has been shown (Willstätter and Escher, Abstr., 1910, i, 330) to belong to the carotene group, and it is now proved that lutein from the yolk of eggs is a xanthophyll isomeric with, and closely related to, that derived from chlorophyll.

The methods of separating lutein from the phosphatides, fats, and cholesterol of the yolk are described: the pure pigment crystallises slowly from carbon disulphide in well formed prisms, or quickly in fire-red conglomerates of pointed, microscopic needles, m. p. 195—196° (corr.). It crystallises from methyl alcohol in prisms with V-shaped indentations, which are amber-yellow with metallic lustre.

Lutein forms an additive compound with iodine in ethereal solution; the *iodide* is a dark violet powder consisting of microscopic, pointed needles. It absorbs oxygen to the extent of 23% of its weight.

In alcoholic solution it shows absorption bands in the blue and indigo-blue, corresponding with those of xanthophyll from leaves, but differing from carotene.

E. F. A.

[Preparation of Thionaphthen Derivatives.] KALLE & Co. (D.R.-P. 239089. Compare Abstr., 1911, i, 666, 667, 1009).—An account of the preparation of substances having the general formula  $RS \cdot C_6H_3(S \cdot CH_2 \cdot CO_2H) \cdot CO_2H$ , some of which have been previously described (Abstr., 1911, i, 666).

The following new compounds are mentioned :

2-Carboxy-5-methylthiolphenylthiolacetic acid, yellowish-white needles, m. p. 220° (decomp.).

3-Keto-6-methylthiol-(1)-thionaphthen-2-carboxylic acid, a colourless powder, and 3-keto-6-methylthiol-(1)-thionaphthen, glistening needles, m. p. 133—134°.

F. M. G. M.

[Preparation of Thionaphthen Derivatives.] KALLE & Co. (D.R.-P. 239092).—*o*-Nitro-*m*-xylidine was diazotised, and converted by the action of potassium cyanide and copper sulphate into 2-nitro-*m*-xylonitrile, needles, m. p. 126°; this when heated at 100° during twelve hours with 80% sulphuric acid yielded 6-nitro-2 : 4-dimethylbenzoic acid, yellow needles, m. p. 180°, and on reduction furnished the corresponding 6-amino-2 : 4-dimethylbenzoic acid, a yellow, crystalline powder, m. p. 126° (decomp.). The foregoing amino-acid when diazotised, xanthogenated, and treated with chloroacetic acid yielded 4-carboxy-*m*-xyl-yl-5-thiolacetic acid,  $CO_2H \cdot C_6H_2Me_2 \cdot S \cdot CH_2 \cdot CO_2H$ , a microcrystalline powder, m. p. 158—159°, which on fusion with sodium hydroxide furnished keto-4 : 6-dimethylthionaphthencarboxylic acid, red flakes, and was subsequently converted into keto-4 : 6-dimethylthionaphthen, needles, m. p. 93°, which rapidly darkens on exposure to light.

F. M. G. M.

[Preparation of Anthraquinonethioxanthones.] FRITZ ULLMANN (D.R.-P. 238983. Compare Abstr., 1911, i, 1010).—Anthraquinone-thioxanthone, orange-red leaflets, m. p. 335°, is prepared by heating anthraquinone-1-*o*-thiolbenzoic acid with phosphorus pentachloride in nitrobenzene solution; the anthraquinone-thioxanthone, m. p. 272°, described previously (Abstr., 1910, i, 270) has now been obtained by fusing anthraquinone-2-*o*-thiolbenzoic acid with *p*-toluenesulphonyl chloride at 205°, whilst anthraquinonyl-1 : 5-di-*o*-thiolbenzoic acid and phosphorus pentachloride furnish an anthraquinone-dithioxanthone, glistening, orange needles, which do not melt at 350°.

F. M. G. M.

[Preparation of "Thioindigo" Derivatives.] KALLE & Co. (D.R.-P. 239673).—When 3-oxy-(1)-thionaphthen-2-carboxylic acid and its derivatives containing a free or substituted amino-group in the benzene nucleus are oxidised in either alkaline solution or neutral suspension, they yield "thioindigo" derivatives.

"6 : 6'-Diaminothioindigo" was obtained as a brown, flocculent precipitate by the oxidation of an aqueous alkaline solution of 6-amino-

3-oxy-(1)-thionaphthen-2-carboxylic acid with air at 70—80°; other oxidising agents can also be employed. F. M. G. M.

**Lysine Platinichloride.** MAX SIEGFRIED (*Zeitsch. physiol. Chem.*, 1912, 76, 234—237).—The platinichloride of active lysine, when dried over sulphuric acid, has the composition  $C_6H_{14}O_2N_2, PtH_2Cl_6, EtOH$ , and crystallises in needles more slender and darker than those of the platinichloride of inactive lysine, which forms stouter, paler yellow prisms, having the composition  $C_6H_{14}O_2N_2, PtH_2Cl_6$ . Racemic and active lysine may be sharply differentiated in this manner.

E. F. A.

**Hæmopyrrole.** RICHARD WILLSTÄTTER and YASUHIKO ASAHINA (*Ber.*, 1911, 44, 3707—3710).—Hæmopyrrole from hæmin or from chlorophyll has been shown to contain phyllopyrrole,  $C_9H_{15}N$ , *iso*-hæmopyrrole,  $C_8H_{13}N$ , and another base,  $C_8H_{13}N$ . The constitutions 2:3:4- and 2:4:3-dimethylethylpyrrole respectively were ascribed to the two latter compounds (Willstätter and Asahina, this vol., i, 41), but further investigation is necessary, as neither of them proves to be identical with the 2:4-dimethyl-3-ethylpyrrole synthesised by Knorr and Hess (*Abstr.*, 1911, i, 1019; compare also Fischer and Bartholomäus, this vol., i, 50).

The synthesis of Knorr and Hess is confirmed; 2:4-dimethyl-3-ethylpyrrole has b. p. 84°/10 mm., 197°/710 mm.,  $D_4^{20}$  0.913. The *stypnate* forms four-sided prisms, m. p. 136°; the *chloropicrate* gives prisms, m. p. 140°. On oxidation with nitrous acid, methylethyl-maleinimideoxime is obtained, crystallising in prisms, m. p. 215—216° (Knorr and Hess give 201°).

The pyrrole base was reduced with hydrogen iodide and phosphorus at 240°, and finally with platinum and hydrogen. The *pyrrolidine* obtained has b. p. 145°, and forms a *platinichloride*, crystallising in pointed prisms, m. p. 220°, and an  *$\alpha$ -naphthylcarbamide*, crystallising in irregularly-defined, rhombic plates, m. p. 109—110°. It is essentially different from *isohæmopyrrolidine*.

E. F. A.

**Asymmetric Selenites.** LUIGI MARINO and V. SQUINTANI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 666—670. Compare Marino, *Abstr.*, 1908, ii, 833).—When absolutely dry, recently sublimed selenious anhydride is mixed with an equimolecular quantity of a solution of pure piperidine in anhydrous benzene cooled with ice, a colourless, crystalline mass is deposited. The reaction is complete in eight or ten hours. The product, after being washed with anhydrous benzene, gives on analysis figures corresponding with the formula  $C_5H_{11}N \cdot SeO_2$ , but allowance has to be made for absorbed water, owing to the extremely hygroscopic nature of the substance. The compound has m. p. 70—71°, but traces of water may lower it to 64—65°. It probably reacts with alcohol, but the reaction product has not been isolated. The piperidine group is not involved in the reaction.

R. V. S.

**Cyclic Ammonium Bases.** JOHANNES GADAMER (*J. pr. Chem.*, 1911, [ii], 84, 817—820).—A reply to Decker and Kaufman (*Abstr.*,

1911, i, 807), who erroneously attributed to the author the view that the carbinol bases have in all cases the structure of amino-aldehydes or ketones. F. B.

**Action of Methylamine and Aniline on Benzoyldehydracetic Acid.** [Mutual Replacement of Ammonia and Amines in Pyridone Derivatives.] PAVEL I. PETRENKO-KRITSCHENKO and JOH. SCHÖTTE (*Ber.*, 1911, 44, 3648—3654. Compare Abstr., 1911, i, 1020).—The interaction of benzoyldehydracetic acid with methylamine and aniline has been studied, whereby the *methyl-* and *phenyl-lactams* of benzoyldehydracetic acid have been obtained. These have m. p. 188° and 203° respectively. Unlike the lactam described previously (*loc. cit.*), neither of these compounds yields a pyridonecarboxylic acid when warmed with alkali. The methyl-lactam, on treatment with hydrochloric acid, yielded 2 : 6-diphenyl-4-pyridone, the *platinichloride* of which, m. p. 218—221° (decomp.), was analysed. When similarly treated, the phenyl-lactam yielded 2 : 6-diphenyl-1 : 4-pyridone.

The methyl- and phenyl-lactams were also prepared by the action of alcoholic solutions of methylamine and aniline on the lactam. Conversely, the methyl-lactam, when treated with alcoholic ammonia, yields the lactam which was identified by conversion into 2 : 6-diphenyl-4-pyridone-3-carboxylic acid and 2 : 6-diphenyl-4-pyridone; on treatment with an alcoholic solution of aniline, it yields the phenyl-lactam.

Similarly, the anilino-group of the phenyl-lactam is replaceable under the action of ammonia or methylamine. H. W.

**The Condensation of Acetonedicarboxylic Ester with Aldehydes, Ammonia, and Amines.** PAVEL I. PETRENKO-KRITSCHENKO (*J. pr. Chem.*, 1912, [ii], 85, 1—37).—A résumé of the results of already published investigations by the author and various co-workers (Abstr., 1906, i, 452; 1907, i, 708; 1908, i, 564; 1909, i, 605, 959; 1910, i, 188). D. F. T.

**Preparation of Derivatives and Homologues of Indole.** GESELLSCHAFT FÜR TEERVERWERTUNG (D.R.-P. 238138).—When arylhydrazones (or their keto- or aldehyde derivatives) are heated with zinc chloride they furnish indole derivatives. 2-Methylindole was obtained in 75% yield by heating acetonephenylhydrazone (1 part) in 3 parts of solvent naphtha with zinc chloride (1 part) at 150° during one hour, extracting with water, and subsequently fractionating in a vacuum.

3-Methylindole, previously prepared by E. Fischer in 38% yield, was produced in 80% yield from propionaldehydephenylhydrazone at 200°, whilst ethyl phenylhydrazonopyruvate furnished a 60% yield of 2-indolecarboxylic acid at 130°. F. M. G. M.

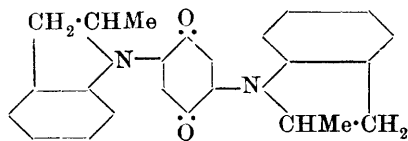
**New Synthesis of Benzylidene-2-methylquinoline.** VON ISMAILSKY (*J. pr. Chem.*, 1912, [ii], 85, 90—92).—In the presence of sodium hydroxide solution, *o*-aminobenzaldehyde slowly condenses with excess of styryl methyl ketone, yielding benzylidene-2-methylquinoline. The product agrees entirely with previous descriptions

(Wallach and Wüsten, Abstr., 1883, 1096; Jacobsen and Reimer, Abstr., 1884, 335; Doebner and Peters, Abstr., 1890, 176; Eibner, Abstr., 1901, i, 64). D. F. T.

**Condensation of para-Quinones with Indoles and Pyrroles Containing Hydrogen in the 3-Position.** RICHARD MÖHLAU and ALFRED REDLICH *Ber.*, 1911, 44, 3605—3618).—2-Methylindole and *p*-benzoquinone (2 mols.) react in boiling alcohol to form 2-methyl-indyl-3-benzoquinone,  $\text{CH} \begin{smallmatrix} \diagup \text{CH} \cdot \text{CO} \\ \diagdown \text{CO} \cdot \text{CH} \end{smallmatrix} \text{C} = \text{C} \begin{smallmatrix} \diagup \text{CMe} \\ \diagdown \text{C}_6\text{H}_4 \end{smallmatrix} \text{NH}$ , dark violet, bronze needles, m. p. about 185°, and quinol in quantitative yield. That the reaction occurs directly at the 3-hydrogen atom, not at the iminic hydrogen atom, is proved, not only by the fact that the colourless leuco-compound, obtained by the action of hydrazine hydrate, forms a diacetate, m. p. 132° (a triacetate should be formed had the reaction occurred in position 1), but also because 1:2-dimethylindole and *p*-benzoquinone yield in a similar manner an almost quantitative amount of 1:2-dimethylindyl-3-benzoquinone,  $\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}$ , m. p. about 160°, violet-black needles. In a similar manner, 2-methylindole and toluquinone yield a corresponding substance,  $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}$ , m. p. about 195° (decomp.), reddish-violet needles; the colourless diacetate of its leuco-compound has m. p. 146°. 2-Phenylindole and *p*-benzoquinone give about 40% of 2-phenylindyl-3-benzoquinone,  $\text{C}_{20}\text{H}_{13}\text{O}_2\text{N}$ , m. p. about 205°, blue needles; 2:5-dimethylindole reacts with *p*-benzoquinone and with toluquinone to form about 90% of 2:5-dimethylindyl-3-benzoquinone,  $\text{C}_{16}\text{H}_{13}\text{O}_2\text{N}$ , m. p. about 201° (decomp.), violet-black, bronze needles, and 2:5-dimethylindyl-3-toluquinone,  $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}$ , reddish-violet needles.

As is to be expected from the preceding, pyrroles unsubstituted in positions 3 and 4 react with *p*-quinones (4 mols., two of which are utilised in oxidising the initially-formed leuco-compound) to form diquinonylpyrroles; thus 2:5-dimethylpyrrole yields 3:4-diquinonyl-2:3-dimethylpyrrole,  $\text{NH} \begin{smallmatrix} \diagup \text{CMe} \cdot \text{C} \cdot \text{C}_6\text{H}_4\text{O}_2 \\ \diagdown \text{CMe} \cdot \text{C} \cdot \text{C}_6\text{H}_4\text{O}_2 \end{smallmatrix}$ , black, microcrystalline powder, whilst 5-phenyl-2-methylpyrrole yields 3:4-diquinonyl-5-phenyl-2-methylpyrrole,  $\text{C}_{23}\text{H}_{15}\text{O}_4\text{N}$ , brownish-black powder.

Whilst with the preceding indoles and pyrroles only one nucleus enters the benzoquinone molecule, it is found that the more strongly basic 2-methyldihydroindole reacts like the following bases with *p*-quinones, in that two nuclei enter the quinone molecule; thus 2-methyldihydroindole yields a substance (annexed formula), m. p. 187°, brown needles; methylaniline yields bismethylanilinoquinone,



( $\text{NPhMe}_2$ ) $\text{C}_6\text{H}_2\text{O}_2$ , reddish-brown leaflets; tetrahydroquinoline yields bistetrahydroquinolinoquinone, ( $\text{C}_9\text{NH}_{10}$ ) $\text{C}_6\text{H}_2\text{O}_2$ , m. p. 189°, brown needles, and 4-methyltetrahydroquinoline yields bis-6-methyltetrahydroquinolinoquinone, ( $\text{C}_9\text{H}_9\text{MeN}$ ) $\text{C}_6\text{H}_2\text{O}_2$ , m. p. 197°. C. S.

**Products of the Condensation of 9-Methylcarbazole and Phthalic Anhydride.** FRANZ EHRENREICH (*Monatsh.*, 1911, 32, 1103—1114. Compare Scholl and Neovius, *Abstr.*, 1911, i, 567).—By the interaction of molecular proportions of 9-methylcarbazole and phthalic anhydride, the main product is 9-methylcarbazole-3-phthaloylic acid,  $C_6H_4 \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CO \\ CO \end{smallmatrix} C_6H_3 \cdot CO \cdot C_6H_4 \cdot CO_2H$ , together with small quantities of 9-methylcarbazole-3:6-diphthaloylic acid,



When twice as much phthalic anhydride is used, the quantity of the latter is increased considerably.

9-Methylcarbazole is conveniently prepared by the action of methyl iodide or of methyl sulphate at the ordinary temperature on potassium carbazole.

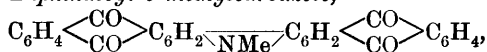
9-Methylcarbazole-3-phthaloylic acid, prepared by the interaction of the components in benzene solution with aluminium chloride, crystallises in large, well-formed rhombs, m. p.  $232^\circ$ ; it shows a characteristic, cherry-red coloration with concentrated sulphuric acid, changing to green on the addition of strong nitric acid. The methyl group is only very slowly and partly eliminated on boiling with hydrogen iodide, and the attraction of alkyl to nitrogen is apparently increased by the phthaloyl group; indeed, no trace of halogen alkyl is obtained on heating the diphthaloyl derivative with hydrogen iodide.

The same *methyl* ester is obtained from the silver salt and methyl iodide, or from the acid chloride and methyl alcohol; it crystallises in monoclinic prisms, m. p.  $146^\circ$ .

9-Methylcarbazole-3:6-diphthaloylic acid crystallises in slender needles, m. p.  $330^\circ$ ; the cherry-red coloration with sulphuric acid turns yellow on the addition of strong nitric acid.

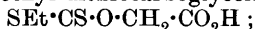
The *dimethyl* ester crystallises in large, colourless prisms, m. p.  $196^\circ$ .

2:3:6:7-Diphthaloyl-9-methylcarbazole,



prepared by heating 9-methylcarbazole-3:6-diphthaloylic acid with sulphuric acid at  $90^\circ$  (compare Scholl and Neovius, *loc. cit.*), crystallises in reddish-yellow plates, which have not melted at  $400^\circ$ . With concentrated sulphuric acid a bluish-violet solution is obtained, which becomes orange when strong nitric acid is added. E. F. A.

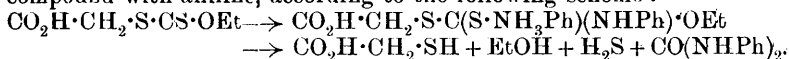
**Ester Acids of Thiocarboxylic Acids with Aliphatic Alcohol Acids.** V. BROR HOLMBERG (*J. pr. Chem.*, 1911, [ii], 84, 634—686. Compare *Abstr.*, 1910, i, 361, 834).—A detailed account of the action of amines towards the following acids: xanthoacetic acid,  $OEt \cdot CS \cdot S \cdot CH_2 \cdot CO_2H$ ; ethyl dithiocarboglycollic acid,



dithiocarbodiglycollic acid,  $CO_2H \cdot CH_2 \cdot S \cdot CS \cdot O \cdot CH_2 \cdot CO_2H$ ; carbodithioglycollic acid,  $CO(S \cdot CH_2 \cdot CO_2H)_2$ , and trithiocarbodiglycollic acid,  $CS(S \cdot CH_2 \cdot CO_2H)_2$ .

The previously-observed formation of diphenylcarbamide by the action of aniline on xanthoacetic acid is considered by the author to

be due to the intermediate formation and decomposition of an additive compound with aniline, according to the following scheme :



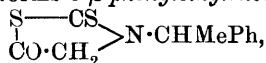
Evidence in support of the author's view is furnished (1) by the non-formation of diphenylcarbamide in acid solution and in the absence of excess of aniline, and (2) by the isolation of similar additive compounds of the thiocarbamylglycollic acids with amines (see below).

$\beta$ -Phenylethylamine reacts with xanthoacetic acid, yielding an oily *thiourethane*,  $\text{CHMePh}\cdot\text{NH}\cdot\text{CS}\cdot\text{OEt}$ .

Ethyl dithiocarboglycollic acid forms with aniline in aqueous solution the *aniline* salt,  $\text{SEt}\cdot\text{CS}\cdot\text{O}\cdot\text{CO}_2\cdot\text{NH}_2\text{Ph}$ , m. p.  $77\cdot5$ — $78^\circ$ ; when heated with aniline in alcoholic solution, diphenylcarbamide is produced.

Dithiocarbodiglycollic acid reacts with ethylamine to form ethylthiocarbamylthioglycollic acid and the anhydride of ethylthiocarbamylglycollic acid mentioned below. With aniline in ethereal solution it yields the *aniline* salts,  $\text{C}_5\text{H}_6\text{O}_5\text{S}_2\cdot 2\text{NH}_2\text{Ph}$ , lustrous, pale yellow leaflets, m. p.  $97$ — $97\cdot5^\circ$ , and  $\text{C}_5\text{H}_6\text{O}_5\text{S}_2\cdot\text{NH}_2\text{Ph}$ , m. p.  $110$ — $110\cdot5^\circ$ . When heated with aniline in aqueous solution, dithiocarbodiglycollic acid gives rise to a mixture of substances, the nature of which depends on the ratio of aniline to acid, and the temperature and duration of the reaction; the following compounds were isolated from the product: *s*-diphenylthiocarbamide, phenylrhodanine, trithiocarbodiglycollic acid, glycollic acid, thioglycollic acid, phenylthiocarbamylglycollic acid and its anhydride, and phenylthiocarbamylglycollanilide.

Trithiocarbodiglycollic acid reacts with primary amines, yielding thioglycollic acid and rhodanines (compare Abstr., 1910, i, 361); with  $\beta$ -phenylethylamine it forms 3- $\beta$ -phenylethylrhodanine,

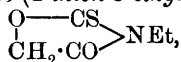


pale yellow, tabular crystals, m. p.  $111$ — $112^\circ$ .

Ethyltrithiocarboglycollic acid and aniline in aqueous solution yield phenylrhodanine and ethyl trithiocarbonate.

*N*-Substituted derivatives of thiocarbamylglycollic acid are readily obtained by the interaction of amines and ethyldithiocarboglycollic acid.

*Ethylthiocarbamylglycollic acid*,  $\text{NH}_2\text{Et}\cdot\text{CS}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared from ethylamine in aqueous solution, crystallises in stellar aggregates of small, white needles, m. p.  $97\cdot5$ — $98^\circ$ ; the *sodium* salt is amorphous; the *barium* salt,  $(\text{NH}_2\text{Et}\cdot\text{CS}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2)_2\text{Ba}\cdot 3\text{H}_2\text{O}$ , forms colourless plates. It is oxidised by bromine to *ethylcarbamylglycollic acid*, colourless prisms, m. p.  $85$ — $86^\circ$ , and when warmed in aqueous solution forms an *anhydride* (2-thion-3-ethyl-4-oxazolidone),



which crystallises in colourless plates, m. p.  $49$ — $40\cdot5^\circ$ .

*Diethylthiocarbamylglycollic acid*,  $\text{NEt}_2\cdot\text{CS}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , prepared from diethylamine, crystallises in flat, colourless prisms, m. p.  $90\cdot5$ — $91^\circ$ ,

and yields crystalline *sodium* and *barium* salts; the *ethyl* ester is an oil.

*Phenylthiocarbamylglycollic acid*,  $\text{NHPh}\cdot\text{CS}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p. 111—112°, obtained together with phenylrhodanine and diphenylcarbamide by heating aniline with ethyldithiocarboglycollic acid in aqueous solution, crystallises with one molecule of acetic acid in long, colourless prisms, which lose their acetic acid on exposure to air; the *sodium* salt and *barium* salt,  $(\text{NHPh}\cdot\text{CS}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2)_2\text{Ba}\cdot 3\text{H}_2\text{O}$ , were analysed. It readily loses water, forming the *anhydride* (2-thion-

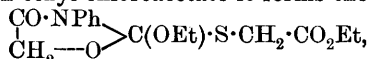
3-phenyl-4-oxazolidone),  $\begin{array}{c} \text{O} - \text{CS} \\ | \quad \diagup \\ \text{CH}_2 - \text{CO} \end{array} > \text{NPh}$ , which crystallises in stout, irregular plates or short prisms, m. p. 172—173°, and dissolves in aqueous sodium carbonate to form the sodium salt of the original acid. When heated in neutral or alkaline solution, it yields glycollic acid and diphenylcarbamide; in aqueous ammonia, phenylthiocarbamide is produced. Oxidation with potassium permanganate yields phenylcarbamyglycollic acid.

*Phenylthiocarbamyglycollanilide*,  $\text{NHPh}\cdot\text{CS}\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$ , prepared by heating the acid with aniline in aqueous solution, forms lustrous, white needles, m. p. 133—134°.

2-Thion-3-phenyl-4-oxazolidone is oxidised by bromine to 2:4-diketo-3-phenyloxazolidine. When dissolved in alcoholic sodium

ethoxide, it forms a gelatinous *sodium* salt,  $\begin{array}{c} \text{CO}\cdot\text{NPh} \\ | \quad \diagup \\ \text{CH}_2 - \text{O} \end{array} > \text{C}(\text{SNa})\cdot\text{OEt}$ , which is decomposed by acetic acid, yielding 2-ethoxy-2-thiol-3-phenyl-4-oxazolidone,  $\begin{array}{c} \text{CO}\cdot\text{NPh} \\ | \quad \diagup \\ \text{CH}_2 - \text{O} \end{array} > \text{C}(\text{SH})\cdot\text{OEt}$ . This crystallises in colour-

less needles, m. p. 73—73.5°, and dissolves in alkalis, forming salts of phenylthiocarbamyglycollic acid. The above-mentioned sodium compound reacts with ethyl iodide, yielding a reddish-yellow oil, probably  $\begin{array}{c} \text{CO}\cdot\text{NPh} \\ | \quad \diagup \\ \text{CH}_2 - \text{O} \end{array} > \text{C}(\text{SEt})\cdot\text{OEt}$ , which, on treatment with aqueous sodium hydroxide, is converted into ethyl mercaptan and phenylcarbamyglycollic acid; with ethyl chloroacetate it forms the compound,



which, by dilute hydrochloric acid, is hydrolysed and converted into 2:4-diketo-3-phenylthiazolidine, and by acetic acid is hydrolysed to phenylcarbamyglycollic acid and a substance crystallising in small, flat prisms or white needles, m. p. 171—172°. The latter substance

is probably *diphenylisohydantoin*,  $\begin{array}{c} \text{CO}\cdot\text{NPh} \\ | \quad \diagup \\ \text{CH}_2 - \text{O} \end{array} > \text{C}\cdot\text{NPh}$ .

The interaction of chloroacetanilide and the sodium salt of 2-thiol-2-ethoxy-3-phenyl-4-oxazolidone yields a thiazolidone compound,  $\begin{array}{c} \text{CH}_2 - \text{S} \\ | \quad \diagup \\ \text{CO}\cdot\text{NPh} \end{array} > \text{C}\cdot\text{NPh}$  or  $\begin{array}{c} \text{S} - \text{CH}_2 \\ | \quad \diagup \\ \text{CO}\cdot\text{NPh} \end{array} > \text{C}\cdot\text{NPh}$ , which forms pale yellow crystals, m. p. 174—175°.

The prolonged action of alcoholic sodium ethoxide on 2-thion-3-phenyl-4-oxazolidone at the ordinary temperature gives rise to

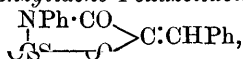
sodium phenylthiocarbamylglycollate; at 100°, xanthanilide is produced.

Piperidine combines with 2-thion-3-ethyl-4-oxazolidone in alcoholic solution to form 2-thiol-2-piperidyl-3-ethyl-4-oxazolidone,  $\text{CO}\cdot\text{NEt} \begin{array}{c} \diagup \\ \text{CH}_2-\text{O} \end{array} \text{C}(\text{SH})\cdot\text{N}\cdot\text{C}_5\text{H}_{10}$ , colourless prisms, m. p. 146—147°, and with the corresponding phenyl derivative, yielding 2-thiol-2-piperidyl-3-phenyl-4-oxazolidone,  $\text{CO}\cdot\text{NPh} \begin{array}{c} \diagup \\ \text{CH}_2-\text{O} \end{array} \text{C}(\text{SH})\cdot\text{C}_5\text{NH}_{10}$ , which forms white needles, m. p. 130—132°.

2-Thion-3-ethyl-4-oxazolidone condenses with benzaldehyde in the presence of sodium ethoxide, yielding  $\alpha$ -keto- $\beta$ -diphenylbutyrolactone (Erlenmeyer and Knight, Abstr., 1894, i, 592); the same compound, accompanied by *s*-diphenylthiocarbamide, is obtained by the condensation of 2-thion-3-phenyl-4-oxazolidone with benzaldehyde by sodium ethoxide.

2-Thion-5-benzylidene-3-ethyl-4-oxazolidone,  $\text{NEt}\cdot\text{CO} \begin{array}{c} \diagup \\ \text{CS}-\text{O} \end{array} \text{C}\cdot\text{CHPh}$ , prepared by condensing 2-thion-3-ethyl-4-oxazolidone with benzaldehyde in the presence of piperidine, crystallises in colourless plates or short prisms, m. p. 94·5—95°; when the condensation is effected by means of acetic anhydride, a *stereoisomeride*, crystallising in long, pale yellow prisms, m. p. 137·5—138°, is obtained.

2-Thion-3-phenyl-5-benzylidene-4-oxazolidone,



prepared by condensing 2-thion-3-phenyl-4-oxazolidone and benzaldehyde by means of acetic anhydride, forms slender, golden-yellow needles, m. p. 181·5—182°.

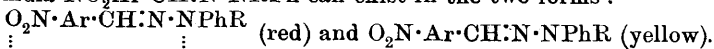
3-Phenylrhodanine reacts with piperidine in alcoholic solution, yielding phenylpiperidylthiocarbamide,  $\text{NHPh}\cdot\text{CS}\cdot\text{C}_5\text{NH}_{10}$ , thin, white prisms, m. p. 100—100·5°, and with alcoholic sodium ethoxide to form a sodium salt, which on acidification with acetic acid yields

4-keto-2-thiol-2-ethoxy-3-phenylthiazolidine,  $\text{CO}\cdot\text{NPh} \begin{array}{c} \diagup \\ \text{CH}_2-\text{S} \end{array} \text{C}(\text{SH})\cdot\text{OEt}$ ; this crystallises in colourless, flat, prismatic needles, m. p. 61·5—62°.

The formation of the latter compound furnishes additional evidence in support of the thiazolidine formula assigned to the rhodanines.

F. B.

**Nitro-derivatives and Nitro-hydrazones.** ROBERTO CIUSA (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 578—583. Compare Hantzsch, Abstr., 1910, i, 475).—The author refers to the different coloured modifications of hydrazones of nitro-aromatic aldehydes which he has described, and suggests that they are chromo-isomerides like the nitro-anilines of Hantzsch. According to him, a nitrohydrazone of the formula  $\text{NO}_2\cdot\text{Ar}\cdot\text{CH}\cdot\text{N}\cdot\text{NRPh}$  can exist in the two forms:



Since the hydrazones contain a  $\text{-C}\cdot\text{N-}$  linking, they can exist in

*syn*- and *anti*-forms, and it is suggested that the red isomerides are the *syn*-forms, because that configuration would favour the origin of the internal additive product containing a secondary valence.

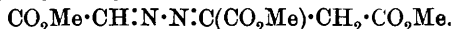
R. V. S.

**Constitution of Buchner's so-called Pyrazolinecarboxylic Acids.** CARL BÜLOW (*Ber.*, 1911, 44, 3710—3716).—By the interaction of phenylhydrazine and acraldehyde, Fischer and Knoevenagel obtained phenylpyrazoline,  $\text{NPh} \begin{smallmatrix} \text{N}=\text{CH} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix}$ . Subsequently

pyrazoline,  $\text{NH} \begin{smallmatrix} \text{N}=\text{CH} \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix}$ , was obtained by Curtius and Wirsing by the interaction of hydrazine and acraldehyde. This is very unstable towards oxidising agents, but it can be distilled unchanged, and is stable towards hydrochloric acid.

On the other hand, the pyrazolinecarboxylic acids described by Buchner (*Abstr.*, 1893, i, 430; 1894, i, 348), obtained from aliphatic diazo-compounds and unsaturated mono- or di-carboxylic acids of the ethylene series, are characterised by giving up all their nitrogen on heating or distillation and forming *cyclo*propanecarboxylic acids. When boiled with dilute mineral acids, hydrazine is eliminated. Lastly, they are readily converted into pyrazole derivatives.

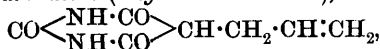
These facts are not in agreement with the relatively stable nature of heterocyclic five-membered rings, and it is considered that Buchner's acids are more correctly formulated as mixed azines of glyoxylic and oxalacetic acid esters; thus the product from ethyl diazoacetate and ethyl fumarate has the formula



Azines such as benzyldeneazine,  $\text{CHPh} : \text{N} : \text{N} : \text{CHPh}$ , give up the whole of their nitrogen on heating, and the other properties of Buchner's acids are shown to be in accord with formulating them as mixed azines instead of as pyrazolinecarboxylic acids. E. F. A.

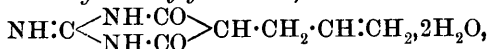
**Pyrimidines. LIV. Condensation of Carbamide and Guanidine with Esters of Allylmalonic and Some Alkyl-substituted Allylmalonic Acids.** TREAT B. JOHNSON and ARTHUR J. HILL (*Amer. Chem. J.*, 1911, 46, 537—549).—In an earlier paper (*Abstr.*, 1911, i, 502) it has been shown that ethyl allylmalonate reacts with thiocarbamide to form ethyl 2-amino-4-keto-7-methyltetrahydrohexathiazole-5-carboxylate instead of the expected allylthiobarbituric acid, whilst ethyl benzylallylmalonate and diallylmalonate condense with thiocarbamide with production of acylthiocarbamides or their  $\gamma$ -lactones. In view of this abnormal behaviour, experiments have been carried out to ascertain whether barbituric acid derivatives are formed by the condensation of ethyl allylmalonates with carbamide and guanidine.

5. *Allylmalonylcarbamide (allylbarbituric acid)*,



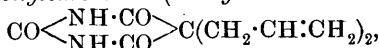
m. p. 167°, obtained by the action of carbamide on ethyl malonate in

presence of sodium ethoxide, crystallises in nearly colourless plates, and is hydrolysed by potassium hydroxide with formation of allylmalonic acid. *5-Allylmalonylguanidine*,



m. p. 265—266°, crystallises in pink prisms or hexagonal tablets.

*5:5-Diallylmalonylcarbamide (diallylbarbituric acid)*,



m. p. 173°, obtained by the action of carbamide on ethyl diallylmalonate, forms colourless, rhombohedral crystals, and on hydrolysis with potassium hydroxide yields diallylmalonic acid. *5:5-Diallylmalonylguanidine*,  $\text{NH}:\text{C} \begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{array} > \text{C}(\text{CH}_2\cdot\text{CH}:\text{CH}_2)_2$ , crystallises in colourless, rhombohedral prisms, does not melt below 300°, and is hydrolysed by potassium hydroxide with formation of diallylmalonic acid.

*5-Benzyl-5-allylmalonylcarbamide (5-benzyl-5-allylbarbituric acid)*,



prepared by the condensation of carbamide with ethyl benzylallylmalonate, crystallises in prisms; it can also be obtained by the action of allyl iodide on silver benzylbarbiturate. The compound is not hydrolysed smoothly by potassium hydroxide. When guanidine is heated with ethyl benzylallylmalonate in presence of sodium ethoxide, *benzylallyliminomalonuric acid*,  $\text{NH}_2\cdot\text{C}(\text{NH})\cdot\text{NH}\cdot\text{CO}\cdot\text{C}(\text{CH}_2\text{Ph})(\text{CH}_2\cdot\text{CH}:\text{CH}_2)\cdot\text{CO}_2\text{H}$ , or, more probably,  $\text{NH}:\text{C} \begin{array}{c} \text{NH}—\text{CO} \\ \text{NH}_3\cdot\text{O}\cdot\text{CO} \end{array} > \text{C}(\text{CH}_2\text{Ph})\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$ , is produced,

which crystallises in needles, does not melt below 300°, and is immediately transformed by dilute hydrochloric acid into 5-benzyl-5-allylmalonylguanidine *hydrochloride*. *5-Benzyl-5-allylmalonylguanidine*,  $\text{NH}:\text{C} \begin{array}{c} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CO} \end{array} > \text{C}(\text{CH}_2\text{Ph})\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$ , can also be obtained by the action of benzyl iodide on 5-allylmalonylguanidine; it forms a fine, colourless powder, and does not melt below 300°. Attempts to obtain pure benzylallylmalonic acid by the hydrolysis of this compound with potassium hydroxide were not successful.

*Benzylallylmalonic acid*,  $\text{CH}_2\cdot\text{CH}:\text{CH}_2\cdot\text{C}(\text{CH}_2\text{Ph})(\text{CO}_2\text{H})_2$ , was obtained as a viscid, uncrystallisable liquid by the hydrolysis of its ethyl ester with potassium hydroxide; the *silver* salt was prepared.

E. G.

**Preparation of 1-p-Dimethylaminophenyl-2:3:4-trimethyl-5-pyrazolone.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 238256).—1-p-Aminophenyl-2:3:4-trimethyl-5-pyrazolone, m. p. 225—227°, prepared by the reduction of 1-p-nitrophenyl-2:3:4-trimethyl-5-pyrazolone, crystallises from water in colourless crystals containing 2H<sub>2</sub>O. When heated at 90—100° with methyl iodide, it yields 1-p-dimethylaminophenyl-2:3:4-trimethyl-5-pyrazolone, which crystallises with 2H<sub>2</sub>O, and has m. p. 140° (anhydrous).

The following compounds are also described: 1-p-Aminophenyl-

3 : 4-dimethyl-5-pyrazolone, a colourless, crystalline powder, m. p. 232°, obtained by reducing the corresponding nitro-compound. 5-Ethoxy-1-p-aminophenyl-3 : 4-dimethylpyrazole, m. p. 95—97°. 1-p-Acetylaminophenyl-3 : 4-dimethyl-5-pyrazolone, a colourless, crystalline powder, m. p. 272—273°. 5-Ethoxy-1-p-acetylaminophenyl-3 : 4-dimethylpyrazole, m. p. 130°. 5-Acetoxy-1-p-acetylaminophenyl-3 : 4-dimethylpyrazole, m. p. 167—168°. 1-p-Methylaminophenyl-3 : 4-dimethyl-5-pyrazolone, needles or leaflets (1H<sub>2</sub>O), m. p. 108—110°. 1-p-Dimethylaminophenyl-3 : 4-dimethyl-5-pyrazolone, m. p. 199—200°. 1-p-Acetylmethylaminophenyl-3 : 4-dimethyl-5-pyrazolone crystallises with 2H<sub>2</sub>O, m. p. 80° or 162° (anhydrous). 5-Ethoxy-1-p-methylaminophenyl-3 : 4-dimethylpyrazole is an oil; its nitroso-derivative has m. p. 75°.

1-p-Acetylmethylaminophenyl-2 : 3 : 4-trimethyl-5-pyrazolone has m. p. 139—140°. 1-p-Methylaminophenyl-2 : 3 : 4-trimethyl-5-pyrazolone has m. p. 168°.

F. M. G. M.

[Preparation of Substituted Pyrazolones.] FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 238373).—It is found that 4-iso-valeryl-amino-1-phenyl-3-methyl-5-pyrazolone and its derivatives can be methylated (methyl sulphate) without eliminating the isovaleryl group in position 4; the following compounds are described: 4-iso-Valeryl-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone forms colourless crystals, m. p. 203°. 4-iso-Valeryl-amino-1-phenyl-3-methyl-5-pyrazolone forms colourless crystals, m. p. 230°. 4-iso-Valeryl-amino-5-ethoxy-1-phenyl-3-methylpyrazole has m. p. 115°. 5-Chloro-4-isovaleryl-amino-1-phenyl-3-methylpyrazole has m. p. 120°. 4-iso-Valeryl-amino-5-isovaleryloxy-1-phenyl-3-methylpyrazole has m. p. 122—123°. 4- $\alpha$ -Bromoisovaleryl-amino-1-phenyl-2 : 3-dimethyl-5-pyrazolone forms colourless crystals, m. p. 206°. 4- $\alpha$ -Bromoisovaleryl-amino-5- $\alpha$ -bromoisovaleryloxy-1-phenyl-3-methylpyrazole, colourless crystals, m. p. 114—116°, is obtained by treating an aqueous solution of 4-amino-1-phenyl-3-methyl-5-pyrazolone hydrochloride with  $\alpha$ -bromoisovaleryl bromide in the presence of sodium acetate.

F. M. G. M.

Hydantoins. VIII. Action of Bromine on Tyrosinehydantoin. TREAT B. JOHNSON and CHARLES HOFFMAN (*Amer. Chem. J.*, 1912, 47, 20—27).—It has been found by Wheeler, Hoffman, and Johnson (*Abstr.*, 1911, i, 923) that tyrosinehydantoin is converted by chlorine into the 3 : 5-dichloro-derivative, and that the latter is hydrolysed by barium hydroxide with formation of 3 : 5-dichlorotyrosine.

It is now shown that iodine reacts in a similar manner with tyrosinehydantoin with production of a nearly theoretical yield of 3 : 5-di-iodotyrosinehydantoin. With bromine, however, tyrosinehydantoin behaves abnormally, giving 3 : 5-dibromobenzylidenehydantoin as the chief product of the reaction, and only a small quantity of 3 : 5-dibromotyrosinehydantoin.

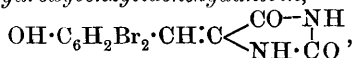
3 : 5-Di-iodotyrosinehydantoin,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{I}_2 \cdot \text{CH}_2 \cdot \text{CH} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$ , m. p. 235° (decomp.), crystallises in hexagonal plates.

3 : 5-Dibromo-4-hydroxybenzoylhydantoinic acid (3 : 5-dibromotyrosinehydantoinic acid),  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{OH}$ , m. p.

191°, obtained by the action of potassium cyanate on 3:5-dibromotyrosine, forms rhombohedral plates or square prisms, and is hydrolysed by concentrated hydrochloric acid with formation of 3:5-dibromotyrosinehydantoin,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Br}_2 \cdot \text{CH}_2 \cdot \text{CH} \begin{smallmatrix} \text{CO-NH} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$ , m. p. 223—225° (decomp.),

which crystallises in prisms.

3:5-Dibromo-4-hydroxybenzylidenehydantoin,



m. p. above 295° (decomp.), obtained by condensation of 3:5-dibromo-4-hydroxybenzaldehyde with hydantoin, forms small, brownish-yellow needles, yields a yellow ammonium salt, and is reduced by hydriodic acid with production of 3:5-dibromotyrosinehydantoin. 3:5-Dibromo-4-hydroxybenzylidenehydantoin is also produced by the action of bromine on tyrosinehydantoin and on 3:5-dibromotyrosinehydantoin.

E. G.

**The Reduction of Aromatic Aldazines.** THEODOR CURTIUS (*J. pr. Chem.*, 1912, [ii], 85, 37—77. Compare Abstr., 1900, i, 610).—The paper first gives a summarised account of the results of the investigations published hitherto by different workers on the products obtained by the reduction of benzaldazine (benzylidenehydrazine) and its substituted derivatives under various conditions.

[With FRANZ SCHNEIDERS.]—Benzylhydrazine easily undergoes atmospheric oxidation, giving a deposit of benzaldehydebenzylhydrazone (private communication from August Darapsky).

Towards the esters of  $\beta$ - and  $\gamma$ -ketonic acids, benzylhydrazine behaves like phenylhydrazine. Warmed with benzoylacetate ester it yields 3-phenyl-1-benzyl-5-pyrazolone, a white, crystalline powder, m. p. 204—205°. Ferric chloride solution is without action on the substance (contrast the 1-benzyl-3-methyl compound below). When treated in glacial acetic acid solution with sodium nitrite, 4-oximino-3-phenyl-1-benzyl-5-pyrazolone is obtained; it forms deep red needles, m. p. 161—162°.

On warming benzylhydrazine with ethyl lævulate, 1-benzyl-3-methyl-6-pyridazinone,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CMe} = \text{N} \end{smallmatrix} \text{N} \cdot \text{CH}_2\text{Ph}$ , is obtained; this crystallises from light petroleum in colourless, prismatic crystals, m. p. 56—57°.

When cautiously added to ethyl acetoacetate, benzylhydrazine yields 1-benzyl-3-methyl-5-pyrazolone, a white, crystalline solid, m. p. 175—176°, b. p. 192—194°/14 mm.; the intermediate benzylhydrazone of acetoacetic ester could not be isolated. The product is acid to litmus, and the copper, cobalt, nickel, and silver salts are described; the hydrochloride forms prismatic crystals, m. p. 120°.

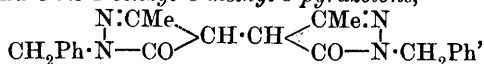
1-Benzyl-3-methyl-5-pyrazolone is exceedingly reactive. Ferric chloride solution in the cold gives a brown coloration, and on boiling causes oxidation to the corresponding pyrazole-blue. Heated with phosphorus pentachloride, it yields 4-dichloro-1-benzyl-3-methyl-5-pyrazolone, which crystallises in leaves, m. p. 59—61°; the analogous 4-dibromo-compound forms small, hard crystals with a tinge

of yellow (m. p. 81—83°); these two dihalogen compounds are, unlike the original substance, indifferent to both acid and alkali.

4-p-Tolueneazo-1-benzyl-3-methyl-5-pyrazolone, obtained by the action of toluenediazonium sulphate, forms slender, yellow needles, m. p. 123—124°.

1-Benzyl-4-benzylidene-3-methyl-5-pyrazolone, obtained by the action of benzaldehyde on benzylmethylpyrazolone, forms red crystals, m. p. 111—112°.

On heating benzylmethylpyrazolone with phenylhydrazine, ammonia is evolved, and 4-bis-1-benzyl-3-methyl-5-pyrazolone,

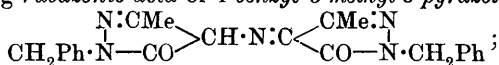


obtained, which forms white needle crystals, melting above 330°; by oxidation with various oxidising agents it passes smoothly into

1-benzyl-3-methylpyrazole-blue,  $\text{CH}_2\text{Ph}\cdot\text{N}\begin{array}{c} \text{N}:\text{CMe} \\ | \\ \text{CO} \end{array} > \text{C}:\text{C} < \begin{array}{c} \text{CMe}:\text{N} \\ | \\ \text{CO} \end{array} \cdot\text{N}\cdot\text{CH}_2\text{Ph}$ ;

this crystallises in almost black needles, m. p. 142—144°, and is decomposed by strong acids and boiling alkali solutions. Careful oxidation of benzylmethylpyrazolone by potassium permanganate gives a white acid substance of indefinite m. p., which could not be further purified; the silver salt was obtained as a white precipitate, m. p. 185—189°; excess of permanganate causes oxidation to benzaldehyde and benzoic acid.

On treating 1-benzyl-3-methyl-5-pyrazolone in dilute hydrochloric acid solution with sodium nitrite, 4-oximino-1-benzyl-3-methyl-5-pyrazolone is obtained, crystallising in yellow needles or prisms, m. p. 152—152.5°. By reduction with zinc dust in acetic acid solution, the oximino-compound gives a solution of 4-amino-1-benzyl-3-methyl-5-pyrazolone, which was not isolable, and attempts to isolate it as the benzylidene derivative merely caused oxidation to the corresponding rubazonic acid of 1-benzyl-3-methyl-5-pyrazolone,



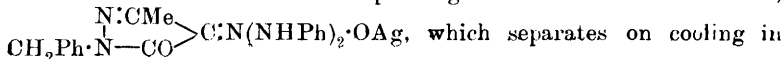
this, more conveniently prepared by oxidation of the amino-compound with ferric chloride, forms cinnabar-red crystals, m. p. 160—161°; its solutions in alkalis are violet-red.

The ammonium salt of 4-oximino-1-benzyl-3-methyl-5-pyrazolone forms a yellow powder (m. p. 175—176°); with silver nitrate it yields the silver salt as a reddish-brown, insoluble, amorphous powder, which decomposes completely at 179°.

On the other hand, silver nitrate decomposes an acetic acid solution of the free oximino-compound, nitrous fumes are evolved, and finally microscopic needles of the silver salt of 4-nitro-1-benzyl-3-methyl-5-pyrazolone are obtained, which decompose at 245—246°.

4-Nitro-1-benzyl-3-methyl-5-pyrazolone can be obtained from the silver salt, or by oxidation of the oximino-compounds with nitric acid; it forms colourless needles, m. p. 144—145° (decomp.).

The silver salt of the nitro-compound gives with aniline a substance,



yellow, capillary crystals; treatment with solvents removes aniline from the substance, regenerating the original silver salt.

1-Benzyl-2:3-dimethyl-5-pyrazolone (1-benzylantipyrine) is obtained by methylating 1-benzyl-3-methyl-5-pyrazolone. It forms anhydrous, hygroscopic crystals, m. p. 84—86°; from moist solvents, it crystallises with  $\frac{1}{2}$ H<sub>2</sub>O, and then has m. p. 102—103°. The *picrate* forms long, yellow needles (from hot water), m. p. 143—145°. 4-Oximino-1-benzyl-2:3-dimethylpyrazolone is an unstable, deep green, viscous oil. If benzylantipyrine is oxidised with concentrated nitric acid, 4-nitro-1-benzyl-2:3-dimethylpyrazolone is obtained as colourless, prismatic crystals, m. p. 161—162°.

The physiological action of benzylantipyrine was investigated; it appears to possess certain advantages over ordinary antipyrine.

[With GUSTAV SPRENGER.]—*p*-Methylbenzylhydrazine (compare Abstr., 1900, i, 612) is best prepared by reduction of *p*-methylbenzaldazine by sodium amalgam; on dilution with water and cooling, crystals of the *p*-methylbenzylhydrazone of *p*-tolualdehyde separate, and can be decomposed by hydrochloric acid. The *dihydrochloride*, m. p. 150° (decomp.), the *sulphate*, m. p. 178—179°, and the *oxalate*, m. p. 180°, were obtained.

Benzaldehyde-*p*-methylbenzylhydrazone forms large, transparent tablets, m. p. 88°; the *diacetyl* derivative, C<sub>6</sub>H<sub>4</sub>Me·CH<sub>2</sub>·N<sub>2</sub>HAc<sub>2</sub>, forms crystals, m. p. 75° (indefinite). The stable *nitroso*-compound, C<sub>6</sub>H<sub>4</sub>Me·CH<sub>2</sub>·N(NO)·NH<sub>2</sub>, crystallises from water in needles, m. p. 78°, and when warmed with dilute sulphuric acid yields *p*-methylbenzylazoimide, C<sub>6</sub>H<sub>4</sub>Me·CH<sub>2</sub>·N<sub>2</sub>, b. p. 94°/12 mm. (compare Curtius and Darapsky, Abstr., 1902, i, 844). With ethyl acetoacetate, *p*-methylbenzylhydrazine gives 1-*p*-methylbenzyl-3-methyl-5-pyrazolone (compare Abstr., 1900, i, 612); its *hydrochloride* has m. p. 130°. By treatment with nitrous acid the above pyrazolone is converted into yellow 4-oximino-1-*p*-methylbenzyl-3-methyl-5-pyrazolone, m. p. 154°. By methylation the pyrazolone is converted into 1-*p*-methylbenzyl-2:3-dimethyl-5-pyrazolone, which forms prismatic crystals, m. p. 78°. The substance behaves analogously to antipyrine and benzylantipyrine towards nitrous acid and ferric chloride. Its physiological effect has not yet been investigated.

D. F. T.

Ethyl Cyanoanilide-*o*-carboxylate. RALPH H. MCKEE (*J. pr. Chem.*, 1911, [ii], 84, 821—826).—By the interaction of ethyl cyanoimidocarbonate and ethyl anthranilate, Finger and Zeh (Abstr., 1910, i, 382) obtained a compound which they considered to be ethyl cyanoanilide-*o*-carboxylate. The author has investigated the action of cyanogen bromide on ethyl anthranilate, and finds that the resulting compound, which undoubtedly has the structure of ethyl cyanoanilide-*o*-carboxylate, is different from Finger and Zeh's compound. The latter substance is considered to be ethylbenzoyleneisocarbamide,

[2-ethoxyquinazoline],  $\begin{array}{c} \text{CO} \text{---} \text{N} \\ | \quad \diagup \\ \text{C}_6\text{H}_4 \cdot \text{NH} \end{array} \text{C} \cdot \text{OEt}$  or  $\begin{array}{c} \text{CO} \cdot \text{NH} \\ | \quad \diagup \\ \text{C}_6\text{H}_4 \cdot \text{N} \end{array} \text{C} \cdot \text{OEt}$ , and this

view is supported by the formation of the corresponding methyl compound by the interaction of methyl cyanoimidocarbonate and ethyl anthranilate. According to Finger and Zeh the products obtained

from both the methyl and ethyl cyanoimidocarbonates should be identical. Finger and Günzler had already shown that it is a quinazoline derivative (Abstr., 1911, i, 237).

*Methyl cyanoimidocarbonate*,  $\text{NH}\cdot\text{C}(\text{CN})\cdot\text{OEt}$ , prepared by the action of hydrogen chloride on methyl alcohol and potassium cyanide, is a colourless oil, b. p.  $115^\circ/760$  mm., having an odour of mice excrement. It reacts with ethyl anthranilate at  $80^\circ$  in the presence of cuprous chloride, yielding 2-methoxyquinazalone,  $\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}(\text{O})\text{N}=\text{C}\cdot\text{OMe}$ , m. p.  $231\text{--}232^\circ$  (corr.), which is hydrolysed by hydrochloric acid to 2:4-diketodihydroquinazoline, m. p.  $357^\circ$  (corr.); Griess (*Ber.*, 1869, 2, 416) gives  $344^\circ$ .

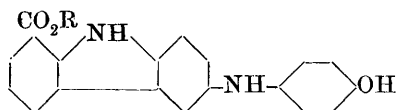
*Methyl cyanoanilide-o-carboxylate*,  $\text{CN}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}$ , obtained by the action of cyanogen bromide on methyl anthranilate in ethereal solution, crystallises in needles, m. p.  $105^\circ$  (corr.). When heated at  $100^\circ$ , it polymerises to tri-o-carbomethoxyphenylmelamine,  $\text{C}_{27}\text{H}_{24}\text{O}_6\text{N}_6$ , which has m. p. about  $160^\circ$ .

*Ethyl cyanoanilide-o-carboxylate*, prepared from cyanogen bromide and ethyl anthranilate, has m. p.  $93\text{--}94^\circ$ , and polymerises to tri-o-carbomethoxyphenylmelamine,  $\text{C}_{30}\text{H}_{30}\text{O}_6\text{N}_6$ , m. p.  $190^\circ$  with previous sintering.

Methyl anthranilate forms a *picrate*,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , crystallising in deep yellow, microscopic needles, m. p.  $106^\circ$  (corr.); the *picrate* of ethyl anthranilate has m. p.  $116^\circ$  (corr.). F. B.

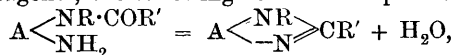
**Preparation of Derivatives of Indophenols.** LEOPOLD CASSELLA & Co. (D.R.-P. 238857).—Indophenols prepared from carbazolecarb-

oxylic acids and nitrosophenols have previously been described; these substances on reduction furnish leuco-derivatives having the annexed general constitution,



which, when slowly dropped into a hot solution of sodium polysulphide, yield dark blue sulphur cotton dyes which are extremely fast to light, washing, or chlorine. F. M. G. M.

**Preparation of Anthraquinone Derivatives.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 238981. Compare following abstract).—When acyl o-diaminoanthraquinones are treated with dehydrating reagents, the following action takes place:



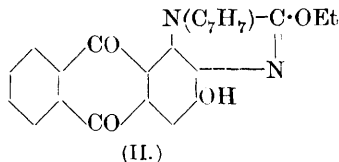
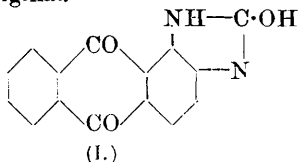
where A is an anthraquinone residue (substituted or otherwise), R hydrogen, alkyl, or aryl, and R' alkyl, aryl, or an ethoxy-group.

1:2-Phenylantraquinoneiminazole, prepared from benzoyl-1:2-diaminoanthraquinone, and 4-amino-1:2-phenylantraquinoneiminazole, obtained from benzoyl-1:2:4-triaminoanthraquinone by the action of sulphuric acid at  $150^\circ$ , form yellow crystals and glistening, metallic needles respectively.

1:2-Hydroxyantraquinoneiminazole (I), prepared by the action of carbonyl chloride on 1:2-diaminoanthraquinone, crystallises from quinoline in needles.

4-Hydroxy-2-ethoxy-1-p-tolylantraquinoneiminazole (II), yellow needles, was obtained by the fusion (at 100°) of *p*-toluidine with dinitro- $\beta$ -aminoanthraquinoneurethane; it yields a *sulphonic acid* when heated with fuming sulphuric acid.

1:2-Methylantraquinoneiminazole, yellow needles, obtained from 1:2-diaminoanthraquinone and acetic anhydride, and the compound, from the same base and formic acid, are also mentioned in the original.



F. M. G. M.

**Preparation of Anthraquinone Derivatives.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 238982).—Condensation products of benzaldehyde and  $\beta$ -aminoanthraquinones have been described by Kaufler (Abstr., 1904, i, 207); this condensation is now found to take place readily with *o*-diaminoanthraquinones and either aliphatic or aromatic aldehydes.

The compounds prepared from 1:2-diaminoanthraquinone and 1:2:4-triaminoanthraquinone respectively with benzaldehyde are identical with those obtained from the benzoyl derivatives of these compounds when heated with sulphuric acid (compare preceding abstract), whilst 1:2-diaminoanthraquinone with para-acetaldehyde in concentrated sulphuric acid at 0–10° yields the 1:2-methylantraquinoneiminazole also previously described.

F. M. G. M.

[Preparation of Anthraquinoneacridone Derivatives.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 238977 and 238978).—Anthraquinoneacridone can be conveniently nitrated with nitro-sulphuric acid at 0–5°; the nitrated product is yellow, and does not fuse at 300°; when reduced with sodium sulphide at 100°, it furnishes *aminoanthraquinoneacridone* (not melted at 300°).

*Benzoylaminoanthraquinoneacridone* separates in crystalline form when a nitrobenzene solution of aminoanthraquinoneacridone is boiled with benzoyl chloride; the *acetyl* compound has also been prepared. The second patent states that the foregoing benzoylaminoanthraquinoneacridone can be obtained by boiling a nitrobenzene solution of bromoanthraquinoneacridone with benzamide in the presence of copper and sodium carbonate during twenty-four hours.

F. M. G. M.

**Nature of the Indanthren Fusion of 2-Aminoanthraquinone: 2-Hydroxylamino- and 2:2'-Azoxyanthraquinone.** ROLAND SCHOLL and FRITZ EBERLE (*Monatsh.*, 1911, 32, 1035–1042).—2-Hydroxylaminoanthraquinone, obtained in small quantity by reduction of 2-nitroanthraquinone, could not be converted into indanthren by fusion with an alkali hydroxide. In alkaline solution hydroxylaminoanthraquinone is very readily oxidised by atmospheric

oxygen to 2:2'-azoxyanthraquinone. This compound could not be reduced to the corresponding hydrazoanthraquinone, 2-aminoanthraquinone always resulting.

The formation of indanthren from 2-aminoanthraquinone is explained on the assumption that on fusion with an alkali hydroxide 2-aminodihydro-1:2'-dianthraquinonylamine,

$\text{NH}_2 \cdot \text{C}_{14}\text{H}_6(\text{OH})_2 \cdot \text{NH} \cdot \text{C}_{14}\text{H}_7\text{O}_2$ ,

is formed, and that this loses hydrogen, forming dihydroindanthren,

$$\text{C}_{14}\text{H}_6(\text{OH})_2 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} \text{C}_{14}\text{H}_6\text{O}_2.$$

*Hydroxylaminoanthraquinone*,  $\text{C}_{14}\text{H}_7\text{O}_2 \cdot \text{NH} \cdot \text{OH}$ , was obtained as an orange-red solid, sintering at  $140^\circ$ , m. p.  $158-160^\circ$ . It dissolves in dilute sodium hydroxide with an intense green coloration.

2:2'-*Azoxyanthraquinone*,  $\text{ON}_2(\text{C}_6\text{H}_3 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C}_6\text{H}_4)_2$ , crystallises in small, light brown prisms and prismatic plates, m. p.  $342.5^\circ$ . The solution in concentrated sulphuric acid is red. A solution in hot acetone gives a very characteristic cornflower-blue coloration on the addition of a few drops of sodium hydroxide. E. F. A.

[Preparation of Dimethylindanthren.] BADISCHE ANILIN & SODA-FABRIK (D.R.-P. 238979).—3:3'-*Dimethylindanthren*, a bluish-grey, crystalline powder, can be prepared by boiling an acetic acid solution of 2-amino-3-methylanthraquinone (1 part) with lead peroxide (3 parts) during three hours, or by boiling a naphthalene solution of 1-bromo-2-amino-3-methylanthraquinone with copper oxide and anhydrous sodium acetate during four to five hours. A similar compound can be obtained from 2-amino-6(7)-methylanthraquinone.

F. M. G. M.

**Action of Semicarbazide on Hydroxamic Acids.** HANS RUPE and F. FIEDLER (*J. pr. Chem.*, 1911, [ii], 84, 809—816).—It has been shown previously (Rupe and Kessler, *Abstr.*, 1910, i, 93) that the action of semicarbazide hydrochloride on aliphatic oximino-ketones leads to the replacement of the oximino-group by the semicarbazide residue,  $\text{N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ . A similar elimination of the oximino-group is found to take place with hydroxamic acids, resulting in the formation of semicarbazides. The reaction is, however, not a general one. The replacement occurs readily with benzhydroxamic and acethydroxamic acids, and with difficulty in the case of phenyl-acethydroxamic acid, whilst with salicylhydroxamic and cinnamhydroxamic acids no reaction takes place.

Benzoylsemicarbazide, obtained by heating benzhydroxamic acid with semicarbazide hydrochloride in aqueous solution, has m. p.  $215^\circ$ , and may also be prepared by the action of ethyl benzoate or benzoic anhydride on semicarbazide. The high m. p. ( $225^\circ$ ) given by Widmann and Cleve (*Abstr.*, 1898, i, 335) is due to the presence of hydrazodicarboxylamide. The *acetyl* derivative,  $\text{C}_{10}\text{H}_{11}\text{O}_3\text{N}_3$ , forms lustrous, white leaflets, m. p.  $174^\circ$ , and is instantly hydrolysed by cold aqueous sodium hydroxide.

*Cinnamoylsemicarbazide*,  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}_3$ , prepared by heating cinnamic

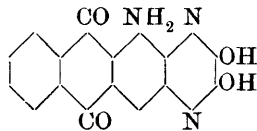
anhydride with semicarbazide, crystallises in needles; the *acetyl* derivative forms slender, white needles, m. p. 177—178°.

*Phenylacetylsemicarbazide*,  $C_9H_{11}O_2N_3$ , obtained from the acid chloride or anhydride in a similar manner, or by the interaction of phenylhydroxamic acid and semicarbazide hydrochloride in aqueous solution, crystallises in slender needles, m. p. 167—168°. F. B.

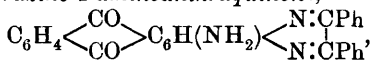
**Azines and Quinonediazides of the Anthraquinone Series.**  
 ROLAND SCHOLL, FRITZ EBERLE, and WALTER TRITSCH (*Monatsh.*, 1911, 32, 1043—1056).—(1) *Azines from Triaminoanthraquinone*.—On condensing 1:2:3-triaminoanthraquinone with *o*-dicarbonyl compounds, azines of entirely different nature are to be expected, according as the pyrazine nucleus becomes attached in the angular 1:2-position or the linear 2:3-position. The linear derivatives should possess the same properties as the azines from 2:3-diaminoanthraquinone (Scholl and Kacer, *Abstr.*, 1905, i, 88), characterised by their giving brown reduction products with alkaline sodium hyposulphite (Scholl and Edlbacher, *Abstr.*, 1911, i, 756).

Oxalic acid, benzil, 1:2-naphthaquinone, phenanthraquinone, and isatin yield azines with triaminoanthraquinone, which all form insoluble brown products in alkaline sodium hyposulphite. The azines are accordingly regarded as linear (for nomenclature see Scholl, *Abstr.*, 1911, i, 677). 1:2:3-Triaminoanthraquinone has m. p. 325° (decomp.).

*Dihydroxy-2:3-pyrazino-1-aminoanthraquinone* (annexed formula), produced on condensation with oxalic acid, sublimes in lustrous, dark brown needles. It is not melted at 400°; in boiling with dilute sodium hydroxide, it dissolves, giving a red solution, from which a red sodium salt separates on cooling.



*Diphenyl-2:3-pyrazino-1-aminoanthraquinone*,



prepared by condensation of triaminoanthraquinone and benzil, crystallises in tiny red or brownish-red needles, m. p. 241°; it sublimes without decomposition, and gives a red coloration with concentrated sulphuric acid.

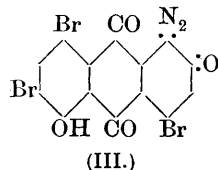
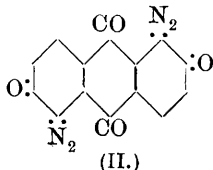
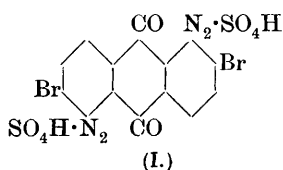
2:3(1':2'-)-*Naphthazino-1(or 4)-aminoanthraquinone* is obtained as a dark brown, amorphous compound, m. p. 266—267°.

2:3(9':10'-)-*Phenanthrazino-1-aminoanthraquinone* crystallises in well formed, reddish-brown, lustrous needles, m. p. 361°.

2:3-*Indazino-1(or 4)-aminoanthraquinone* forms a dark brown, indefinitely crystalline powder, m. p. above 400°. When heated with sodium hyposulphite and sodium hydroxide it forms a reddish-brown vat, which dyes cotton yarn light brown.

(2) *Quinoneuzides of the Anthraquinone Series*.—The quinonediazides of the anthraquinone series in contrast to those of the benzene series cannot be coupled with naphthol or naphthylamine to azo-dyes. With resorcinol they couple only very slowly on prolonged heating.

2 : 6-Dibromoanthraquinone-1 : 5-bisdiazonium sulphate (I), produced on diazotising dibromodiaminoanthraquinone, separates in yellowish-red crystals, m. p. 185—186°. When boiled with dilute sulphuric acid it is converted into anthraquinone-2 : 1 : 6 : 5-bisquinonediazide (II).

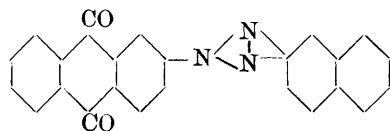


This crystallises in well-formed, metallic-green, lustrous crystals, which explode at 156°.

4 : 6 : 8-Tribromo-5-hydroxyanthraquinone-2 : 1-quinonediazide (III), prepared by diazotising 2 : 4 : 6 : 8-tetrabromo-1 : 5-diaminoanthraquinone and boiling the crude diazo-product, was obtained in a brown, crystalline form from acetone, which blackens and sinters above 360°.

E. F. A.

[Preparation of  $\psi$ -Azimino-compounds.] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 238253). When the azo-compounds



obtained by the combination of  $\beta$ -diazoanthraquinones with  $\beta$ -naphthylamine are oxidised they yield  $\psi$ -azimino-compounds, such as  $\alpha\beta$ -naphthylene- $\psi$ -azimino- $\beta$ -anthraquinonyl (annexed

formula). The sulphonic derivatives are soluble in water, and form valuable cotton dyes.

F. M. G. M.

Action of Hydrazoic Acid on Cyanogen. Formation of Cyanotetrazole. E. OLIVERI-MANDALÀ and T. PASSALACQUA (*Gazzetta*, 1911, 41, ii, 430—435. Compare Oliveri-Mandalà, *Abstr.*, 1910, i, 343; 1911, i, 337; Oliveri-Mandalà and Coppola, *Abstr.*, 1910, i, 593; Oliveri-Mandalà and Alagna, *Abstr.*, 1911, i, 243; Dimroth and Fester, *Abstr.*, 1910, i, 645).—When cyanogen is passed into a 40% aqueous solution of azoimide, cyanotetrazole [*tetrazole-5-carboxylonitrile*],  $C_2HN_5$ , is produced. The substance becomes slightly red at 70° and melts at 99°, forming a reddish-brown liquid. It yields ammonia quantitatively when boiled with potassium hydroxide solution. The silver salt,  $C_2N_5Ag$ , and the barium salt,  $(C_2N_5)_2Ba \cdot 3\frac{1}{2}H_2O$ ,

were prepared.

When the silver salt of cyanotetrazole is treated with ethyl iodide, 1-ethyltetrazole-5-carboxylonitrile,  $\begin{matrix} C(CN) \cdot NEt \\ | \\ N \text{---} N \text{---} N \end{matrix}$ , is obtained; it is a colourless liquid, b. p. 127°/46 mm. On distillation at ordinary pressure, it explodes at about 200°. 1-Ethyltetrazole-5-carboxylamide,  $C_4H_7ON_5$ , is prepared by heating at 50—60° an alkaline solution of 1-ethyltetrazole-5-carboxylonitrile with hydrogen peroxide solution;

it crystallises in minute, lustrous scales, m. p. 125—126°. 1-Ethyl-tetrazole-5-carboxylic acid,  $C_4H_6O_2N_4$ , is obtained by heating 1-ethyl-tetrazole-5-carboxylonitrile with methyl-alcoholic potassium hydroxide, and neutralising the potassium salt with sulphuric acid. The acid crystallises in acicular prisms, m. p. 124—125°. In addition to the potassium salt,  $C_4H_5O_2N_4K$ , the silver salt,  $C_4H_5O_2N_4Ag$ , was prepared. When 1-ethyltetrazole-5-carboxylic acid is kept at 130—140° it loses carbon dioxide, and 1-ethyltetrazole (identified as platini-chloride) is obtained, identical with the *N*-ethyltetrazole formerly described.

R. V. S.

**Identity of the Guanine Pentoside from Molasses with Vernine.** ERNST SCHULZE and GEORG TRIER (*Zeitsch. physiol. Chem.*, 1912, 76, 145—147).—Vernine (guanine-*d*-ribose), for which the composition  $C_{10}H_{13}O_5N_5 \cdot 2H_2O$  was recognised by Schulze and Castoro (Abstr., 1904, ii, 506), is identical with the guanosine obtained by Levene and Jacobs from nucleic acid, and with the guaninepentoside isolated by Andrlik (Abstr., 1911, i, 397) from molasses. In 1.5% sulphuric acid it has  $[\alpha]_D^{20} - 8.4^\circ$ .

E. F. A.

**The Fastness to Light of Hydroxyazo-compounds. Some Derivatives of  $\alpha$ -Methoxynaphthalenes.** N. WOROSHOZOFF (*Zeitsch. Farb.-Ind.*, 1911, 10, 169—173).—It is found that the alkylation of the hydroxy-group in hydroxyazo-compounds increases the fastness to light of the colouring matters obtained therefrom, and that methylation can be conveniently carried out by shaking an alkaline solution of the compound with methyl sulphate.

*Sodium 1-methoxynaphthalene-4-sulphonate*, prepared by shaking  $\alpha$ -naphthol-4-sulphonic acid with methyl sulphate in the presence of sodium hydroxide, separates in glistening leaflets.

*4-Nitro-1-methoxynaphthalene*, yellow needles, m. p. 81°, is obtained by slowly adding an intimate mixture of the foregoing acid (10 parts) and anhydrous sodium carbonate (0.6 part) in small portions to a cooled solution of 1.5 grams of carbamide in 20 c.c. of nitric acid (D 1.4); on reduction with stannous chloride and hydrochloric acid it furnishes *4-methoxy- $\alpha$ -naphthylamine hydrochloride* in colourless crystals; the free base is a dark oil; its *acetyl* derivative has m. p. 180—181°.

F. M. G. M.

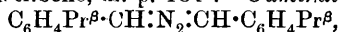
**Salicylic Acid Azo-dyes.** EUGÈNE GRANDMOUGIN (*Ber.*, 1911, 44, 3756).—A claim for priority against Bulow (Abstr., 1911, i, 338).

D. F. T.

**Decomposition of Azines by Heat. I. and II.** PAUL PASCAL and LÉON NORMAND (*Bull. Soc. chim.*, 1911, [iv], 9, 1029—1037, 1059—1068).—Curtius and Jay (Abstr., 1889, 393) showed that benzaldazine decomposes when heated, forming stilbene, and Bouveault obtained di-*p*-methylstilbene in a similar way from tolualdazine (Abstr., 1897, i, 347, 530), but failed to generalise the reaction. In the first of these papers the authors show that, in general, the aromatic aldazines melt with very slight decomposition, but when the tempera-

ture is raised above the melting point, evolution of gas commences and increases with rise of temperature, the principal reaction being the production of nitrogen and the stilbene corresponding with the aldazine used. At the higher temperatures some ammonia and hydrogen are formed, with, as a solid product, the corresponding phenanthrene, due to loss of H atoms at positions contiguous to the azine side-chain. The rate of decomposition was determined by measuring the gas evolved. By plotting temperatures as abscissæ and volumes of (1) nitrogen and (2) ammonia disengaged as ordinates, two curves were obtained cutting one another on the temperature axis, and thus giving the temperature of decomposition, which is sometimes  $50^{\circ}$  below that actually observed subjectively. When the evolution of gas ceases, the contents of the tubes were distilled, and give as a rule (1) a mixture of aldazine and the stilbene; (2) green oils containing the phenanthrene; (3) red oils, and (4) a resinous or coke-like residue. In the case of the "red oils" from benzaldazine the chief constituent is a substance, m. p.  $261^{\circ}$ , b. p.  $460^{\circ}$ , crystallising in long needles and giving a yellow picrate, m. p.  $198^{\circ}$ ; it may be identical with the product  $C_{28}H_{23}N_3$  obtained by Curtius from benzoin-hydrazine. The amounts of this substance and its homologues produced increase with rise in the molecular weight of the aldazine employed.

Benzaldazine,  $CHPh:N_2:CHPh$ , begins to decompose at  $275^{\circ}$ , furnishing stilbene, phenanthrene, and the product  $C_{28}H_{23}N_3$  already referred to. Tolualdazine,  $C_6H_4Me:N_2:C_6H_4Me$ , begins to decompose at  $314^{\circ}$ , forming di-*p*-methylstilbene, m. p.  $181^{\circ}$ . *Cuminaldazine*,



m. p.  $113.6^{\circ}$ , forms yellow leaflets, and begins to decompose at  $281^{\circ}$ , yielding di-*p*-isopropylstilbene,  $C_6H_4Pr^{\beta}:CH:N_2:CH:C_6H_4Pr^{\beta}$ , m. p.  $129^{\circ}$ , which separates from alcohol in colourless scales, and yields a *dibromide*, m. p.  $186-187^{\circ}$  (approx., decomp.), crystallising in small, brilliant, colourless spangles.

*p*-Methylbenzaldazine,  $CHPh:N_2:CH:C_6H_4Me$ , m. p.  $112^{\circ}$ , forms pale yellow crystals from alcohol, and when heated gives *p*-methylstilbene m. p.  $119.6^{\circ}$ . Aldazines in which the benzene nucleus is replaced by naphthalene decompose only at high temperatures, and the unsaturated product is difficult to free from tarry by-products. Furfuraldazine,  $C_4OH_4:CH:N_2:CH:C_4OH_4$ , is decomposed by heat, yielding furfurylstilbene, m. p.  $97.4^{\circ}$ .

The aliphatic azines of low molecular weight distil easily, and decompose only at a red heat. The higher terms decompose slowly on distillation, forming a fluorescent liquid with an odour of petroleum and of pyridine bases; there is no evolution of nitrogen or ammonia.

*Di-p-chlorobenzaldazine*, m. p.  $211^{\circ}$ , forms yellow spangles from alcohol or boiling benzene; it begins to decompose at  $284^{\circ}$ , furnishing di-*p*-chlorostilbene, m. p.  $153.8^{\circ}$ , in silver-grey spangles, which yields a *dibromide*, m. p.  $195-197^{\circ}$ . *Di-p-iminobenzaldazine*, m. p.  $245^{\circ}$ , obtained by the interaction of *p*-aminobenzaldehyde with hydrazine sulphate, is a yellow powder; it begins to decompose at  $307^{\circ}$ , giving off a little nitrogen and much ammonia, so that it was impossible to isolate di-*p*-aminostilbene from the accompanying tarry by-products.

Di-*o*-methoxybenzaldazine begins to decompose at 270°, and yields 80% of di-*o*-methoxystilbene, m. p. 136°, which separates from alcohol in colourless crystals and gives a *dibromide*, m. p. 190°; the corresponding *meta*-compound furnishes di-*m*-methoxystilbene, m. p. 97·5°, the *dibromide* of which, m. p. 183·5—184·5°, is colourless and crystalline. Di-*p*-methoxybenzaldazine begins to decompose at 289°, and yields di-*p*-methoxystilbene, m. p. 213°. Di-*o*-ethoxybenzaldazine, m. p. 131·6°, forms yellow crystals, and commences to decompose at 287°, giving di-*o*-ethoxystilbene, m. p. 87·5°, colourless crystals, the *dibromide* of which, m. p. 218—219°, forms pale yellow crystals. Di-*p*-ethoxybenzaldazine, m. p. 172·3°, crystallises in pale yellow lamellæ, and begins to decompose at 308°, furnishing di-*p*-ethoxystilbene, m. p. 208°.

Di-*o*-benzyloxybenzaldazine, m. p. 157·7°, yellow plates, gives di-*o*-benzyloxystilbene, m. p. 117·6°, in small, brilliant, colourless spangles, whilst the corresponding para-compound, m. p. 209·3°, pale yellow leaflets, decomposes less easily, forming a bulky "coke" from which no stilbene derivative has yet been isolated. T. A. H.

**Decomposition of Azines by Heat. III.** PAUL PASCAL and LÉON NORMAND (*Bull. Soc. chim.*, 1912, [iv], 11, 21—25. Compare preceding abstract).—The *methoxynaphthalaldazine* gives only a small yield of dimethoxynaphthylethylene at 362°. *Veratraldazine* gives but little 3 : 4 : 3' : 4'-tetramethoxystilbene, whilst the *azine* from piperonaldehyde,  $N_2(\cdot CH \cdot C_6H_3 \cdot O_2 \cdot CH_2)_2$ , does not yield a corresponding stilbene. The main conclusions arrived at from results described in this and the preceding abstracts are as follows.

Aromatic azines decompose at about 300°, evolving nitrogen and ammonia, and giving stilbene derivatives, the yields being increased if the position ortho to the group  $\cdot CH \cdot N_2 \cdot$  is filled by any radicle. In the same homologous series the yield diminishes on ascending the series. If a substituent group, such as amino-, in the nucleus of the azine possesses a residual affinity, the yield of stilbene compound is considerably lowered. Esterification in the case of several hydroxy-groups attached to each aromatic nucleus does not prevent decomposition.

A study of the physical constants of the azines and stilbenes shows that the introduction of one or more atoms of oxygen into the molecule produces a rise in the melting point. The reverse is the case if a hydroxyl group is replaced by a methoxy- or ethoxy-group. Finally, the more symmetrical the molecule the higher is the melting point.

W. G.

**The Existence of Sulphur Fixed as Sulphite in Wool.** H. STRUNK and HANS PRIESS (*Zeitsch. physiol. Chem.*, 1912, 76, 136—144).—Raikow (Abstr., 1905, i, 725; 1907, i, 666; compare Grandmougin, *Chem. Zeit.*, 1907, 31, 174) has stated that wool, when kept for some time in contact with large quantities of concentrated phosphoric acid, liberates small quantities of sulphurous acid. This is confirmed, but the amount, 0·0064 gram of sulphur dioxide from 300 grams of wool, is too small for it to be assumed that part of the

sulphur in the keratin molecule is united with oxygen as sulphite. Dry wool has a very pronounced affinity for hydrogen sulphide; this is sufficient to explain the variations experienced in the amount of sulphur in wool. The hydrogen sulphide fixed by the wool is easily oxidised to sulphurous and sulphuric acids, and it is probable that a small quantity of sulphurous acid may arise in the wool of the living animal in such manner.

E. F. A.

**The Separation of Rennet and Pepsin.** W. E. BURGE (*Amer. J. Physiol.*, 1912, 29, 330—334).—The passage of a direct current of 10 milliamperes for twenty-four hours through a solution containing both enzymes causes a complete destruction of peptic activity, but leaves the rennet apparently unchanged.

W. D. H.

**Activation of Sucrase [Invertase] by Different Acids.** GABRIEL BERTRAND, M. ROSENBLATT, and (Mme.) M. ROSENBLATT (*Compt. rend.*, 1912, 154, 1515—1518).—The effect of the more common organic and inorganic acids on the diastatic activity of sucrase has been determined under conditions more precisely defined than those of other observers. In each case the optimum concentration of acid was determined. The results, which are displayed in tabular form, show that, generally speaking, the order of efficiency in which the acids stand as activating agents is the same as Ostwald's order for their activity as catalysts in hydrolysis. Hydrochloric and nitric acids, however, are exceptions to the rule, being less effective as activators than as catalysts.

W. O. W.

**Action of Phosphatase.** HANS EULER and SIXTEN KULLBERG (*Zeitsch. physiol. Chem.*, 1912, 76, 241. Compare Abstr., 1911, i, 1051; this vol., i, 61).—Reference is made to von Lebedeff's work, which does not agree with that of the authors; perhaps different kinds of yeast will explain the discrepancy; no further experimental work is adduced.

W. D. H.

**4-Amino-3-hydroxyphenylarsinic Acid and its Products of Reduction.** LUDWIG BENDA (*Ber.*, 1911, 44, 3578—3582. Compare this vol., i, 61—64).—3-Nitro-4-aminophenylarsinic acid can be diazotised in the usual way, yielding a solution of a diazonium salt, which loses the  $\cdot\text{AsO}(\text{OH})_2$  group when boiled with dilute sulphuric acid. However, by treatment with sodium acetate to destroy the mineral acid, the solution of the diazonium salt exchanges its nitro- for a hydroxyl group; the solution of the resulting diazonium salt can be coupled with alkaline  $\beta$ -naphthol to form a red azo-dye, which is reduced by sodium hyposulphite or by sodium hydroxide and aluminium, yielding 1-amino-2-naphthol and 4-amino-3-hydroxyphenylarsinic acid,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{AsO}(\text{OH})_2$ , the sodium salt,  $\text{C}_6\text{H}_7\text{O}_4\text{NAsNa} \cdot 5\text{H}_2\text{O}$ , and silver salt of which are described.

Under suitable conditions, the red azo-dye is reduced by sodium hyposulphite, yielding 4:4'-diamino-3:3'-dihydroxyarsenobenzene,  $\text{As}_2[\text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{OH}]_2$ , the hydrochloride and sulphate of which are described.

C. S.

## Organic Chemistry.

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**Catalysis and the Formation of Petroleum.** CARL ENGLER and E. SEVERIN (*Zeitsch. angew. Chem.*, 1912, 25, 153—158).—Repetition of Künkler's experiments on the distillation of crude oleic and stearic acids at atmospheric pressure (*Chem. Zentr.*, 1910, i, 2031) shows that decomposition begins at 340° and 358° respectively, and that the formation of hydrocarbons is small and commences at about 400°. The suggestion of Künkler and Schwedhelm (Abstr., 1909, i, 281) that soaps may first be formed by the interaction of lime or alumina with fats, and that these under the influence of heat may give rise first to ketones, and eventually to the hydrocarbons of petroleum, is untenable, since ketones have not been found either in bitumens or petroleum, and no indication of the existence of soaps in bitumen could be found by the authors. Various investigators have suggested that rock-forming materials by their action on organic remains may play some part in the formation of petroleum, and some support to this view is afforded by the work of Sabatier, Senderens, and Mailhe on the catalytic decomposition of aliphatic acids and their esters by metallic oxides (compare Ipatieff, Abstr., 1904, ii, 644, 645; 1911, i, 937), and Gräfe (*Petroleum*, 1910, 6, 71) has pointed out that *Lycopodium* spores distilled with fuller's earth afford a distillate similar in character to Scottish shale oil. The authors have therefore examined the distillates obtained from mixtures of oleic or stearic acid with diatomite, fuller's earth, quartz sand, and finely powdered quartz, and find that these materials lower the temperature of decomposition and give rise to distillates richer in hydrocarbons than are obtained when the acids are distilled alone. Powdered quartz is the most efficient of the four, followed by fuller's earth, which is better than either diatomite or sand (compare Hviid, *Petroleum*, 1910, 6, 429). The distillates, full details of which are given in the original, in general resemble those obtained by distillation of fatty acids under pressure (Abstr., 1888, 928), but contain more undecomposed acid and less low-boiling hydrocarbons. The conclusion is drawn that in the conversion of organic remains into petroleum, the influence of rock-forming materials as well as of time, temperature, and pressure must be taken into account.

T. A. H.

**Presence of Cholesterol in Java Naphthas.** CARL ENGLER and WILHELM STEINKOPF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1820—1825).—The work of Koss (Abstr., 1911, i, 761), which was carried out partly under the supervision of the authors, and also its unauthorised publication are severely criticised.

T. H. P.

**Valency of Carbon in So-called Unsaturated Compounds.** ALEXEI E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1690—1735).—A discussion of the various explanations which have

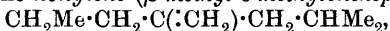
been advanced of the unsaturated character of the carbon atom in different classes of organic compounds. T. H. P.

**$\beta\beta\gamma$ -Trimethylpentane.** LATHAM CLARKE and WEBSTER NEWTON JONES (*J. Amer. Chem. Soc.*, 1912, 34, 170—174).—In continuation of a study of the octanes (Abstr., 1911, i, 354, and earlier abstracts),  $\beta\beta\gamma$ -trimethylpentane has now been synthesised. By the action of magnesium ethyl bromide on pinacolin,  $\beta\beta\gamma$ -trimethylpentan- $\gamma$ -ol was produced, and was converted into  $\gamma$ -iodo- $\beta\beta\gamma$ -trimethylpentane by the action of iodine and amorphous phosphorus. On treating this carbinyl iodide with alcoholic potassium hydroxide,  $\beta\beta$ -dimethyl- $\gamma$ -methylenepentane was obtained, and on passing this over finely divided nickel at 160° in a current of hydrogen,  $\beta\beta\gamma$ -trimethylpentane was produced.

$\beta\beta\gamma$ -Trimethylpentan- $\gamma$ -ol,  $\text{CMe}_3 \cdot \text{CMe}(\text{OH}) \cdot \text{CH}_2\text{Me}$ , b. p. 149—152°/760 mm., is a colourless liquid with a camphor-like odour. The octylene ( $\beta\beta$ -dimethyl- $\gamma$ -methylenepentane),  $\text{CMe}_3 \cdot \text{C}(\text{CH}_2) \cdot \text{CH}_2\text{Me}$ , b. p. 110·4—110·8°/760 mm., is a colourless, mobile liquid with a faint, musty odour.  $\beta\beta\gamma$ -Trimethylpentane,  $\text{CMe}_3 \cdot \text{CHMe} \cdot \text{CH}_2\text{Me}$ , b. p. 110·5—110·8°/760 mm.,  $D_{15}^{25}$  0·7219,  $n_D^{25}$  1·4164, is a colourless, mobile liquid with a very faint odour. E. G.

**$\beta\delta$ -Dimethylheptane.** LATHAM CLARKE and SYDNEY A. BEGGS (*J. Amer. Chem. Soc.*, 1912, 34, 60—62).—In continuation of the work on the nonanes (following abstract),  $\beta\delta$ -dimethylheptane has been synthesised.

When  $\beta$ -methyl- $\delta$ -pentanone (methyl *isobutyl* ketone), obtained by the hydrolysis of ethyl *isopropyl*acetoacetate, is treated with magnesium *n*-propyl iodide, the nonylene ( $\beta$ -methyl- $\delta$ -methylenheptane),



b. p. 132—133°, is obtained as a colourless liquid with an odour resembling that of petroleum. The position of the double bond was not established, but there is little doubt that the formula assigned to the compound is correct. On passing a mixture of the nonylene and hydrogen over freshly reduced nickel,  $\beta\delta$ -dimethylheptane,



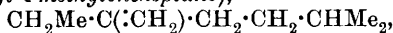
b. p. 132·9—133°/752 mm.,  $D_{15}^{25}$  0·7206,  $n_D^{25}$  1·4014, is produced as a colourless liquid with a petroleum-like odour. E. G.

**$\beta\epsilon$ -Dimethylheptane.** LATHAM CLARKE and SYDNEY A. BEGGS (*J. Amer. Chem. Soc.*, 1912, 34, 54—60).—In a study of the octanes (Abstr., 1911, i, 354, and earlier abstracts), certain relations have been discovered between the chemical constitution and physical properties. An investigation has been undertaken in order to ascertain whether similar relations occur in the nonane series, and an account is now given of the synthesis and properties of  $\beta\epsilon$ -dimethylheptane which has been obtained previously in an impure state by Welt (Abstr., 1896, i, 332).

The synthesis was effected in the following manner.  $\beta$ -Methyl- $\epsilon$ -hexanone, obtained by the hydrolysis of ethyl *isobutyl*acetoacetate, was converted into  $\beta\epsilon$ -dimethyl- $\epsilon$ -heptanol by means of magnesium

ethyl bromide. The iodide of this alcohol was prepared, and when boiled with alcoholic potassium hydroxide yielded  $\beta$ -methyl- $\epsilon$ -methyleneheptane, which was then reduced to  $\beta\epsilon$ -dimethylheptane.

$\beta\epsilon$ -Dimethyl- $\epsilon$ -heptanol,  $\text{CH}_2\text{Me}\cdot\text{CMe}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}_2$ , b. p. 172—174°, is a colourless liquid with an odour of musty apples. The nonylene ( $\beta$ -methyl- $\epsilon$ -methyleneheptane),



b. p. 139—140°, is a colourless liquid with a sweet, petroleum-like odour.  $\beta\epsilon$ -Dimethylheptane,  $\text{CH}_2\text{Me}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}_2$ , b. p. 135.6—135.9°/760 mm.,  $D_{15}^{25}$  0.7190,  $n_D^{25}$  1.4020, obtained by passing a mixture of the nonylene and hydrogen over freshly reduced nickel at 160—180°, is a colourless liquid with a petroleum-like odour.

E. G.

**Conjugated *aci*-Nitro-compounds.** ARTHUR HANTZSCH and KURT VOIGT (*Ber.*, 1912, 45, 85—117).—A number of nitro-compounds, chiefly aliphatic substances containing  $\text{NO}_2$  attached to carbon, have been examined spectrometrically to determine how the absorption spectrum is affected when the real nitro-group is changed to an *aci*-nitro-group. The chief result of the investigation has been the discovery of a new type of nitro-compound, which is called a conjugated *aci*-nitro-compound.

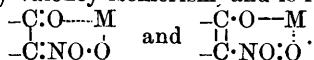
The nitro-group may be present in a substance in three forms, each of which has its characteristic absorption curve. Aliphatic real nitro-compounds show very feeble selective absorption, the curves exhibiting a very flat band or a kink beginning at oscillation frequency 3413. It is immaterial whether the nitro-group is the only negative substituent in the molecule or whether another ( $\text{NO}_2$ ,  $\text{NOH}$ ,  $\text{CO}$ ,  $\text{CO}_2\text{H}$ ,  $\text{CO}_2\text{Et}$ ,  $\text{CO}\cdot\text{NH}_2$ ,  $\text{CN}$ ,  $\text{Ph}$ ) is present, provided that the introduction of the latter does not produce a constitutive change in the nitro-group. A simple *aci*-nitro-group,  $\text{>C:NO}\cdot\text{OH}$ , causes weak general absorption; such groups are present only in the salts of the nitroparaffins,  $\text{CHR:NO}\cdot\text{OM}$ . When, however, an *aci*-nitro-group is present together with another negative group, X (one of those mentioned above), then, without exception, the substance exhibits very strong, selective absorption, the curve exhibiting a very deep band for thicknesses corresponding with 10 to 100 mm. of  $N/10,000$  solution. Since the introduction of a negative group into a real nitro-compound has little optical influence, whilst a simple *aci*-nitro-group alone causes general absorption, it follows that the strong selective absorption exhibited by a substance containing both an *aci*-nitro- and another negative group must be conditioned by the influence of these two groups on one another. This influence is represented by a peculiarly constituted, six-membered ring, produced by the union, by a supplementary valency, of a metallic or hydrogen atom, or of an alkyl group with a negative atom of the negative (unsaturated) group X:  $\text{R}\cdot\text{C}\begin{smallmatrix} \text{X} \\ \text{NO}\cdot\text{O} \end{smallmatrix}$  ( $\text{Na}, \text{H}, \text{Me}$ ). For

examples, X is a nitro-group in *aci*-dinitro-compounds (salts of di- and tri-nitromethane), an  $\text{R}\cdot\text{CO}$  group in  $\alpha$ -*aci*-nitroketones (the nitro-barbituric acids; ethyl *aci*-nitromalonate), and a cyano-group in  $\alpha$ -cyano-

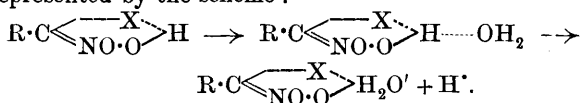
*aci*-nitro-compounds (fulminuric esters ; *aci*-nitrocyanophenylmethane). An *aci*-nitro-group in this state is called a conjugated *aci*-nitro-group. Its presence explains why the introduction of a third negative group into the molecule exerts so slight an optical influence ; the third group can only have a feeble auxochromic effect. *aci*-Nitrophenylmethane and its salts contain a conjugated *aci*-nitro-group ; consequently the benzene nucleus, by means of a supplementary valency (in the ortho- or para-position), can form part of the six-membered complex.

Certain conjugated *aci*-nitro-compounds (fulminuric acid and the nitrobarbituric acids) are so stable that they cannot be converted, even by concentrated sulphuric acid, into real nitro-compounds. Furthermore, substances containing a simple *aci*-nitro-group together with another unsaturated group are incapable of existence ; therefore, when a real nitro-compound containing another unsaturated group is transformed into an *aci*-nitro-compound, a conjugated *aci*-nitro-group is always produced.

The chromoisomerism of certain conjugated *aci*-nitro-compounds, for example, the yellow and the colourless salts of the nitrobarbituric acids, cannot be explained by regarding the yellow salt as containing a conjugated *aci*-nitro-group and the colourless salt as containing a simple *aci*-nitro-group, because the latter group cannot exist in such compounds. Both salts contain the conjugated *aci*-nitro-group. The colour of the yellow salt is due to a shifting of the absorption band towards the red end of the spectrum. Chromoisomerism in such cases, therefore, is merely valency isomerism, and is represented thus :



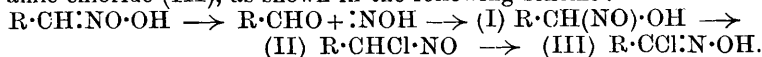
When the ionisation of a substance containing a conjugated *aci*-nitro-group is unaccompanied by secondary changes, the ions are optically identical with the undissociated acid, and therefore contain the peculiar six-membered ring. This result leads to Werner's theory that the formation of ions is, in the first step, a case of hydrate formation. For the particular examples under discussion, the ionisation is represented by the scheme :



In conclusion, attention is drawn to the extensive optical and chemical analogies between negatively substituted nitro-compounds on the one hand, and negatively substituted ketones (ethyl acetoacetate) on the other. C. S.

**Aliphatic Nitro-compounds. XII. Constitution of *aci*-Nitro-compounds.** WILHELM STEINKOPF and BORIS JÜRGENS (*J. pr. Chem.*, 1911, [ii], 84, 686—713. Compare Abstr., 1911, i, 530).—The formation of hydroxamic chlorides by the action of hydrogen chloride on aliphatic nitro-compounds is referred by the authors to the decomposition of the *aci*-nitro-compound into the corresponding aldehyde and nitroxyl, which then combine to form a nitroso-alcohol (I) ; the latter compound reacts with hydrogen chloride, yielding a chloronitroso-

compound (II), which then undergoes transformation into the hydroxamic chloride (III), as shown in the following scheme :



This view is supported (1) by the observations of Nef (Abstr., 1895, i, 3), and also of Hantzsch and Veit (Abstr., 1899, i, 401), who find that *aci*-nitro-derivatives of hydrocarbons readily decompose into aldehyde, nitrous oxide, and water; (2) by the formation of hydroxamic acids by the direct combination of aldehydes and nitroxyl (Angeli), and (3) by the production of blue or green colorations, due to the formation of chloronitroso-compounds,  $\text{R}\cdot\text{CHCl}\cdot\text{NO}$ , when salts of the nitro-derivatives of aliphatic hydrocarbons are acidified in aqueous or ethereal solution. Attempts have been made to isolate these coloured compounds in the case of nitromethane, nitropropane, and nitroethane, but only with the last-mentioned compound were the attempts successful. When a suspension of the sodium salt of *aci*-nitroethane in a large volume of ether is treated with an excess of hydrogen chloride, and the resulting solution, after removal of the sodium chloride, rapidly evaporated, chloronitrosoethane (Piloty and Steinbock, Abstr., 1902, i, 735) was obtained. If a small volume of ether is used and excess of hydrogen chloride avoided, the product consists of ethyl-nitrolic acid. The formation of the latter compound is due to the action of nitrous acid, produced by the decomposition of the intermediately formed nitroso-alcohol,  $\text{NO}\cdot\text{CMeH}\cdot\text{OH}$ , on unchanged nitroethane.

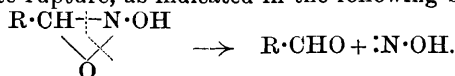
Salts of nitro-compounds, such as nitroacetic acid and nitroacetone, which contain strongly negative groups do not give blue or green colorations when treated with acids, and the conclusion is therefore drawn that in these cases decomposition of the *aci*-nitro-compound into aldehyde and nitroxyl does not take place.

This view is supported by the behaviour of *o*-nitroacetophenone, which on treatment with hydrogen chloride in ethereal solution yields *o*-chloro-*o*-oximinoacetophenone (Thiele and Haeckel, Abstr., 1903, i, 160), without the intermediate formation of a coloured nitroso-compound. *aci*-Phenylnitromethane, which contains the feebly negative phenyl group, occupies an intermediate position; with ethereal hydrogen chloride, it develops the blue coloration very slowly, instead of instantly as in the case of the nitro-derivatives of aliphatic hydrocarbons, and this coloration gradually disappears owing to the formation of benzhydroxamic acid.

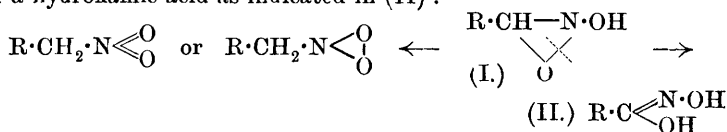
These differences in the behaviour of nitro-compounds are best explained on the assumption that the *aci*-nitro-derivative has the constitution,  $\text{CRH}-\text{N}\cdot\text{OH}$ , proposed by Hantzsch, and not the



Michael-Nef formula,  $\text{CHR}\cdot\text{NO}\cdot\text{OH}$ , now generally accepted. The stability of the carbazoxy-ring depends on the nature of the substituents. When  $\text{R} = \text{H}$  or alkyl, the ring is unstable, and readily suffers complete rupture, as indicated in the following scheme :



On the other hand, when R is a strongly negative group, the stability of the ring is greatly increased, so that rupture occurs only at one point, either between C and O, with the formation of a nitro-compound as shown in (I) below, or between N and O, with the formation of a hydroxamic acid as indicated in (II) :



The evidence furnished by Nef in favour of the formula



for *aci*-nitro-compounds is subjected to a critical examination, and the conclusion is drawn that Hantzsch's formula affords a simpler and less forced explanation of the behaviour of these compounds.

Numerous examples of the reactions of nitro-compounds and of a large number of other classes of compounds containing the carbazoxy-ring are cited in support of the authors' view. F. B.

**Specific Gravity Table of Alcohol-Water Mixtures at 17.5°.** WILHELM FRESSENIUS and LEO GRÜNHUT (*Zeitsch. anal. Chem.*, 1912, 51, 123—124).—A useful table giving  $D_4^{17.5}$  for a number of mixtures of alcohol and water, together with the corresponding alcohol % by weight and by volume, and also alcohol in grams per 100 c.c. L. DE K.

**Action of Potassium Hydroxide on Secondary Alcohols; Diagnosis of Primary and Secondary Alcohols of High Molecular Weight.** MARCEL GUERBET (*Compt. rend.*, 1912, 154, 222—225. Compare this vol., i, 67).—When secondary alcohols are heated at 230° with potassium hydroxide, some oxidation occurs with production of potassium salts of acids, but the greater part of the alcohol forms condensation products; thus *isopropyl* alcohol yields formic and acetic acid, together with  $\beta$ -methylpentan- $\delta$ -ol and  $\beta\delta$ -dimethylheptan- $\zeta$ -ol. The corresponding higher homologues are obtained from *sec.*-butyl alcohol and octyl alcohol. The ease with which the reaction is carried out renders it suitable for distinguishing between secondary and primary alcohols. W. O. W.

**Specific Gravity and Hygroscopic Power of Glycerol.** ANTON KAILAN (*Zeitsch. anal. Chem.*, 1912, 51, 81—101).—Anhydrous glycerol has  $D_4^{15}$  1.26413. The density between 14° and 20° can be calculated by the expression  $D_4^t = 1.26413 + (15 - t) 0.000632$ , and a table is given of densities from 14.3° to 20.6°. Boiling points under various pressures between 9 and 32 mm. are also recorded.

Glycerol rapidly absorbs moisture from the air, and a number of determinations of the hygroscopic power of anhydrous and hydrated samples are given. It appears that a mixture containing 80% of glycerol is in equilibrium with air containing an average amount of moisture.

The author also noticed that alcohol containing but little water absorbs, in the same circumstances, water four times more rapidly than does a similar glycerol. L. DE K.

**Preparation of Epichlorohydrin from Dichlorohydrin and Alkalis.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 239077).—When dichlorohydrin (129 parts) in 200 parts of water is slowly treated with 133 parts of 30% sodium hydroxide solution, it yields 85 parts of epichlorohydrin; the sodium hydroxide may be replaced by its equivalent of potassium or ammonium hydroxide, but the above concentrations must be carefully maintained. F. M. G. M.

**Tautomerism of the Dialkyl Phosphites.** THADDEUS MILOBENDZKI (*Ber.*, 1912, 45, 298—303).—Previous investigations (Abstr., 1897, i, 391; 1908, ii, 488; 1903, i, 733; 1907, i, 8, 1899, i, 659) have indicated that dialkyl hydrogen phosphite in the free condition has the constitution (I)  $\text{O}:\text{P}(\text{OR})_2$ . From the behaviour of the esters in aqueous solution, the author shows that they also exist in the tautomeric form (II)  $\text{OH}\cdot\text{P}(\text{OR})_2$ .

Silver salts of the composition  $\text{Ag}\cdot\text{PO}(\text{OR})_2$  are precipitated from aqueous solutions of diisopropyl hydrogen phosphite (b. p. 74—75°/9 mm.) and diethyl hydrogen phosphite (b. p. 66—67°/9 mm.) by the successive addition of silver nitrate and aqueous alkalis (ammonia, sodium hydroxide, and barium hydroxide); the addition of the reagents in the reverse order produces no precipitate.

According to the author the silver salts,  $\text{OAg}\cdot\text{P}(\text{OR})_2$ , are readily soluble in water, and the non-formation of a precipitate, when the alkali is added before the silver nitrate is due to the transformation of the keto-ester (I) into the enolic form (II).

The silver salts,  $\text{Ag}\cdot\text{PO}(\text{OR})_2$ , dissolve in excess of alkali owing to change into the tautomeric form, induced by the hydroxyl ions; on acidifying the alkaline solutions, the original salt is precipitated.

Dialkyl hydrogen phosphites show the phenomenon of gradual neutralisation. The percentage of the ester (I) present in aqueous solutions has been determined by adding the equivalent amount of aqueous ammonia, followed immediately by the addition of silver nitrate; the amount of silver salt,  $\text{Ag}\cdot\text{PO}(\text{OR})_2$ , precipitated corresponds with that of the ester of the formula (I) originally present; with diethyl hydrogen phosphate the amount is 35%.

That the enolic modifications of the esters are capable of existing in aqueous solution has also been shown by neutralising with aqueous barium hydroxide, and then adding the equivalent amount of sulphuric acid; the solutions thus obtained do not show the phenomenon of gradual neutralisation, nor yield insoluble silver salts.

Triethyl phosphite is hydrolysed by excess of aqueous sodium hydroxide to sodium diethyl hydrogen phosphite; dialkyl hydrogen phosphites are not hydrolysed by alkalis.

Experiments are also described showing that *sodium diethyl phosphite*, prepared from sodium and diethyl hydrogen phosphite in ethereal solution, exists in aqueous solution in the form  $\text{NaO}\cdot\text{P}(\text{OEt})_2$ .

F. B.

**Constitution of Glycerophosphoric Acid Prepared by Esterification of Phosphoric Acid or Sodium Dihydrogen Phosphate.** PAUL CARRÉ (*Compt. rend.*, 1912, 154, 220—222.\* Compare Abstr., 1904, i, 133, 215).—Sodium glycerophosphate,

\* and *Bull. Soc. chim.*, 1912, 11, 169—172.

prepared by Poulenc's method, was converted into glycerophosphoric acid by the process previously described. The product is identical in every respect with the acid formed in the direct esterification of phosphoric acid by glycerol. The same acid is obtained when glycerol bromohydrin (3 mols.) is heated with silver phosphate and the resulting unstable *ester*,  $\text{OP}[\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}]_3$ , submitted to hydrolysis. Poulenc's compound must, therefore, be a salt of  $\alpha$ -glycerophosphoric acid, and not of the  $\beta$ -acid as stated by Paolini (Abstr., 1911, ii, 774). The author has been unable to obtain Paolini's brucine salt crystallising with  $7\text{H}_2\text{O}$ . W. O. W.

**Preparation of Glycol and Glycolhydrin Esters of Phosphoric Acid Glycerides.** ADOLF GRÜN and FRITZ KADE (D.R.-P. 240075).—Compounds of general formula  $\text{X}\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{PO}(\text{OH})\cdot\text{O}\cdot\text{C}_3\text{H}_5(\text{O}\cdot\text{CO}\cdot\text{R})_2$ , where R is an alkyl group and X halogen or hydroxyl, can be readily prepared by the action of phosphoric oxide on distearin and ethylene-glycol or halogenhydrins.

The following products are described: the *compound*,  
 $\text{C}_2\text{H}_4\text{Cl}\cdot\text{O}\cdot\text{PO}(\text{OH})\cdot\text{O}\cdot\text{C}_3\text{H}_5(\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{35})_2$ ,  
 m. p.  $65-66^\circ$ ; the *compound*,  
 $\text{OH}\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{PO}(\text{OH})\cdot\text{O}\cdot\text{C}_3\text{H}_5(\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{35})_2$ ,  
 from  $\alpha\beta$ -distearinphosphoric acid ester, ethylenechlorohydrin, and glycol. The *trimethylamine salt*,  
 $\text{C}_2\text{H}_4\text{Cl}\cdot\text{O}\cdot\text{PO}(\text{O}\cdot\text{NHMe}_3)\cdot\text{O}\cdot\text{C}_3\text{H}_5(\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{35})_2$ ,  
 m. p.  $69^\circ$ ; and by the interaction of another molecule of trimethylamine, the *salt*,  
 $\text{NMe}_3\text{Cl}\cdot\text{C}_2\text{H}_4\cdot\text{O}\cdot\text{PO}(\text{O}\cdot\text{NHMe}_3)\cdot\text{O}\cdot\text{C}_3\text{H}_5(\text{O}\cdot\text{CO}\cdot\text{C}_{17}\text{H}_{35})_2$ .

F. M. G. M.

**The Agglutination of Lecithins and Lecithin-protein Mixtures by Acids.** J. FEINSCHMIDT (*Biochem. Zeitsch.*, 1912, 38, 244—251).—Aqueous suspensions of lecithins of various origins have agglutination optima at definite hydrogen ion concentrations, which are identical with the isoelectric point. This varies in the different preparations between  $10^{-2}$  and  $10^{-4}$ , that is, in somewhat strongly acid solutions. Neutral salts increase the turbidity of the solutions, but make the actual agglutination point less sharp. When lecithin and protein are mixed, a new complex is formed, in which the agglutination point shifts towards the less acid side; in this case the precipitation is more energetic and coarser. S. B. S.

**Catalytic Decomposition of Formic Esters.** PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1912, 154, 49—52. Compare Abstr., 1911, i, 258—416).—The catalytic decomposition of alkyl formates below  $400^\circ$  is somewhat complicated, and follows a different course from that of esters of higher acids. In general, two principal reactions occur, represented by the equations: (1)  $2\text{H}\cdot\text{CO}_2\text{R} = \text{H}\cdot\text{CHO} + \text{CO}_2 + \text{R}_2\text{O}$ , followed by the dehydration of the aldehyde with production of an unsaturated hydrocarbon; (2)  $\text{H}\cdot\text{CO}_2\text{R} = \text{CO} + \text{R}\cdot\text{OH}$ , followed by dehydration or dehydrogenation of the alcohol. The water set free may effect hydrolysis, the resulting formic acid then decomposing in the manner already described.

The nature of the catalyst considerably influences the course of reaction; thus in the case of methyl formate and titanium oxide, reaction (1) predominates, whilst with zinc oxide reaction (2) occurs almost exclusively. Both reactions take place with thorium dioxide. Finely divided platinum, nickel, and copper readily effect catalysis, principally in accordance with equation (2). W. O. W.

**Catalytic Formation of Saturated Aliphatic Esters from Formic Esters.** PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1912, 154, 175—177. Compare preceding abstract).—When the vapour of methyl formate and isobutyric acid in equimolecular proportions is passed over titanium oxide at 250°, carbon monoxide is liberated, and the condensed liquid contains 20% of methyl isobutyrate, together with methyl alcohol and some isobutaldehyde. The esterification is explained by the decomposition of the methyl formate in the manner previously described, whilst the aldehyde arises from reduction of the acid by formic acid. Thorium oxide acts in the same way, but requires a higher temperature; thus at 300—330°, isovaleric acid and methyl formate give 40% of methyl isovalerate by volume and 16% of isovaleraldehyde. Under these conditions the amount of ketone formed is inconsiderable, but at 370° the condensed liquid contains 50% of ester, 10% of isovalerone, 15% of isovaleraldehyde, and also methyl alcohol.

Similar results have been obtained with higher acids and other alkyl formates. The direct reduction of acids by means of formic acid will be described in a further communication. W. O. W.

**Optically Active Dialkylacetic Acids.** EMIL FISCHER, JULIUS HOLZAPFEL, and HANS VON GWINNER (*Ber.*, 1912, 45, 247—257. Compare Fischer and Flatau, *Abstr.*, 1909, i, 628).—*α*-isoButylhexoic acid has been resolved into optically active components by crystallisation of the brucine salt. The difference between the butyl and isobutyl radicles is apparently enough to cause pronounced optical asymmetry. *α*-isoButylvaleric acid has also been resolved, but definite results were not obtained with *α*-isopropylvaleric acid.

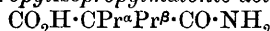
*Ethyl butylisobutylmalonate*, prepared by the interaction of *n*-butyl bromide on ethyl isobutylmalonate and sodium, has b. p. 137—140°/10 mm. When hydrolysed by means of sodium hydroxide, *butyl isobutylmalonic acid* is obtained in colourless crystals, m. p. 136—138°. The neutral solution of the ammonium salt gives a colourless precipitate with silver nitrate, and crystalline precipitates of the corresponding salts with barium and calcium chlorides. On heating at 160°, *butylisobutylacetic* [*α*-isobutylhexoic] acid is obtained as a colourless oil, b. p. 145—145·5° (corr.)/10 mm. The brucine salt forms small, microscopic prisms. The first separations were hydrolysed by heating with sulphuric acid. The optically active *d*-*α*-isobutylhexoic acid had  $[\alpha]_D^{25} + 5\cdot73^\circ$ .

*Ethyl propylisobutylmalonate* was obtained as an oil, b. p. 126°/9·5 mm.

*Propylisobutylmalonic acid* crystallises in stunted prisms or plates, m. p. 147—149° (corr., decomp.).

*Propylisobutylacetic* [*α*-isobutylvaleric] acid is a colourless oil,  $D^{20}_D$  0.8928, b. p. 122° (corr.)/8.5 mm.; it forms a colourless *silver* salt, crystallising from ammonia in microscopic, slender needles. The *calcium* salt also consists of microscopic, slender needles. The *brucine* salt forms microscopic, small prisms, and yields *d*-*α*-isobutylvaleric acid as a colourless oil, m. p. 100°/0.5 mm.,  $D^{22}_D$  0.8876,  $[\alpha]^{20}_D + 9.8^\circ$ .

The monoamide of *propylisopropylmalonic acid*,



obtained by heating cyanoisopropylvaleric acid with concentrated sulphuric acid, crystallises in colourless bunches of intergrown prisms, m. p. 137° (corr., decomp.). When heated over the flame in a distillation flask, *α*-isopropylvaleramide is obtained at about 250°. It crystallises in slender, colourless needles, m. p. 131—133° (corr.).

By the action of sulphuric acid and sodium nitrite at 80°, *propylisopropylacetic* [*α*-isopropylvaleric] acid is obtained, b. p. 116° (corr.)/12 mm., 112—113°/9 mm.,  $D^{17}_D$  0.9076.

A partial resolution was obtained by means of the quindine salt, the acid formed having  $[\alpha]^{22}_D + 0.77^\circ$ . E. F. A.

**Composition of Linseed Oil and the Distribution of Oxygen in Dried Layers of the Oil.** II. E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1509—1524. Compare Abstr., 1910, i, 810).—The author criticises Fokin's work (Abstr., 1907, i, 820), the results of his own experiments being in agreement with Genthe's theory (*Zeitsch. angew. Chem.*, 1906, 19, 2087), except that he finds that when a layer of the oil, 100—108 sq. cm. in area, weighs 0.1—0.15 gram, 15—16% of oxygen is taken up, although setting occurs when only 12% has been absorbed.

Experiments in which a cobalt dryer was employed give for the rates at which oxygen is fixed results corresponding with the formula  $dx/dt = k(A-x)(B+x)$  or  $k = \frac{1}{t(A+B)} \cdot \log\left(\frac{A}{A-x} \cdot \frac{B+x}{B}\right)$ , where  $A$  represents the total amount of oxygen absorbed expressed as reduction of pressure,  $x$  the atmospheric pressure, and  $B$  a constant. After the oil has combined with 12% of its weight of oxygen, a solid phase is formed, and the further velocity of the absorbing process is expressed by  $dx/dt = k(A-fx)(B+fx)$ , where  $f$ , the correction coefficient, is less than unity, and corresponds with the product of combination of the solid phase,  $kf$  being a constant magnitude.

In parallel with this chemical process proceeds a physical one of diffusion of the oxygen into the oil, the amounts of oxygen in successive layers, starting from the surface, being in the proportions of  $n, n^2, n^3, n^4 \dots n^x$ , where  $n$  is less than 1 (0.5, 0.6, etc.). The quantity of oxygen combined is related to the factor  $n$ , according to the expression  $S/Q = n/(1-n)$ , where  $Q$  is the quantity of combined oxygen corresponding with the iodine number, and  $S$  is the amount of oxygen found in each separate case. Assuming complete distribution

of the oxygen by diffusion, the value of  $n$  must be taken as two-thirds.  
T. H. P.

**Molecular Rearrangements in the Camphor Series. IX. Lauronolic Acid and Campholactone.** WILLIAM A. NOYES and CHARLES E. BURKE (*J. Amer. Chem. Soc.*, 1912, 34, 174—183).—Tiemann (Abstr., 1901, i, 6) found that lauronolic acid prepared from bromocamphoric anhydride has a rotatory power which differs considerably from that of the acid obtained by the distillation of camphanic acid, and suggested that the acid produced by the latter method consisted of a mixture of optical isomerides. This has now been proved to be the case.

Lauronolic acid, prepared from active bromocamphoric anhydride by Aschan's method (Abstr., 1895, i, 154), has been obtained in the form of rosettes of long needles; it has m. p.  $6.5-8^{\circ}$ , b. p.  $230-235^{\circ}$  under the ordinary pressure, vapour pressure 99—100 mm. at  $184^{\circ}$ ,  $D_4^{25}$  1.0109,  $D_4^{25}$  1.0133,  $D_4^{10}$  1.0249,  $[\alpha]_D^{25} + 187.7^{\circ}$ ,  $n_D$  1.47586, and the dissociation constant  $K$   $1.36 \times 10^{-5}$ . The calcium salt crystallises with  $3H_2O$ , instead of only  $2H_2O$  as stated by Brecht (Abstr., 1911, i, 417), and when heated with soda-lime yields laurolene.

When hydrogen iodide is passed into a solution of lauronolic acid in light petroleum, the *hydriodide* is obtained in the form of yellow plates, and is very unstable. On reducing this compound with zinc dust and alcohol, *dihydrolauronolic acid*,  $C_8H_{15} \cdot CO_2H$ , is produced, which has  $D_4^{25.5}$  0.9008,  $[\alpha]_D^{25.5} + 1.74^{\circ}$ , vapour pressure 100 mm. at  $178^{\circ}$  and 749 mm. at  $215^{\circ}$ , and  $[n]_D$  1.45786; the *amide* has m. p.  $50-51^{\circ}$ .

By decomposing inactive bromocamphoric anhydride prepared from synthetical camphor, inactive lauronolic and camphanic acids were obtained. Inactive lauronolic acid has m. p.  $5-8.5^{\circ}$ , vapour pressure 100 mm. at  $192^{\circ}$ ,  $D_4^{25}$  1.0318, and  $[n]_D$  1.47655; its *calcium* salt crystallises with  $1H_2O$ .

Campholactone, prepared in various ways from lauronolic acids of widely different rotatory powers, has m. p.  $50^{\circ}$  and  $[\alpha]_D^{22} - 21.7^{\circ}$ , and when warmed with barium hydroxide solution is converted into the corresponding hydroxy-acid, m. p.  $143^{\circ}$  and  $[\alpha]_D^{27} + 16.0^{\circ}$ . E. G.

**Molecular Rearrangements in the Camphor Series. VIII. Camphonolic Acid and Camphonolactone.** WILLIAM A. NOYES, E. E. GORSLINE, and R. S. POTTER (*J. Amer. Chem. Soc.*, 1912, 34, 62—67).—Four hydroxy-acids and three lactones have been described which retain the tertiary carboxyl group of camphoric acid. The structural formulæ assigned to these compounds have not been well established, and the present work was therefore undertaken with the object of obtaining further evidence as to their constitution.

Camphononic acid, prepared by a modification of Lapworth and Lenton's method (Trans., 1901, 79, 1287), has m. p.  $229-230^{\circ}$ ,  $[\alpha]_D^{27.5}$  in benzene (2.4 grams in 100 c.c.)  $+ 17.8^{\circ}$ ,  $[\alpha]_D^{28}$  in alcohol (2 grams in 100 c.c.)  $- 3.9^{\circ}$ . On reducing this acid with sodium and amyl

alcohol, *amyl camphonolate* is obtained as a yellow, viscous oil of b. p. 222—223°/40 mm.; the *calcium*, *copper*, and *silver* salts were prepared.

It is shown that the lactone obtained by Noyes and Taveau (Abstr., 1906, i, 397) by decomposing the nitroso-derivative of aminolauronic anhydride with sodium hydroxide is identical with *cis*-camphonolactone (annexed formula) prepared by Bredt (Abstr., 1909, i, 498) by the electrolytic reduction of camphononic acid. *cis*-Camphonolactone has m. p. 165—167°,  $[\alpha]_D^{25}$  in alcohol (5 grams in 100 c.c.) -20·2° and  $[\alpha]_D^{25}$  (10 grams in 100 c.c.) -22·3°. The corresponding hydroxy-acid, *cis*-camphonolic acid (annexed formula), has m. p. 202—203° when rapidly heated,  $[\alpha]_D^{25}$  in alcohol (10 grams in 100 c.c.) +29·2°, and on oxidation with chromic acid is converted into camphononic acid. E. G.

**The Melting Point of Oxalic Acid.** EYVIND BÖDTKER (*Chem. Zeit.*, 1912, 36, 105).—Pure crystallised oxalic acid does not appear to have a definite melting point; a small crystal placed in a capillary tube had m. p. 99·5—101·5°, whilst a layer in the capillary tube, 1 mm. in height, had m. p. 100—102·5° when the temperature was raised very slowly and maintained at 100° for about one minute.

W. P. S.

**Conversion of Maleic into Fumaric Acid.** SEBASTIAN M. TANATAR (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1742—1746).—It was discovered by Skraup (Abstr., 1891, 1338) that the interaction of hydrogen sulphide and sulphur dioxide in aqueous solution in presence of maleic acid is accompanied by transformation of the latter acid into fumaric acid; this effect he termed "resonance."

Since the reaction liquid, after filtration from the sulphur formed, contains nothing capable of bringing about this transformation, the author has investigated the action of sulphur on maleic acid. Milk of sulphur is without effect, and the same is apparently the case with the sulphur separated by the action of hydrogen sulphide on ferric chloride in presence of maleic acid. With sodium thiosulphate and a mineral acid, however, which normally give precipitation of sulphur, maleic acid prevents such precipitation and is simultaneously converted into fumaric acid; a similar transformation is produced, also without separation of sulphur, by addition of the thiosulphate to a solution of maleic acid alone. That these solutions contain no dissolved sulphur is shown by extraction with carbon disulphide, and the conclusion is drawn that it is the reaction of the thiosulphuric and maleic acids, with formation of an unknown product, that induces the isomeric change.

This same change is brought about by treatment of maleic acid with ammonia or potassium polysulphide (liver of sulphur), although in the latter case it may be due to the presence of thiosulphate.

T. H. P.

**Relation between the Configuration and Rotation of the Lactones in the Sugar and Saccharinic Acid Groups.** ERNEST ANDERSON (*J. Amer. Chem. Soc.*, 1912, 34, 51—54).—Hudson (Abstr., 1910, i, 220) has pointed out that dextrorotatory sugar lactones have the ring on one side of the structure, whilst levorotatory lactones have it on the other.

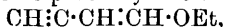
It is now shown that this relation is true, not only for the lactones to which Hudson referred, but for nearly all monobasic and some dibasic acid lactones in the sugar and saccharinic acid groups. The configurations and specific rotations of eighteen such lactones are tabulated. The relation affords a new method for determining the configuration of the lactones formed by certain dibasic acids.

E. G.

**Ethyl Orthotrithioformate.** BROR HOLMBERG (*Ber.*, 1912, 45, 364—365).—In reply to Houben and Schultze (this vol., i, 5) it is claimed that the product obtained by the author (Abstr., 1907, i, 474) was pure.

D. F. T.

**Action of Potassium Hydroxide on Tetrolacetal.** PAUL L. VIGUIER (*Compt. rend.*, 1912, 154, 217—220. Compare Abstr., 1909, i, 691; this vol., i, 7).—When tetrolacetal (diethoxybutinene) is dropped on potassium hydroxide at 180—200°, a liquid distils, and on fractionation yields a compound,  $C_6H_8O$ , b. p. 29—33°/16 mm.,  $D_{19.5}^{20} 0.826$ ,  $n_D^{19.5} 1.462$ . This probably has the constitution



since it forms an explosive *silver* derivative,  $C_6H_7OAg$ , and is hydrolysed by acids, forming an unstable substance having the properties of the *aldehyde*,  $CH:C\cdot CH_2\cdot CHO$ . The latter changes spontaneously into triacetylbenzene, acetoacetaldehyde probably being produced first. Hydroxylamine yields 1-methylisooxazole. On treating the aldehyde with semicarbazide hydrochloride, a *semicarbazone*,  $C_5H_8ON_3Cl$ , is obtained; this yields the corresponding *aldehyde*,  $C_4H_5OCl$ , on hydrolysis.

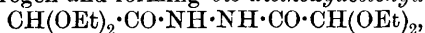
W. O. W.

**Tartardialdehyde.** ALFRED WOHL and BRUNO MYLO (*Ber.*, 1912, 45, 322—349).—From the result of their endeavours, the authors conclude that the synthesis of tartardialdehyde by the symmetrical linking together of two molecules each containing two carbon atoms presents excessive difficulties, and they have finally attained success by other means.

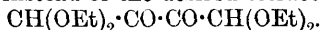
The action on acetyl chloride of copper hydride gives ethyl acetate and ethylidene diacetate, whilst the action of copper on the additive product of dibromoacetaldehyde and acetyl bromide yields bromovinyl acetate. Dibromoacetaldehyde also reacts slowly with magnesium methoxide, the product being a  $\beta\beta\delta$ (or  $\delta\delta\beta$ )-tribromo- $\gamma$ -keto-*n*-butyl alcohol, b. p. 77—79°/14—16 mm.

Glyoxal sodium bisulphite in acetic anhydride solution reacts with hydrogen chloride producing unstable *s*-dichloroglycol diacetate, b. p. 110—115°/14 mm. (compare Prud'homme, *Zeit. Chem.*, 1870, 380).

Ethyl diethoxyacetate in ethereal solution with potassium gives as chief product an undistillable syrupy substance, *β*-hydroxy-γ-keto-succindialdehyde diethylacetal,  $\text{CH}(\text{OEt})_2 \cdot \text{CO} \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OEt})_2$ ; the substance was not obtainable in a pure state, and the action of sodium gave still less satisfactory results. The action of sodium on the piperidide of diethoxyacetic acid (Wohl and Lange, Abstr., 1908, i, 943) yields *monoethoxyacetopiperidide*, b. p. 72—74°/0.08—0.11 mm. *Diethoxyacetohydrazide*, obtained from the ethyl ester with hydrazine in alcoholic solution, forms capillary crystals, m. p. 43—45°, and has b. p. 110°/0.05 mm.; it reacts with mercuric oxide or metaboric acid, eliminating nitrogen and forming *bis-diethoxyacetohydrazide*,



which crystallises in needles, m. p. 67—70°; the mercury, copper, and lead compounds are described. Iodine removes mercury from the mercury compound with the formation of *azo-α-ketodi-β-ethoxyethane*,  $\text{CH}(\text{OEt})_2 \cdot \text{CO} \cdot \text{N} \cdot \text{N} \cdot \text{CO} \cdot \text{CH}(\text{OEt})_2$ , a viscous, colourless oil, b. p. 131—134°/0.07—0.08 mm., which on warming decomposes, giving ethyl orthoformate, instead of the desired tetraethoxydiacetyl,



Success was attained by starting with di-magnesium acetylene dibromide (from acetylene and magnesium ethyl bromide), which on treatment with ethyl orthoformate gives acetylenedialdehyde diethylacetal,  $\text{CH}(\text{OEt})_2 \cdot \text{C} \equiv \text{C} \cdot \text{CH}(\text{OEt})_2$ ,  $D^{18.5}$  0.955 (compare Jotsitch, *Chem. Zeit.*, 1907, 31, 979); by reduction with hydrogen in the presence of colloidal palladium, this passes into *maleinaldehyde diethylacetal*, b. p. 112—112.5°/11 mm.,  $D^{23}$  0.926, which is oxidisable by potassium permanganate (compare Wohl, Abstr., 1898, i, 556) into *tartardialdehyde diethylacetal*, a viscous oil, b. p. 157—160°/11 mm. The hydrolysis of this acetal is most satisfactorily accomplished by *N*/10-sulphuric acid in the cold, when a sweet solution of *tartardialdehyde* is obtained; this solution on slow evaporation deposits microscopic needles, which, having a bitter taste and being sparingly soluble in water, probably represent a polymeric form; they re-dissolve slowly in warm water, giving a sweet solution, which from its cryoscopic behaviour contains the substance in a unimolecular condition; this solution on evaporation gives a sweet amorphous residue.

The *diphenylhydrazone* of tartardialdehyde forms yellow crystals, m. p. 197.5° (corr., decomp.); no osazone was obtainable; the *di-semicarbazone* has m. p. 227.5° (corr., decomp.); the dioxime, 153.5° (corr., decomp.).

Oxidation of the tartardialdehyde by bromine water gives meso-tartaric acid; for this reason the above ethylenic aldehyde is supposed to be that corresponding with maleic acid.

D. F. T.

**Dihydroxyacetone as an Intermediate Product of Alcoholic Fermentation.** ARTHUR SLATOR (*Ber.*, 1912, 45, 43—46).—It is sometimes assumed that dihydroxyacetone is an intermediate product of the alcoholic fermentation of dextrose (compare Buchner and Meisenheimer, Abstr., 1910, ii, 737). If this is the case, dihydroxyacetone must be fermented by the yeast at least as quickly as

dextrose. Experiments are quoted to show that during twenty minutes no dihydroxyacetone is fermented, although an equal weight of dextrose is entirely fermented by the same yeast during this time. The conclusion is drawn that dihydroxyacetone is not directly fermented, and that it is therefore not an intermediate product of alcoholic fermentation.

E. F. A.

**The Physico-chemical Bases of the Seliwanoff Lævulose Reaction.** HARRY KOENIGSFELD (*Biochem. Zeitsch.*, 1912, 38, 310—320).—It is shown that the Seliwanoff reaction for lævulose is also yielded by dextrose when the latter is present in a concentration higher than 2%, and also when the hydrochloric acid exceeds 12—12.5% in strength. As the reaction appears to be due to hydroxy-methylfurfuraldehyde formed from the lævulose, and as under certain conditions lævulose can be formed from dextrose, the author draws the conclusion that the latter sugar only gives a positive result in the Seliwanoff reaction when the conditions are such that it can be converted in appreciable quantity into the former sugar. This hypothesis is supported by the investigation of the action of acids and bases on dextrose, which, it is shown, probably changes under certain conditions into fructose.

S. B. S.

**Chemistry of the Wood Dextrins.** C. A. YLLNER (*Zeitsch. angew. Chem.*, 1912, 25, 103—107).—The dextrins obtained by Hönig and Schubert (Abstr., 1887, 125) are mixtures of homologues, from which the individual substances can be obtained only after repeated precipitation. The reducing power increases with the rotation of the dextrin; 1 gram of a dextrin with the rotation  $+25^{\circ}$  corresponds with approximately 0.1 gram of cuprous oxide, a rotation of  $+50^{\circ}$  corresponding with about 0.2 gram of cuprous oxide.

The velocity and extent of hydrolytic decomposition with acids was determined.

T. S. P.

**Photolytic Decomposition of Smokeless Powders by Ultra-violet Light. Influence of Stabilisers. Damaged Powders.** DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1912, 154, 201—203. Compare this vol., ii, 210).—Exposure of nitroglycerol to the light from a quartz-mercury lamp results in decomposition with production of the following gases:  $\text{CO}_2$  (24 vols.), CO (19.5 vols.),  $\text{N}_2$  (39 vols.),  $\text{N}_2\text{O}$  (7 vols.), NO (9 vols.), with a considerable amount of nitrogen peroxide, which, however, is not evolved from the gelatinised material treated with stabilisers. At a distance of 20 mm. from the lamp, powders stabilised with amyl alcohol withstood decomposition better than those containing diphenylamine, whereas at 50 mm. diphenylamine was the more effective stabiliser. Damaged French naval powders showed themselves less resistant to the rays than sound powders of the same composition.

W. O. W.

**General Method for the Preparation of Aliphatic Amines by Catalytic Reduction of Alkyl Nitrites.** GEORGES GAUDION (*Ann. Chim. Phys.*, 1912, [viii], 25, 125—136).—The author has applied Sabatier and Senderens' method (Abstr., 1905, i, 333) of catalytic

reduction by means of finely divided nickel or copper in presence of hydrogen to a series of alkyl nitrites, and finds that these are reduced, giving the corresponding secondary amine, with small amounts of the primary amine and very small quantities of the tertiary amine. Nickel generally acted at a lower temperature than copper; thus in the case of *isoamyl* nitrite the former gave good results at 220—230°, and the latter at 350°.

Several possible explanations of the reaction are discussed, and it is considered that it is best explained by assuming that the alkyl nitrites are first isomerised into the corresponding nitro-paraffins, which are then reduced in the ordinary way. This explanation is the more probable in view of the fact that the reaction seems to take place in the same way as the catalytic reduction of the nitro-paraffins investigated by Sabatier and Senderens (Abstr., 1902, i, 701). T. A. H.

**Ammonium and Sulphonium Perchlorates. Relations between Solubility and Constitution.** KARL A. HOFMANN, KURT HÖBOLD, and FRITZ QUOOS (*Annalen*, 1912, 386, 304—317. Compare Abstr., 1910, i, 818; 1911, i, 608).—Ammonium and sulphinium perchlorates are eminently suitable substances for the study of the relationship between solubility and constitution, because they do not form hydrates, are nearly allied crystallographically, and, whilst not being hydrolysed in aqueous solution, are electrolytically dissociated to the same order of magnitude; several factors, therefore, which might possibly mask the relationship are eliminated from the field. The following perchlorates are described (the numbers in brackets denote the grams of water in the saturated solution at 15° containing one gram-molecule of the salt):  $\text{NH}_4 \cdot \text{ClO}_4$  (635);  $\text{NHMe}_3 \cdot \text{ClO}_4$  (800);  $\text{NMe}_4 \cdot \text{ClO}_4$  (32,640);  $\text{NMe}_3\text{Et} \cdot \text{ClO}_4$  (1710);  $\text{NMe}_3\text{Pr} \cdot \text{ClO}_4$ , doubly refracting, rhombic plates or prisms, m. p. 118° (1310);  $\text{NMe}_3(\text{C}_3\text{H}_5)_2 \cdot \text{ClO}_4$ , thin, rectangular plates, m. p. 90° (100);  $\text{ClO}_4 \cdot \text{NMe}_3 \cdot \text{C}_4\text{H}_9$ , almost rectangular plates, m. p. 186° (5810);  $\text{ClO}_4 \cdot \text{NMe}_3 \cdot \text{C}_5\text{H}_{11}$ , doubly refracting, rhombic plates or prisms (10,300);  $\text{NMe}_3\text{Ph} \cdot \text{ClO}_4$ , rhombic crystals, m. p. 175° (decomp.) (1315);  $\text{CH}_2\text{I} \cdot \text{NMe}_3 \cdot \text{ClO}_4$ , rhombic or monoclinic plates, m. p. 184° (decomp.) (9535);  $\text{ClO}_4 \cdot \text{NMe}_3 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$ , thin, doubly refracting, rhombic plates, sinters at 86° (150);  $\text{NEt}_4 \cdot \text{ClO}_4$  (6130);  $\text{NMeEt}_3 \cdot \text{ClO}_4$ , rhombic plates (915);  $\text{NEt}_3\text{Pr} \cdot \text{ClO}_4$ , quadratic prisms, m. p. 275° (3090);  $\text{NMe}_3\text{Et}_2 \cdot \text{ClO}_4$  (150);  $\text{C}_2\text{H}_4(\text{NMe}_3 \cdot \text{ClO}_4)_2$ , rhombic plates (200);  $\text{C}_2\text{H}_4(\text{NMe}_3 \cdot \text{ClO}_4)_2$ , stout, rhombic plates (28,700);  $\text{C}_3\text{H}_6(\text{NMe}_3 \cdot \text{ClO}_4)_2$ , doubly refracting leaflets (23,500);  $\text{SMe}_3 \cdot \text{ClO}_4$ , stout, rhombic prisms or elongated plates, m. p. above 267° (1280);  $\text{SMe}_2\text{Et} \cdot \text{ClO}_4$ , elongated, rhombic plates (840);  $\text{SMe}_2\text{Pr} \cdot \text{ClO}_4$  (1700);  $\text{ClO}_4 \cdot \text{SMe}_2 \cdot \text{C}_4\text{H}_9$  (1650);  $\text{C}_2\text{H}_4(\text{SMe}_2 \cdot \text{ClO}_4)_2$ , rhombic prisms, m. p. 250° (2360);  $\text{ClO}_4 \cdot \text{SMe}_2 \cdot \text{CH} \cdot \text{CH}_2$ , elongated plates (1368);  $\text{C}_3\text{H}_6(\text{SMe}_2 \cdot \text{ClO}_4)_2$  (2480).

The most striking result is the sparing solubility of the quaternary ammonium perchlorates in comparison with the great solubility of methylammonium perchlorate (120), dimethylammonium perchlorate (70), diethylammonium perchlorate (115), and ethylammonium perchlorate (70). Another striking fact is the enormous difference in the

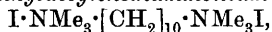
solubilities of quaternary ammonium perchlorates containing like alkyl groups from those containing unlike alkyl groups; for example,  $\text{NMe}_4 \cdot \text{ClO}_4$  (32,640),  $\text{NMe}_3\text{Et} \cdot \text{ClO}_4$  (1710). These two groups of perchlorates also differ in their stability towards alkaline potassium permanganate, those of the type  $\text{NR}_4 \cdot \text{ClO}_4$  being stable, whilst members of the other group are rapidly oxidised, at the ordinary temperature.

The molecular dilutions of glyceryltrimethylammonium perchlorate (150) and of choline perchlorate (70) show how enormously the solubility is increased by the introduction of hydroxyl groups; when the hydroxyl groups are esterified, however, the solubility is very largely diminished, as shown in the case of nitratocholine perchlorate (40,000). Deductions similar to the preceding can be drawn in the case of the sulphinium perchlorates.

C. S.

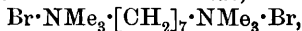
### Decomposition of Quaternary Ammonium Hydroxides.

II. JULIUS VON BRAUN (*Annalen*, 1912, 386, 273—303. Compare Abstr., 1911, i, 610).—The decomposition by heat of diammonium hydroxides of the type  $\text{OH} \cdot \text{NMe}_3 \cdot [\text{CH}_2]_x \cdot \text{NMe}_3 \cdot \text{OH}$  may result in the formation of di-olefines, unsaturated tertiary amines, or ditertiary diamines. Substances in which  $x$  is 3, 5, 7 and 10, have been examined. All four yield by decomposition unsaturated tertiary amines,  $\text{CH}_2 \cdot \text{CH} \cdot [\text{CH}_2]_{x-2} \cdot \text{NMe}_2$ , the amount of which increases as  $x$  increases; thus *hexamethyldecylenediammonium iodide*,



white leaflets, m. p.  $231^\circ$ , obtained from *ak*-di-iododecane (Abstr., 1910, i, 25) and alcoholic trimethylamine at  $100^\circ$ , is converted by the usual treatment into a syrupy mass of *hexamethyldecylenediammonium hydroxide*, by the distillation of which very little di-olefine (unexamined) is formed, the chief product being a mixture of 30% of *dimethyldecenylamine*,  $\text{CH}_2 \cdot \text{CH} \cdot [\text{CH}_2]_8 \cdot \text{NMe}_2$ , b. p.  $118\text{—}120^\circ/17$  mm. (*platinichloride*; *picrate*, m. p.  $137^\circ$ ; *methiodide*, m. p.  $137\text{—}140^\circ$ ), and 50% of *ak-tetramethyldiaminodecane*,  $\text{C}_{14}\text{H}_{32}\text{N}_2$ , b. p.  $157\text{—}158^\circ/17$  mm., (*platinichloride*, m. p.  $189^\circ$  [decomp.]; *picrate*, m. p.  $139\text{—}140^\circ$ ). The distillation of trimethyldecenylammonium hydroxide gives a 75% yield of dimethyldecenylamine; hence the latter can be obtained from hexamethyldecylenediammonium hydroxide with comparative ease and in good yield.

*Hexamethylheptylenediammonium bromide*,



m. p.  $245^\circ$ , prepared from *an*-dibromoheptane and alcoholic trimethylamine at  $100^\circ$ , forms a diammonium hydroxide, the distillation of which yields about 15% of a heptadiene, 28—29% of *dimethylheptenylamine*,  $\text{CH}_2 \cdot \text{CH} \cdot [\text{CH}_2]_5 \cdot \text{NMe}_2$ , b. p.  $166\text{—}169^\circ$  or  $60\text{—}65^\circ/10$  mm. (*picrate*, m. p.  $88^\circ$ ; *methiodide*, m. p.  $120^\circ$ ), and 51% of *an-tetramethyl-diaminoheptane*,  $\text{NMe}_2 \cdot [\text{CH}_2]_7 \cdot \text{NMe}_2$ , b. p.  $225\text{—}230^\circ$  (decomp.) or  $101\text{—}102^\circ/10$  mm. (*picrate*, m. p.  $136^\circ$ ; *dimethiodide*, m. p.  $242^\circ$ ). Unlike the two preceding diammonium hydroxides, hexamethylamlyenediammonium hydroxide, prepared from the iodide (*loc. cit.*), begins to decompose during the evaporation of its aqueous solution. Its complete decomposition yields mainly trimethylamine, water, and piperylene, very little *tetramethyldiaminopentane*, b. p.  $193\text{—}194^\circ$

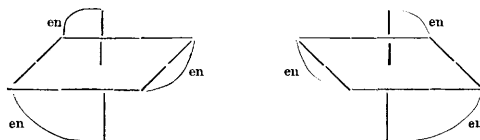
(*platinichloride*, m. p. 218° [decomp.]; *picrate*, m. p. 149°), and *dimethylpentenylamine* (isolated as the *methiodide*, m. p. 200°) being produced. Similar results are obtained by the decomposition of hexamethylbutylenediammonium hydroxide and hexamethylpropylenediammonium hydroxide; in the latter case, the non-nitrogenous product is not allene, but a mixture of viscous oxidation products, from which an unsaturated substance,  $C_6H_{10}O$  (*semicarbazone*, m. p. 192°), probably an isomeride,  $CH_3 \cdot CO \cdot CH_2 \cdot CMe \cdot CH_2$ , of mesityl oxide, has been isolated.

The experiments indicate that in the decomposition of diammonium hydroxides, whilst the lower members of the series decompose simultaneously at both ends of the chain, the higher members experience changes first at one end of the chain only. For example:  $OH \cdot NMe_3 \cdot [CH_2]_{10} \cdot NMe_3 \cdot OH \rightarrow Me \cdot OH + OH \cdot NMe_3 \cdot [CH_2]_{10} \cdot NMe_2$  and  $H_2O + NMe_3 + OH \cdot NMe_3 \cdot [CH_2]_8 \cdot CH : CH_2$ ; then  $OH \cdot NMe_3 \cdot [CH_2]_{10} \cdot NMe_2 \rightarrow MeOH + NMe_2 \cdot [CH_2]_{10} \cdot NMe_2$  and  $H_2O + NMe_3 + CH_2 : CH \cdot [CH_2]_8 \cdot NMe_2$ , whilst  $OH \cdot NMe_3 \cdot [CH_2]_8 \cdot CH : CH_2 \rightarrow MeOH + NMe_2 \cdot [CH_2]_8 \cdot CH : CH_2$  and  $H_2O + NMe_3 + C_{10}H_{18}$ .

It has been shown (*loc. cit.*) that the presence of an ethylenic linking in an aliphatic group in a quaternary ammonium hydroxide facilitates the elimination of the group when the point of unsaturation is adjacent to the nitrogen atom. The decomposition of the hydroxides  $OH \cdot NMe_3 \cdot [CH_2]_x \cdot CH : CH_2$  shows that the loosening influence of the ethylenic linking weakens as its distance from the nitrogen atom increases; trimethyldecenylammonium hydroxide yields not more hydrocarbon than does the corresponding saturated quaternary ammonium hydroxide.

C. S.

**The Asymmetric Cobalt Atom. V.** ALFRED WERNER (*Ber.*, 1912, 45, 121—130).—According to the author's theory, there are two possible salts of triethylenediaminecobalt which stand to each other in the relation of object and mirror-image, and are not superposable. These may be represented thus:



Such compounds form the simplest possible case of molecular asymmetry, being specially characterised by having all the co-ordination positions of the central atom occupied by structurally identical groups, the asymmetry being caused by the special spatial arrangement of these groups. Such asymmetry the author denotes as *molecular asymmetry II* (compare Abstr., 1911, i, 838), and he has been successful in resolving some of the salts into the optically active isomerides. Resolution by means of the camphorsulphonates,  $\alpha$ -bromocamphorsulphonates, etc., was unsuccessful, since the salts would not crystallise. Triethylenediaminecobaltic tartrate was obtained in the

crystalline condition, however, and proved to be a partial racemate, which underwent slight resolution on fractional crystallisation, the extent of the resolution being ascertained by taking advantage of the very strong rotation dispersion of these compounds. The lesser soluble crystals contained an excess of the *lævo*-isomeride, the final mother liquors containing the excess of the *dextro*-isomeride; the pure isomerides could then be isolated by making use of the fact that their bromides were readily soluble in concentrated hydrobromic acid, the racemic bromide being almost insoluble. The yields of the active components were very poor by this method, which was then replaced by the following: The chloride tartrate,  $\left[ \text{Co en}_3 \right] \text{C}_4\text{H}_4\text{O}_6^{\text{Cl}}$ , does not form a partial racemate, and by one recrystallisation can be separated into the sparingly soluble *d*-triethylenediaminecobaltic chloride-*d*-tartrate and the readily soluble *l*-triethylenediaminecobaltic chloride-*d*-tartrate, from which other salts can be obtained without difficulty. The bromide tartrates behave similarly to the chloride tartrates.

The specific rotations of the various salts are very large, and the rotation dispersion is very marked, as shown by the following table:

	$[\alpha]_D$ .	$[\alpha]_C$ .	$[M]_D$ .	$[M]_C$ .
Chloride .....	$\begin{cases} +152^\circ \\ -154 \end{cases}$	$\pm 45^\circ$	$\begin{cases} +552.5^\circ \\ -560 \end{cases}$	$\pm 153.6^\circ$
Bromide .....	$\begin{cases} +117 \\ -115 \end{cases}$	$\pm 32$	$\begin{cases} +602.5 \\ -592 \end{cases}$	$\pm 165$
Nitrate .....	$\begin{cases} +132 \\ -130 \end{cases}$	$\begin{cases} +46 \\ -44 \end{cases}$	$\begin{cases} +561 \\ -552 \end{cases}$	$\begin{cases} +195.5 \\ -187 \end{cases}$

The active salts are very stable; their solutions can be evaporated down with concentrated hydrochloric or hydrobromic acid without suffering any loss of activity. The active isomerides are much more readily soluble than the racemates.

The triethylenediaminecobaltic salts,  $(\text{Co en}_3)\text{X}_3$ , are best prepared as follows: 10 grams of cobalt chloride are dissolved in 150 grams of 10% ethylenediamine and oxidised by leading air through the solution. The brown solution so obtained is acidified with hydrochloric acid, evaporated to crystallisation, the crystals dissolved in water, and ammonium nitrate added to the solution, whereby 1:6-dichlorodiethylenediaminecobaltic nitrate is precipitated. After collecting this salt the filtrate is precipitated with sodium bromide, giving pure triethylenediaminecobaltic bromide.

*Triethylenediaminecobaltic tartrate*,  $(\text{Co en}_3)_2(\text{C}_4\text{H}_4\text{O}_6)_3$ , is obtained from the bromide by double decomposition with silver tartrate; it crystallises in spherical aggregates of light yellow needles. *Triethylenediaminecobaltic chloride-tartrate*,  $\left[ \text{Co en}_3 \right] \text{C}_4\text{H}_4\text{O}_6^{\text{Cl}}$ , is prepared by interaction of 1 molecule of the chloride with 1 molecule of silver tartrate, the precipitate of silver chloride being extracted with boiling water until pure white in colour. The solutions thus obtained are concentrated and allowed to crystallise, columnar and tabular crystals separating; these are collected and the filtrate further concentrated.

A second crop of crystals often separates, and then the concentrated solution sets to a jelly-like mass. The crystals consist of *d-triethylenediaminecobaltic chloride-tartrate*,  $\left[ \text{Co en}_3 \right] \text{Cl} \cdot \text{C}_4\text{H}_4\text{O}_6 \cdot 5\text{H}_2\text{O}$ , and are purified by one recrystallisation from water; they have  $[\alpha]_{\text{D}} + 101^\circ$ ,  $[\text{M}]_{\text{D}} + 517.6^\circ$ ,  $[\alpha]_{\text{C}} + 35^\circ$ ,  $[\text{M}]_{\text{C}} + 179.4^\circ$ . The gel consists of the corresponding *laevo*-salt, mixed with small quantities of the *d*-isomeride.

*d-Triethylenediaminecobaltic bromide-tartrate*,  $\left[ \text{Co en}_3 \right] \text{Br} \cdot \text{C}_4\text{H}_4\text{O}_6 \cdot 5\text{H}_2\text{O}$ , is obtained similarly, and forms a felted mass of light yellow, silky needles, which, in contact with the solution, slowly change to much darker, stout, plate-shaped crystals; they have  $[\alpha]_{\text{D}} + 98^\circ$ ,  $[\text{M}]_{\text{D}} + 555^\circ$ ,  $[\alpha]_{\text{C}} + 38^\circ$ ,  $[\text{M}]_{\text{C}} + 211.7^\circ$ . The corresponding *laevo*-isomeride forms a gel.

*d-Triethylenediaminecobaltic bromide*,  $[\text{Co en}_3] \text{Br}_3 \cdot 2\text{H}_2\text{O}$ , is prepared from either the bromide-tartrate or the chloride-tartrate by trituration with warm concentrated hydrobromic acid. The solution, after filtering, deposits large, hexagonal plates, which are probably an acid bromide; on recrystallisation from water, large, columnar crystals of the bromide are obtained. The *l*-bromide,  $[\text{Co en}_3] \text{Br}_3 \cdot 2\text{H}_2\text{O}$ , is similarly prepared from the gel of *l*-bromide-tartrate or *l*-chloride-tartrate, the sparingly soluble racemic bromide remaining undissolved. The *d*- and *l*-chlorides,  $[\text{Co en}_3] \text{Cl}_3 \cdot \text{H}_2\text{O}$ , are obtained from the bromides by reaction with silver chloride; they crystallise in small, golden-yellow, needle-shaped crystals. The *d*- and *l*-nitrates,  $[\text{Co en}_3] (\text{NO}_3)_3$ , are prepared from the bromide by treatment with the theoretical quantity of silver nitrate; they form pyramidal crystals, which are readily soluble in water.

T. S. P.

**Preparation of Hexamethylenetetramine Borocitrates.** ATHENSTAEDT and REDEKER (D.R.-P. 238962).—Alkali and magnesium borocitrates have been previously described. The hexamethylenetetramine derivatives have now been obtained by thoroughly mixing the required proportions of the ingredients in either concentrated aqueous or alcoholic solution. They form colourless, crystalline powders, and are readily soluble in water or alcohol.

*Hexamethylenetetramine borocitrates* having the following composition are mentioned:

$\text{C}_6\text{H}_8\text{O}_7 \cdot 3\text{HBO}_2 \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$	decomp. $182^\circ$ ;
$\text{C}_6\text{H}_8\text{O}_7 \cdot 3\text{HBO}_2 \cdot 3\text{C}_6\text{H}_{12}\text{N}_4$	" $192^\circ$ ;
$2\text{C}_6\text{H}_8\text{O}_7 \cdot 2\text{HBO}_2 \cdot 3\text{C}_6\text{H}_{12}\text{N}_4$	" $185^\circ$ ;
$2\text{C}_6\text{H}_8\text{O}_7 \cdot 4\text{HBO}_2 \cdot 3\text{C}_6\text{H}_{12}\text{N}_4$	" $180^\circ$ ;
$2\text{C}_6\text{H}_8\text{O}_7 \cdot 6\text{HBO}_2 \cdot 3\text{C}_6\text{H}_{12}\text{N}_4$	" $178^\circ$ .

F. M. G. M.

**Compounds of Chromic Hydroxide with Amino-acids Derived from Proteins.** LOUIS HUGOUNENQ and ALBERT MOREL (*Compt. rend.*, 1912, 154, 119—120).—Chromic hydroxide (1 mol.) dissolved in a boiling aqueous solution of glycine (6 mols.) gives a purple-red solution which deposits red crystals containing four molecules of the amino-acid and two hydroxyl groups to two atoms

of chromium. The excess of chromic hydroxide is removed by lixiviation or treatment with acid. The filtrate from the red crystals on slow evaporation deposits brilliant, vermilion, acicular prisms of a compound containing six molecules of the amino-acid to two atoms of chromium. Both compounds are soluble in acids, and are slowly decomposed by alkalis. They do not show the ordinary reactions of chromium salts, but resemble more closely the chromoxalates.

W. O. W.

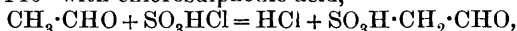
**Action of Amino-acids on Sugars ; Formation of Substances Resembling Melanins.** LOUIS C. MAILLARD (*Compt. rend.*, 1912, 154, 66—68. Compare this vol., i, 13).—Continuing his experiments on the action of natural polyhydric alcohols on amino-acids, the author finds that when glycine is heated on the water-bath with four times its weight of dextrose and the same amount of water, it rapidly loses carbon dioxide and forms dark brown, cyclic, condensation products, the molecules of which contain at least two dextrose residues to one nitrogen atom. They are said to be identical with the melanin pigments obtained in the hydrolysis of proteins. If this is so, the comparatively low yield of amino-acids in such hydrolyses receives an explanation. The reaction is instantaneous between glycine and xylose or arabinose, rapid in the case of galactose and mannose, slow with lactose and maltose, whilst several hours elapse before it occurs in the case of sucrose. Of the common amino-acids, alanine is the most activ

W. O. W.

**The Action of Moist Sulphur on Cholic Acid and Taurine.** J. A. A. AUZIES (*Rev. gen. chim. pure appl.*, 1911, 14, 278—280).—A study of the composition of the gall and bile of cattle and pigs, from which the author corroborates the results of Langheld (*Ab-tr.*, 1908, ii, 211).

Cholic acid,  $\text{OH}\cdot\text{NMe}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , is prepared by mixing calcium chloroacetate (1.92 parts) with trimethylamine (1.18 parts) and heating the *chloride of calcium trimethylammoniumacetate* so obtained with milk of lime at 120—150°.

Taurine is prepared on an industrial scale as follows: Acetaldehyde is heated at 140° with chlorosulphonic acid,



the product converted into its calcium salt,  $(\text{CHO}\cdot\text{CH}_2\cdot\text{SO}_3)_2\text{Ca}$ , which by treatment with ammonium hydroxide yields the aldehyde ammonia,  $[\text{NH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{SO}_3]_2\text{Ca}$ , this loses water (2 mols.) on heating, and is converted into the imine,  $(\text{NH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{SO}_3)_2\text{Ca}$ , which after reduction to the corresponding amine and elimination of calcium with sulphuric acid furnishes the required taurine.

F. M. G. M.

**Preparation of Bromoacylisocarbamide Ethers.** FARBEN-FABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 240353).—When isocarbamide ethers of the general formula  $\text{NH}_2\cdot\text{C}(\text{OR})\cdot\text{NH}$  (R = alkyl or alkylaryl) are treated with bromodiethylacetyl halides, they yield bromo- $\alpha$ -ethylbutyrylisocarbamide ethers, which are of therapeutic value.

*Bromo- $\alpha$ -ethylbutyrylisocarbamide methyl ether*, colourless crystals, m. p. 72°, was obtained by boiling bromo- $\alpha$ -ethylbutyryl bromide with

methyl isocarbamide hydrochloride (Abstr., 1900, i, 340) in aqueous solution, cooling, and rendering alkaline when the product separated.

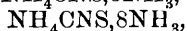
F. M. G. M.

**Specific Rotatory Power of Glutamine. Ammonium Glutamate.** ERNST SCHULZE and GEORG TRIER (*Ber.*, 1912, 45, 257—262).—Supposed pure preparations of glutamine obtained from different plant preparations by precipitation with mercuric nitrate and continued crystallisation show  $[\alpha]_D$  varying from  $+5.4^\circ$  to  $8.9^\circ$ . By purification of the copper salt, these preparations all yield glutamine of constant rotatory power,  $[\alpha]_D +6^\circ$  to  $7^\circ$ . The higher values are due to the presence of traces of glutamic acid, which, acting as an acid, increases the rotatory power of glutamine.

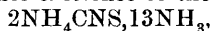
Glutamic acid forms a monobasic ammonium salt,  $[\alpha]_D -3.6^\circ$ , which begins to lose ammonia when kept over concentrated sulphuric acid, and readily loses ammonia when evaporated in aqueous solution. Since glutamine when boiled in aqueous solution is to some extent hydrolysed to the ammonium salt, the presence of glutamic acid is explained.

E. F. A.

**Action of Ammonia on Ammonium Thiocyanate.** WALTER P. BRADLEY and W. B. ALEXANDER (*J. Amer. Chem. Soc.*, 1912, 34, 15—24).—Comparatively few substances become deliquescent on exposure to dry ammonia, and of these ammonium thiocyanate appears to possess the property in the highest degree, the deliquescence continuing up to a temperature of  $88^\circ$ . The absorptive power of the salt was determined at various temperatures between  $0^\circ$  and  $100^\circ$ . At  $0^\circ$ , the product contained 43.10% of ammonia; at  $25^\circ$ , 31.16%; at  $50^\circ$ , 19.40%; at  $75^\circ$ , 6.17%, whilst at  $100^\circ$  none was absorbed. F.p. determinations were made of solutions of ammonium thiocyanate in ammonia, the concentrations ranging from 0% to 100% of the latter. On plotting the results, it is shown that there are certainly three, and probably five, compounds formed. The former are:  $\text{NH}_4\text{CNS}, \text{NH}_3$ , m. p.  $-16^\circ$  (metastable);  $\text{NH}_4\text{CNS}, 3\text{NH}_3$ , m. p.  $-38^\circ$ ; and



m. p. about  $-87^\circ$ . The other two compounds are  $\text{NH}_4\text{CNS}, 6\text{NH}_3$ , m. p.  $-76^\circ$ , and  $\text{NH}_4\text{CNS}, 7\text{NH}_3$ , m. p.  $-84^\circ$ . Indications were also obtained of the possible existence of the compound



m. p. about  $-80^\circ$ . The lowest eutectic point was in the vicinity of  $-96^\circ$ .

E. G.

**The Composition of Prussian Blue.** P. WORINGER (*Chem. Zeit.*, 1912, 36, 78).—Evidence for regarding Prussian blue as a ferrocyanide has been given by Hofmann, Heine, and Höchtlen (Abstr., 1905, i, 38). On the other hand, when a ferric salt is precipitated with an excess of potassium ferrocyanide, the filtrate contains considerable quantities of potassium ferricyanide, formed by the reactions:  $\text{FeCl}_3 + \text{K}_4\text{Fe}(\text{CN})_6 = \text{FeCl}_2 + \text{K}_3\text{Fe}(\text{CN})_6 + \text{KCl} = \text{KFeFe}(\text{CN})_6 + 3\text{KCl}$ , and in the filtrate,  $3\text{KFeFe}(\text{CN})_6 = \text{Fe}_3[\text{Fe}(\text{CN})_6]_2 + \text{K}_3\text{Fe}(\text{CN})_6$ .

If ammonium carbonate solution is added to a boiling suspension of

Prussian blue, ammonium ferricyanide as well as ferrocyanide is found in the filtrate, and the iron remains as  $\text{Fe}_3\text{O}_4$ . This is considered to prove that Prussian blue is a ferricyanide. C. H. D.

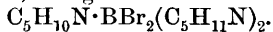
**Organic Boro-Nitrogen Compounds.** ARDEN RICHARD JOHNSON (*J. Physical. Chem.*, 1912, 16, 1—28).—A series of compounds of boron tribromide with amines and nitriles was prepared in which boron as well as nitrogen is supposed to function as quinquevalent. Various additive compounds of boron trichloride, tribromide, and tri-iodide with ammonia are known, in which the proportion of ammonia varies from 1.5 to 15 molecules per molecule of boron compound.

Boron tribromide reacts with amines and nitriles with liberation of heat, and additive compounds of the type  $(\text{X})\text{N}:\text{BBr}_3$  are apparently formed in most cases. The nitriles and tertiary amines, except trimethylamine, give fairly stable crystalline products. Compounds of this type were also isolated from the primary *iso*amylamine and aniline. The compounds of the aliphatic secondary amines immediately lose hydrogen bromide, amorphous products of the type  $\text{R}_2\text{N}\cdot\text{BBr}_2$  resulting. Similarly, the product from ethylamine has the constitution  $\text{NHEt}\cdot\text{BBr}_2$ . With methylamine, the reaction apparently goes a stage further, and the product isolated has the formula  $\text{B}(\text{NHMe})_2\cdot\text{Br}$ . Piperidine and diphenylamine give compounds of the type  $(\text{YNH})_3\cdot\text{BBr}_3$ .

The compounds were prepared by passing the dry gaseous amines into a carbon tetrachloride solution of boron tribromide or by adding the bromide solution from a burette to the anhydrous amine or nitrile dissolved in carbon tetrachloride. In some cases an oily insoluble product containing excess of amine was first formed, and afterwards converted into a solid product by further addition of bromide.

The substances,  $(\text{NHMe})_2\cdot\text{BBr}$ ,  $\text{NHEt}\cdot\text{BBr}_2$ ,  $\text{NH}_2(\text{C}_5\text{H}_{11})\cdot\text{BBr}_3$ ,  $\text{NH}_2\text{Ph}\cdot\text{BBr}_3$ ,  $\text{NMe}_2\cdot\text{BBr}_2$ , and  $\text{NPr}_2\cdot\text{BBr}_2$ , are white, amorphous solids sparingly soluble in carbon tetrachloride. The mono*iso*amylamine compound, which may be handled in the air, turns yellow in sunlight, but does not dissociate very rapidly below  $40^\circ$ . When heated up quickly, it appears to melt and decompose simultaneously. It burns furiously, colouring the flame intensely green.

The *iso*amyl compound,  $\text{N}(\text{C}_5\text{H}_{11})_2\cdot\text{BBr}_2$ , may be crystallised from carbon tetrachloride. It dissolves in water, giving di*iso*amylamine hydrobromide and boric acid. The substance,  $3\text{C}_5\text{H}_{11}\text{N}\cdot\text{BBr}_3$ , is formed from piperidine in a violent reaction, which must be moderated by careful cooling. It has been obtained as a pale yellow precipitate, which readily loses hydrogen bromide when exposed over sodium hydroxide in a desiccator, being converted into the substance,



The latter is a stable solid giving greenish-yellow, fluorescing solutions in organic solvents. The substance,  $3\text{NHPh}_2\cdot\text{BBr}_3$ , is a white precipitate comparatively stable in air.

Trimethylamine reacts with boron tribromide with development of heat. White fumes were given off, and no solid compound could be

isolated. The *substance*,  $\text{NEt}_3 \cdot \text{BBr}_3$ , crystallises from carbon tetrachloride in long, slender prisms. The *substance*,  $\text{NMe}_2\text{Ph} \cdot \text{BBr}_3$ , forms a camphor-like, crystalline, hygroscopic mass. When exposed in a desiccator over sodium hydroxide, the elements of methyl bromide are removed, and the *substance*,  $\text{NMePh} \cdot \text{BBr}_2$ , remains. The latter is very rapidly decomposed by hot alkali with precipitation of boron nitride,  $\text{BN}$ . The *pyridine* compound,  $\text{C}_5\text{H}_5\text{N} \cdot \text{BBr}_3$ , is a snow-white, amorphous mass, fairly stable in the air, but tending to dissociate with rising temperature; at  $120^\circ$  it turns brown and sinters. When placed in a desiccator over sodium hydroxide, the elements of hydrogen bromide are removed, and the *substance*,  $\text{C}_5\text{H}_4\text{N} \cdot \text{BBr}_2$ , remains as a stable powder. It is suggested that boron is probably combined with the carbon as well as the nitrogen of the pyridine nucleus in this compound. The white *substance*,  $\text{C}_9\text{H}_7\text{N} \cdot \text{BBr}_3$ , formed from quinoline is more stable than the pyridine compound, and scarcely fumes in the air.

The *substances*,  $\text{CNMe} \cdot \text{BBr}_3$ ,  $\text{CNEt} \cdot \text{BBr}_3$ , and  $\text{CNPh} \cdot \text{BBr}_3$ , are obtained from their carbon tetrachloride solutions as white crystals. The methyl compound dissociates very rapidly at  $30^\circ$ , and the ethyl compound is slightly more stable. The *substance*,  $\text{CH}_2\text{Ph} \cdot \text{CN} \cdot \text{BBr}_3$ , which is difficult to purify by crystallisation, was obtained as a slightly yellow, crystalline mass. It melts with some decomposition.

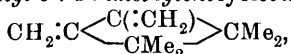
Most of the above boron tribromide compounds decompose or sublime without melting. Some of the nitrile compounds may be heated to nearly  $200^\circ$  before decomposing. Of the amine products those of pyridine and quinoline are the most stable. The products of decomposition by heat probably contain boron nitride in most cases. The *substances* described are violently decomposed by water, absolute alcohol, acetaldehyde, and acetic acid, the products containing boric acid accompanied by hydrogen bromide, ethyl bromide, bromoacetaldehyde, and acetyl bromide respectively. Acetone, the esters, and ether have a less violent action, and crystalline products containing boron and carbon have been obtained. Hydrocarbons usually exert no solvent action on boron bromide compounds, but with prolonged contact in sunlight the hydrocarbon assumes a red to brown tint. A slow decomposition also occurs in contact with chloroform and bromoform. Carbon tetrachloride and tetrabromide, in which the *substances* are but slightly soluble, have no chemical action on them. R. J. C.

**Preparation of Methylcyclopentane.** S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1611—1613).—The preparation of methylcyclopentane by the action of fuming hydriodic acid at  $100$ — $105^\circ$  on cyclopentanylcannabinol (compare Zelinsky, *Abstr.*, 1908, i, 727) and reduction of the iodide thus obtained by means of zinc dust in aqueous alcoholic solution gives a product containing cyclohexane. Hence, when heated with hydriodic acid, the cyclopentanylcannabinol undergoes partial isomerisation into a six-carbon atom ring compound. Similar cases of the ready isomerisation of substituted cyclic carbinols have been observed by Demjanoff (*Abstr.*, 1910, i, 838) and by Kijner (*Abstr.*, 1905, i, 772; 1908, i, 530, 864; 1911, i, 42). T. H. P.

**Polymerisation of Diethylene Hydrocarbons. Polymerisation of *as*-Dimethylallene.** IV. SERGIUS V. LEBEDEF (J. Russ. Phys. Chem. Soc., 1911, 43, 1735—1739).—For an unsymmetrical disubstituted allene, six dimerides are possible, three of each of the

types:  $\begin{array}{c} \text{C}:\text{C}:\text{C} \\ | \quad | \\ \text{C}:\text{C}:\text{C} \end{array}$  and  $\begin{array}{c} \text{C}=\text{C} \\ | \quad | \\ \text{C}=\text{C} \end{array}$  Two of the compounds of the former of these types have been obtained (Abstr., 1911, i, 774), failure to isolate the third being due probably to its high velocity of polymerisation. The author's results indicate that the velocity of polymerisation of hydrocarbons with conjugated systems of double linkings,  $:\text{C}:\text{C}:\text{C}:\text{C}:$ , increases with diminution of the loading of the extreme carbon atoms and with increase of that of the intermediate ones. Hence, of the three dimerides of *as*-dimethylallene of the first type, 1:2-diisopropenylcyclobutane should be the most stable, 1:1:2:2-tetramethyl-3:4-dimethylenecyclobutane should occupy an intermediate position in this respect (*loc. cit.*), and the third, 3:3-dimethyl-2-methylene-1-isopropenylcyclobutane, should readily polymerise. By the choice of suitable conditions, the remaining dimeride (the second) has now been obtained.

1:1:2:2-Tetramethyl-3:4-dimethylenecyclobutane,



has b. p. 140—141°/760 mm., 66—67°/55 mm.,  $D_4^{20}$  0.7927,  $n_D^{20}$  1.46063,  $n_C^{20}$  1.45701,  $n_F^{20}$  1.46988,  $n_G^{20}$  1.47807, and yields tetramethylsuccinic acid when treated with ozone.

The physical properties of these three dimerides, some of which were given wrongly in the previous paper, are as follows:

	B. p.	$D_4^{20}$ .	Optical exaltation.
1:2-Disopropenylcyclobutane .....	179—181°	0.8422	2.34
1:1-Dimethyl-2-methylene-3-isopropenylcyclobutane	149—150	0.7982	2.09
1:1:2:2-Tetramethyl-3:4-dimethylenecyclobutane	140—141	0.7927	1.81

As regards the non-formation of dimerides of the second of the two types given above, it is pointed out that the relations of unsaturated compounds to reactions of combination indicate clearly that the tensions of the affinities in the molecule are distributed unequally. For the complex  $:\text{C}:\text{C}:\text{C}:$  they are directed the most strongly towards the middle carbon atom, so that combination of the two molecules takes place first at this place, there being possible the two annexed arrangements.

$\begin{array}{c} \text{CH}_2:\text{C}^2:\text{C}^3:\text{CMe}_2 \\ \vdots \\ \text{CH}_2:\text{C}^1:\text{C}^2:\text{CMe}_2 \end{array}$  and  $\begin{array}{c} \text{CH}_2=\text{C}^1:\text{C}^2:\text{CMe}_2 \\ \vdots \\ \text{CMe}_2:\text{C}^3:\text{CH}_2 \end{array}$  With the former of these arrangements, further saturation of the free affinities gives the two dimerides, 1:2-diisopropenylcyclobutane and 1:1:2:2-tetramethyl-3:4-dimethylenecyclobutane, whilst with the latter, owing to its symmetrical character, only one dimeride, namely, 1:1-dimethyl-2-methylene-3-isopropenylcyclobutane, is obtained. This scheme hence excludes the possibility of formation of dimerides of the second type.

T. H. P.

**Chemical Action of Light. XXII. Autoxidations. I.** GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1912, 45, 38—43; *Atti R. Accad. Lincei*, 1911, [v], 20, ii, 673—677).—Aromatic hydrocarbons on prolonged exposure to the action of light in presence of water in an atmosphere of oxygen in sealed vessels are partly oxidised to the corresponding carboxylic acids; small quantities of the corresponding aldehydes and of formic acid are also formed.

Thus toluene yields benzoic acid and benzaldehyde; *p*-xylene gives *p*-toluic acid, m. p. 181°, and a little terephthalic acid, as well as traces of the aldehyde; *m*-xylene forms *m*-toluic acid, m. p. 111°, and *isophthalic* acid; *o*-xylene forms *o*-toluic acid, m. p. 107—108°. *p*-Cymene yields some aldehyde, *p*-cuminic acid, m. p. 119°, *p*-propenylbenzoic acid, m. p. 165°, and  $\alpha$ -hydroxy-*p*-cuminic acid, m. p. 156°.

In the dark the hydrocarbons are unchanged. *p*- and *o*-Nitrotoluene, also phenanthrene, are practically unaltered after prolonged exposure to light. E. F. A.

[Orientation in the Benzene Nucleus.] JULIUS OBERMILLER (*Ber.*, 1912, 45, 165—167. Compare Abstr., 1911, i, 960).—The author upholds his claim of priority over Holleman (this vol., i, 20), and maintains that there is no essential difference between their views concerning substitution in the benzene nucleus. F. B.

**Benzene Hexachlorides and their Decomposition into Trichlorobenzenes.** T. VAN DER LINDEN (*Ber.*, 1912, 45, 231—247).— $\alpha$ - and  $\beta$ -Benzene hexachlorides, prepared by the action of chlorine on benzene in sunlight, form a eutectic solidifying at 155.5°. This point was mistaken for the melting point by Matthews (*Trans.*, 1891, 59, 166). In addition to the  $\alpha$ - and  $\beta$ -isomerides, two new benzene hexachlorides are formed in the reaction: all four compounds are stereoisomerides. The  $\gamma$ -isomeride crystallises in needles and lozenge-shaped forms, m. p. 112—113°; the  $\delta$ -isomeride forms slender, lustrous, twin platelets, m. p. 129—132°.

On decomposition of  $\alpha$ -benzene hexachloride with alkali, a mixture of 1:2:4-, 1:2:3-, and 1:3:5-trichlorobenzenes is obtained. The temperature at which decomposition is effected has no influence on the relative proportions of these, or is this proportion altered on replacing potassium hydroxide by sodium hydroxide or substituting methyl alcohol for ethyl alcohol. The proportion is, however, altered by the use of pyridine or quinoline, more of the 1:2:4- and less of the 1:2:3-isomeride being obtained, the amount of the 1:3:5-trichlorobenzene remaining constant.

$\beta$ -Benzene hexachloride, when decomposed by potassium hydroxide in ethyl alcohol, yields the same three trichlorobenzenes as the  $\alpha$ -isomeride, but in different proportions, which are very similar to those obtained on decomposing the  $\alpha$ -isomeride with pyridine. Pyridine, however, has hardly any action on the  $\beta$ -compound.

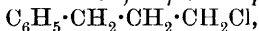
$\gamma$ -Benzene hexachloride yields the three trichlorobenzenes in slightly different proportions than either of the  $\alpha$ - or  $\beta$ -isomerides.

It was not found possible to eliminate the chlorine in stages, neither

could hydrogen chloride be split off by means of aluminium or ferric chlorides.

The fact that a considerable proportion of 1 : 2 : 3-trichlorobenzene is formed indicates that the elimination of hydrogen chloride is not entirely between two neighbouring carbon atoms. E. F. A.

**Preparation of  $\gamma$ -Chloropropylbenzene and its Homologues.**  
EMANUEL MERCK (D.R.-P. 239076).— $\gamma$ -Chloropropylbenzene,



a colourless oil with penetrating odour, b. p. 219—220° or 110°/21 mm., is obtained in 78% yield from  $\gamma$ -chloropropylaniline by diazotisation and subsequent reduction with stannous chloride in alkaline solution. F. M. G. M.

**2-Chloro-3 : 5-dinitrotoluene.** WALTHER BORSCHKE and ANNA FIEDLER (*Ber.*, 1911, 45, 270—273).—2-Chloro-3 : 5-dinitrotoluene is formed in only small quantity by nitrating *o*-chlorotoluene, and does not constitute the main product of the reaction as stated by Nietzki and Rehe (*Abstr.*, 1893, i, 15). It crystallises from alcohol in stout, yellow rhombs, m. p. 63—64°; Nietzki and Rehe give 45°. It is best prepared by heating 2-chloro-3-nitrotoluene or 2-chloro-5-nitrotoluene with a mixture of equal parts of sulphuric and fuming nitric acids for two hours on the water-bath.

The above-mentioned mononitro-compounds are conveniently prepared by nitrating aceto-*o*-toluidide and hydrolysing the product with hydrochloric acid; the resulting mixture of 3-nitro- and 5-nitro-*o*-toluidine is separated by steam distillation, and the amino-group replaced by chlorine according to Ullmann's method.

4-Chloro-3 : 5-dinitrotoluene has m. p. 116—117°, and not 48° as given by Hönig (*Abstr.*, 1887, 1034). F. B.

**Conversion of the Bromonitrobenzenes into the Corresponding Dichlorobenzenes by Phosphorus Pentachloride.** JULIUS SCHMIDT and HANS WAGNER (*Annalen*, 1912, 387, 164—165).—When heated with phosphorus pentachloride in a sealed tube at 180° for six hours, *o*-, *m*-, and *p*-bromonitrobenzenes are converted more or less smoothly into *o*-, *m*-, and *p*-dichlorobenzenes. C. S.

**Action of Nitric Acid on cyclopentane and Methylcyclopentane.** S. S. NAMETKIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1603—1611. Compare *Abstr.*, 1910, i, 830).—Nitrocyclopentane,  $\text{C}_5\text{H}_9\cdot\text{NO}_2$ , obtained by the interaction of aluminium nitrate and cyclopentane in a sealed tube, is a colourless liquid, b. p. 90—91°/40 mm.,  $D_4^{23}$  1.0776,  $n_D^{23}$  1.4518, with the characteristic odour of secondary nitro-compounds. On oxidation with nitric acid, it yields glutaric acid, which is also formed when cyclopentane itself is oxidised.

Nitration of methylcyclopentane by means of nitric acid yields 1-nitro-1-methylcyclopentane and 2-nitro-1-methylcyclopentane, b. p. 98—99°/40 mm.,  $D_4^{22}$  1.0381,  $n_D^{22}$  1.4488 (compare Markownikoff, *Abstr.*, 1899, i, 799).

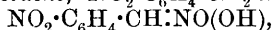
Thus, in the secondary nitro-product of methylcyclopentane the

nitro-group occupies the  $\alpha$ -position, whilst in that of methylcyclohexane it occupies the  $\beta$ -position.

The above two nitro-compounds formed by the nitration of methylcyclopentane are accompanied by succinic and  $\alpha$ -methylglutaric acids; probable schemes are given for the formation of these two acids.

T. H. P.

**The Preparation of  $\omega$ -2-Dinitrotoluene, its Homologues and Derivatives.** SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (D.R.-P. 239953).— $\omega$ -2-Dinitrotoluene,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{NO}_2$  or



m. p.  $67^\circ$ , is readily prepared in 70% yield by heating *o*-nitrotoluene (2 parts) at  $110$ – $120^\circ$  during eight hours with the gradual addition of 70% nitric acid (1 part), *o*-nitrobenzaldehyde and *o*-nitrobenzoic acid being simultaneously produced as by-products. The following compounds are described:  $\omega$ -4-dinitrotoluene, m. p.  $91^\circ$ ; 4-chloro- $\omega$ -2-dinitrotoluene, m. p.  $112^\circ$ ; 4-bromo- $\omega$ -2-dinitrotoluene, m. p.  $113.5^\circ$ ; 6-chloro- $\omega$ -2-dinitrotoluene, m. p.  $82^\circ$ ; whilst *o*-nitro-*m*-xylene yields a mixture of  $\omega$ -6-dinitro-*m*-xylene, m. p.  $86.5^\circ$ , and  $\omega$ -4-dinitro-*m*-xylene, m. p.  $64^\circ$ .

F. M. G. M.

**Preparation of Chloroalkylarylsulphonic Acids and of Chloroalkylarylcarboxylic Acids.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 239311).— $\omega$ -Chlorotoluene-*p*-sulphonic acid is readily prepared by slowly dropping water (18 parts) into  $\omega$ -chlorotoluene-*p*-sulphonyl chloride (225 parts) dissolved in 80 parts of hot alcohol. The sodium salt,  $\text{SO}_3\text{Na} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2\text{Cl}$ , is sparingly soluble in water.

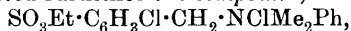
$\omega$ -Dichlorotoluene-*m*-sulphonyl chloride, a crystalline powder insoluble in water and prepared by the action of phosphorus pentachloride on benzaldehyde-*m*-sulphonic acid, is converted by the foregoing treatment into  $\omega$ -dichlorotoluene-*m*-sulphonic acid; the sodium salt is moderately soluble in water.

$\omega$ -Chloro-*p*-toluoyl chloride, a colourless oil, b. p.  $150$ – $155^\circ$  (prepared by chlorinating a hot solution of *p*-toluoyl chloride), when dissolved and maintained at  $0$ – $5^\circ$  in 98% sulphuric acid until the evolution of hydrogen chloride ceases, furnishes  $\omega$ -chloro-*p*-toluic acid, m. p.  $190$ – $192^\circ$  (decomp.), and insoluble in water.

F. M. G. M.

**Preparation of Aromatic Sulphonyl Ammonium Compounds.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 239763).—When sodium  $\omega$ -chlorotoluene-*p*-sulphonate is heated with dimethylaniline at  $70^\circ$ , it yields the compound,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \\ \text{SO}_3 \end{smallmatrix} \text{NMePh}$ , a colourless powder.

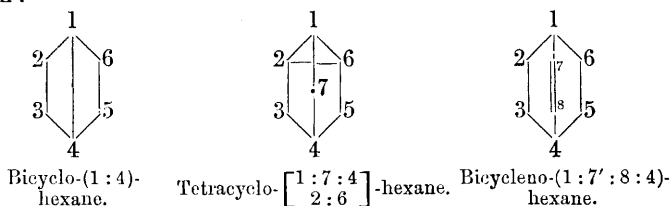
Ethyl  $\omega$ -2-dichlorotoluene-*p*-sulphonate, a colourless oil prepared by hydrolysing the corresponding sulphonyl chloride with sodium ethoxide, when similarly treated furnishes the compound,



in colourless, hygroscopic crystals readily soluble in water and alcohol.

F. M. G. M.

**System of Nomenclature for "Bridged Rings."** VICTOR GRIGNARD (*Bull. Soc. chim.*, 1912, [iv], 11, 124—129).—The author proposes to avoid the inconveniences of von Baeyer's system of nomenclature for such structures by (1) selecting for the nucleus of the name that of the fundamental ring, which is immediately apparent, traversed by one or more bridges; (2) numbering the atoms in the bridges, after those of the fundamental ring, so that the bridges appear to be merely particular substituents attached at two points, and identified in the name by their "characteristic." This characteristic consists of the numbers of all the atoms, which appear in the "bridge," and the highest number in it indicates the total number of carbon atoms in the structure. The number of constituent rings, apart from the fundamental ring, is always twice the number of bridges, and is indicated by prefixes, bicyclo, tetracyclo, etc. Where the bridge contains an ethylenic linking, these prefixes become bicycleno and tetracycleno respectively, and the number of the atom at which the double linking begins is accented in the "characteristic." The following examples of the application of the system may be given:



T. A. H.

**Compounds of Antimony Trichloride and Tribromide with Polynuclear Benzene Hydrocarbons.** BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1805—1820).—Diphenyl and diphenylmethane form with antimony trihalides molecular compounds containing 2 mols. of antimony salt to 1 mol. of hydrocarbon:  $2\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{Ph}$ , m. p.  $71^\circ$ ;  $2\text{SbBr}_3 \cdot \text{C}_6\text{H}_5\text{Ph}$ ,  $60.5^\circ$ ;  $2\text{SbI}_3 \cdot \text{C}_6\text{H}_5\text{Ph}$ ,  $161^\circ$ ;  $2\text{SbCl}_3 \cdot \text{CH}_2\text{Ph}_2$ , m. p.  $100^\circ$ ;  $2\text{SbBr}_3 \cdot \text{CH}_2\text{Ph}_2$ , m. p.  $90^\circ$ . Each concentration-temperature diagram exhibits two eutectic points, as follows:

System.	M. p. Hydro- carbon.	1st eutectic point.		2nd eutectic point.		M. p. $\text{SbX}_3$ .
		Tempera- ture.	n.	Tempera- ture.	n.	
$\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{Ph}$	$70.5^\circ$	$50^\circ$	2.2	$57^\circ$	0.18	$73^\circ$
$\text{SbBr}_3 \cdot \text{C}_6\text{H}_5\text{Ph}$	$70.5$	47	1.75	$60.5$	0.52	94
$\text{SbI}_3 \cdot \text{C}_6\text{H}_5\text{Ph}$	$70.5$	68	89.4	160	0.2	166
$\text{SbCl}_3 \cdot \text{CH}_2\text{Ph}_2$	26	22.5	15.6	67	0.6	73
$\text{SbBr}_3 \cdot \text{CH}_2\text{Ph}_2$	26	22.5	14.6	82	0.18	94

With antimony trichloride and tri-iodide, diphenyl gives stable compounds, which melt without decomposing, whilst with antimony tribromide it yields a compound with a melting point in the region of unstable equilibrium.

Triphenylmethane forms no molecular compound with antimony tribromide, but with the trichloride it gives the compound  $\text{SbCl}_3 \cdot \text{CHPh}_3$ , melting at  $49.5^\circ$  in the region of unstable equilibrium. The diagram consists of three branches, the first eutectic point, corresponding with  $\text{SbCl}_3 \cdot 0.93\text{CHPh}_3$ , lying at  $49^\circ$ , and the second with  $\text{SbCl}_3 \cdot 0.37\text{CHPh}_3$ , at  $35^\circ$ .

The diminished capacity to form compounds with antimony trihalides observed in the case of triphenylmethane may be related to the fact that this hydrocarbon differs considerably in its chemical properties from diphenylmethane; thus, it forms molecular compounds with benzene and other hydrocarbons, and yields metallic derivatives, etc.

Colorations are often observed on fusing these polynuclear hydrocarbons with antimony trihalides (compare Watson Smith, *Abstr.*, 1879, 831). T. H. P.

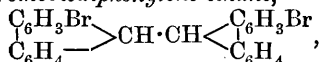
**Halogen Derivatives of Fluorene and Bisdiphenylene-ethylene.** JULIUS SCHMIDT and HANS WAGNER (*Annalen*, 1912, 387, 147—164).—The method of converting 9:9-dichlorofluorene into bisdiphenylene-ethylene by heating with copper powder in benzene (*Abstr.*, 1910, i, 550) has been applied to other halogenated fluorene

derivatives; thus 9:9-dichloro-2-bromofluorene,  $\begin{array}{c} \text{C}_6\text{H}_3\text{Br} \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{---} \text{CCl}_2$ , m. p.

$178^\circ$ , colourless needles, obtained from 2-bromofluorenone and phosphorus pentachloride at  $160\text{--}180^\circ$ , is converted into 2:2'-dibromo-

bisdiphenylene-ethylene,  $\begin{array}{c} \text{C}_6\text{H}_3\text{Br} \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{---} \text{C}:\text{C} \begin{array}{c} \text{C}_6\text{H}_3\text{Br} \\ | \\ \text{C}_6\text{H}_4 \end{array}$ , m. p.  $312^\circ$ , red crystals,

or, by sublimation, yellowish-green needles. This substance is converted into 2:2'-dibromobisdiphenylene-ethane,



m. p.  $272^\circ$ , colourless needles, by heating its ethereal solution with platinum black for eight hours in a current of hydrogen, and reacts additively with chlorine in chloroform and with bromine in carbon disulphide in sunlight to form respectively 9:9'-dichloro-2:2'-dibromo-

bisdiphenylene-ethane,  $\begin{array}{c} \text{C}_6\text{H}_3\text{Br} \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{---} \text{CCl} \cdot \text{CCl} \begin{array}{c} \text{C}_6\text{H}_3\text{Br} \\ | \\ \text{C}_6\text{H}_4 \end{array}$ , m. p.  $268^\circ$ , colour-

less crystals, and 2:2':9:9'-tetrabromobisdiphenylene-ethane, m. p.  $258^\circ$ ; the latter in benzene reacts with silver acetate to form the

diacetate,  $\begin{array}{c} \text{C}_6\text{H}_3\text{Br} \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{---} \text{C}(\text{OAc}) \cdot \text{C}(\text{OAc}) \begin{array}{c} \text{C}_6\text{H}_3\text{Br} \\ | \\ \text{C}_6\text{H}_4 \end{array}$ , m. p.  $285^\circ$ .

9:9-Dichloro-2:7-dibromofluorene,  $\begin{array}{c} \text{C}_6\text{H}_3\text{Br} \\ | \\ \text{C}_6\text{H}_3\text{Br} \end{array} \text{---} \text{CCl}_2$ , m. p.  $260^\circ$ , colour-

less needles, obtained from 2:7-dibromofluorenone and phosphorus pentachloride at  $210\text{--}220^\circ$ , is converted by copper into 2:2':7:7'-tetra-

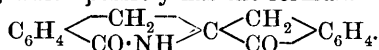
bromobisdiphenylene-ethylene,  $\begin{array}{c} \text{C}_6\text{H}_3\text{Br} \\ | \\ \text{C}_6\text{H}_3\text{Br} \end{array} \text{---} \text{C}:\text{C} \begin{array}{c} \text{C}_6\text{H}_3\text{Br} \\ | \\ \text{C}_6\text{H}_3\text{Br} \end{array}$ , m. p.  $364^\circ$ , red

crystals, from which the following substances have been prepared: 9:9'-dichloro-2:2':7:7'-tetrabromobisdiphenylene-ethane, m. p.  $298\text{--}299^\circ$ ,

colourless needles; 2:2':7:7':9:9'-hexabromobisdiphenylene-ethane, m. p. 310°, colourless crystals; 2:2':7:7'-tetrabromobisdiphenylene-ethane, m. p. 284°, colourless leaflets. The disappearance of colour coincidentally with that of the ethylenic linking is noteworthy.

When heated in a sealed tube at 180° for six hours, fluorenone and phosphorus pentachloride yield 9:9'-dichlorobisdiphenylene-ethane, m. p. 235—236°, 2:7:9:9-tetrachlorofluorene, m. p. 215°, and a little 2:7-dichlorofluorenone (?), m. p. 187—189°. 2:7-Dichlorofluorenone, m. p. 185—186° (which appears to be identical with Goldschmiedt and Schranzhofer's  $\beta$ -dichlorofluorenone), is obtained best by heating 2:7-dinitrofluorenone with phosphorus pentachloride in a sealed tube at 170—180°, and boiling the resulting 2:7:9:9-tetrachlorofluorene with water; it forms an *oxime*, decomp. 243°, *phenylhydrazone*, decomp. 186—187°, and *semicarbazone*, decomp. 345°, and is converted by copper into 2:2':7:7'-tetrachlorobisdiphenylene-ethylene, a red substance, m. p. above 380°. C. S.

**The Preparation and Reactions of Bis- $\alpha$ -hydrindone-(2:2)-spiran.** HERMANN LEUCHS and DAN RADULESCU (*Ber.*, 1912, 45, 189—201).—Dibenzylmalonic acid, the preparation of which is fully described, is converted, by means of phosphorus pentachloride, into *dibenzylmalonyl chloride*, b. p. 216—218°/17 mm., 232—235°/32 mm., m. p. 68—69°. When dissolved in ether and treated with ammonia and aniline respectively, this yields the corresponding *amide* (m. p. 198—199°) and *anilide* (m. p. 196—197°). Boiling alcohol converts it into the *ester*. During distillation of the chloride under diminished pressure, as also when it is heated at 250—270° for some time, hydrogen chloride is evolved, and small quantities of *bis- $\alpha$ -hydrindone-(2:2)-spiran* formed. The latter is best prepared by distilling the chloride under diminished pressure in the presence of 2% of aluminium chloride. It has b. p. 255—257°/12 mm. (corr.), m. p. 174°. Phenylhydrazine converts it into *bis- $\alpha$ -hydrindone-(2:2)-spiranbisphenylhydrazone*, colourless prisms, m. p. 200—201° (decomp.). When treated with hydroxylamine, a *substance*,  $C_{17}H_{13}O_2N$ , is formed (m. p. 214—215°), which possibly has the formula

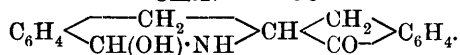


Under the action of sodium hydroxide, *bis- $\alpha$ -hydrindone-(2:2)-spiran* readily yields the *sodium* salt of a strong, monobasic acid, which is stable towards excess of alkali. The free *acid* has m. p. 140—142°, and, when heated at 220°, evolves water vapour with the reformation of spiran. The composition of the acid is probably expressed by the formula  $C_6H_4 \begin{array}{c} \diagup CH_2 \diagdown \\ \diagdown CO_2H \diagup \end{array} HC \begin{array}{c} \diagup CH_2 \diagdown \\ \diagdown CO \diagup \end{array} C_6H_4.$

It can be resolved into optically active forms by crystallisation of the brucine salt from acetone. Attempts were made to prepare the *methyl* ester of the acid by the action of methyl iodide on the *silver* salt. The ester could not be obtained in the crystalline state. When distilled under diminished pressure, it decomposed with the regeneration of spiran.

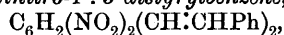
*Bis- $\alpha$ -hydrindone-(2:2)-spiran*, when treated with alcoholic ammonia,

forms two compounds,  $C_{17}H_{13}ON$ , m. p. 246—248° (decomp.), and  $C_{17}H_{15}O_2N$ . The latter, when rapidly heated, melts at 124—128° (decomp.), and is readily transformed into the former by heating it above its m. p., or by treating it with concentrated hydrochloric acid. These substances are probably not the nitrile and amide of the above-described acid, since neither evolves ammonia when treated with potassium hydroxide. The following formulæ are provisionally proposed for them:  $C_6H_4 \begin{array}{c} \text{---CH}_2\text{---} \\ \text{CH:N} \end{array} > C \begin{array}{c} \text{---CH}_2\text{---} \\ \text{CO} \end{array} > C_6H_4$  and

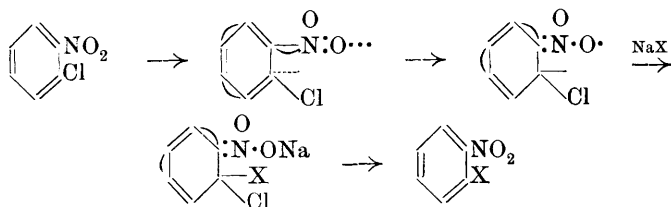


*Anhydrosis-α-hydrindonespiran*, obtained in small quantity by the distillation of dibenzylmalonyl chloride under ordinary pressure in the presence of 4% of aluminium chloride, crystallises from glacial acetic acid in light red needles, m. p. 256—257°. H. W.

**Reactivity of Side-chains in Nuclear Nitrated Homologues of Benzene.** WALTHER BORSCHÉ (*Annalen*, 1912, 386, 351—373).—One of the halogen atoms is readily substituted, the other only with difficulty, when 1:3-dichloro-4:6-dinitrobenzene is warmed in ether with an excess of ethyl sodioacetoacetate. On the other hand, both methyl groups react readily when 4:6-dinitro-*m*-xylene and benzaldehyde (2 mols.) are heated at 190° with a little piperidine; the main product is 4:6-dinitro-1:3-distyrylbenzene,



m. p. 186°, yellow needles, very little 4:6-dinitro-3-methylstilbene,  $C_6H_2Me(NO_2)_2·CH:CHPh$ , m. p. 145°, being formed. Trinitromesitylene, dinitromesitylene, trinitro-*ψ*-cumene, and 2:4-dinitroethylbenzene do not react with benzaldehyde. 2:4:6-Trinitrotoluene yields trinitrostilbene (Ullmann and Gschwind, *Abstr.*, 1908, i, 622). 2:4:6-Trinitro-*m*-xylene, benzaldehyde, and a little piperidine, when heated in boiling amyl alcoholic solution, yield 2:4:6-trinitro-1:3-distyrylbenzene,  $C_{22}H_{15}O_6N_3$ , m. p. 147—148°, yellow needles. Corresponding substances,  $C_{24}H_{19}O_8N_3$ , m. p. 155°, and  $C_{22}H_{13}O_{10}N_5$ , m. p. 268° (decomp.), are obtained with anisaldehyde and *p*-nitrobenzaldehyde respectively. These condensations proceed most smoothly in the toluene series, less readily in the xylene series, and badly or not at all in the mesitylene series. The author is of opinion that in these nitrated methylbenzenes the distribution of the residual affinity of the benzene nucleus is such that, when only one methyl group is present, the influence of the residual affinity is concentrated on the carbon atom of this methyl group, its hydrogen atoms, therefore, becoming more mobile; as, however, the symmetry of the whole molecule is increased by the introduction of two and three methyl groups, the influence of the residual affinity is distributed between the methyl groups, with the result that their hydrogen atoms become less and less mobile. In the case of the chloronitrobenzenes, the elimination of the halogen atom is due, according to the author, not to any weakening of the union between it and the carbon atom, but rather to a striving of the molecule to assume an ortho- or para-quinonoid structure; the reagent is then held additively, the final product being obtained by the elimination of a halide; thus:



Ullmann and Gschwind (*loc. cit.*) have shown that the reactivity of the methyl group in 2:4-dinitrotoluene still persists when one of the nitro-groups is replaced by a carboxylic, sulphonic, or cyanogen group. The author finds, however, that in 6-nitro-4-cyano-*m*-xylene only one methyl group reacts with benzaldehyde and a little piperidine at 190—200°, giving a very poor yield of 6-nitro-4-cyano-3-methylstilbene (?),  $\text{NO}_2 \cdot \text{C}_6\text{H}_2\text{Me}(\text{CN}) \cdot \text{CH}:\text{CHPh}$ , m. p. 183—184°, yellow needles. 2:4-Dicyanotoluene does not react with benzaldehyde.

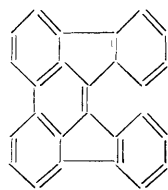
4:6-Dinitro-1:3-distyrylbenzene forms a *tetrabromide*,



m. p. 207—208° (decomp.), and by reduction with stannous chloride and acetic and hydrochloric acids yields 4:6-diamino-1:3-distyrylbenzene, m. p. 204°, yellow crystals with green fluorescence. The base forms fluorescent solutions, yields a *dibenzoyl* derivative which is unchanged at 275°, and reacts with benzaldehyde in boiling alcohol to form the *dibenzylidene* derivative,  $\text{C}_6\text{H}_2(\text{N}:\text{CHPh})_2(\text{CH}:\text{CHPh})_2$ , m. p. 238—239°, deep yellow, non-fluorescent needles. A methyl-alcoholic solution of the base is reduced by hydrogen in the presence of a little colloidal palladium, yielding 4:6-diamino-1:3-di- $\beta$ -phenylethylbenzene,  $\text{C}_6\text{H}_2(\text{NH}_2)_2(\text{CH}_2 \cdot \text{CH}_2\text{Ph})_2$  (*diacetyl* derivative, m. p. 224°; *dibenzoyl* derivative, m. p. 273°).

4-Cyano-*m*-xylene and nitric acid, D 1.52, at 0° yield a mixture of sparingly soluble (in alcohol), yellowish prisms, m. p. 107—108° (probably 6-nitro-4-cyano-*m*-xylene), and easily soluble, white needles, m. p. 120—121° (probably 4-cyano-2-nitro-*m*-xylene). By diazotisation and treatment with cuprous cyanide, 4-cyano-*o*-toluidine yields 2:4-dicyanotoluene, m. p. 144—145°, white needles. C. S.

**Non-Existence of  $\psi$ -Diphenyleneketone [ $\psi$ -Fluorone]. A New Red Hydrocarbon.** RUDOLF PUMMERER (*Ber.*, 1912, 45, 294—298).—The red modification of fluorone, obtained by Kerp (*Abstr.*, 1896, i, 238; compare also Stobbe, *ibid.*, 1911, i, 651) by the distillation of calcium diphenoxide, is shown to be the ordinary yellow variety of fluorone, contaminated with traces of the red substance, first observed by Fittig and Ostermayer (this Journ., 1873, 892), and shown by them to be produced simultaneously in the distillation. This red impurity is insoluble in alcohol and solvents of low b. p., but dissolves to a slight extent in solutions of fluorone, from which it may be removed by shaking in the cold with animal charcoal.



It may be isolated by repeatedly triturating the "red fluorone" with cold alcohol and crystallising the residue from benzene. It forms slender, lancet-shaped crystals, m. p. 306°, yields strongly

yellow, fluorescent solutions, and has the composition  $C_{26}H_{14}$ . On account of its bright red colour, the hydrocarbon is termed by the author *rubicene*.

Its constitution has not yet been definitely established, but arguments are advanced in favour of the formula given on the preceding page. With bromine in chloroform solution, it forms a *bromo*-substitution product; the *picrate* crystallises in very slender, brownish-red prisms.

Kerp's "red fluorone" contains in addition to rubicene a white substance, which remains behind on dissolving the ketone in concentrated sulphuric acid. F. B.

**Isomeric Schiff's Bases.** BRONISLAW PAWLEWSKI (*Chem. Zentr.*, 1912, i, 29; from *Chem. Polski*, 1911, 11, 121—122).—Of the five substances obtained by the author by condensing benzoïn with benzylamine, one, m. p. 88—90°, is the *trans*-modification of *benzylidenebenzylamine*,  $CHPh:N\cdot CH_2Ph$ , and is stereoisomeric therefore with the liquid *benzylidenebenzylamine*, b. p. 200—202°/10—20 mm., described by Mason and Winder (*Trans.*, 1894, 65, 191). C. S.

**The Homo-chromoisomerism of the Phenylmethylpicramides.** ARTHUR HANTZSCH (*Ber.*, 1912, 45, 360—363).—Polemical; a reply to Büllmann (*Abstr.*, 1911, i, 963). D. F. T.

**Nitration of the Acyl Derivatives of *p*-Anisidine.** FRÉDÉRIC REVERDIN and ARMAND DE LUC (*Ber.*, 1912, 45, 349—354).—A continuation of earlier work (*Abstr.*, 1909, i, 377, 913; 1910, i, 470), in which a study has been made of the effect of the substitution of the nitrobenzoyl group into the amino-group of *p*-anisidine on the behaviour of the base towards nitration.

*m*-Nitrobenzenesulphonyl-*p*-anisidide,  $NO_2\cdot C_6H_4\cdot SO_2\cdot NH\cdot C_6H_4\cdot OMe$ , obtained by the action of the acid chloride on the base, forms white needles, m. p. 135°; the *acetyl* derivative forms needles, m. p. 181—182°.

*o*-Nitrotoluene-*p*-sulphonyl-*p*-anisidide, obtained similarly, forms needle crystals, m. p. 81°; *acetyl* derivative, m. p. 161°.

The nitration of the above nitrobenzenesulphonyl-*p*-anisidide with nitric acid, D 1·38, without cooling (max. temperature 36°), gives as chief product an orange-yellow *dinitro*-derivative, m. p. 170°, which can be hydrolysed to the corresponding free base, 2 : 5-dinitro-*p*-anisidine. If the temperature is allowed to rise to 62°, a mixture of the previous dinitro-compound with the isomeric 3 : 5-dinitro-compound, m. p. 165—166°, is obtained; this forms white needles, and hydrolyses to 3 : 5-dinitro-4-aminoanisole. If the mixture during nitration is heated over a free flame, there is obtained the *nitrobenzenesulphonyl* derivative of 2 : 3 : 6-trinitro-4-aminoanisole, which forms small, prismatic crystals, m. p. 189—190°.

When nitrated as an emulsion in acetic acid at 70° with nitric acid D 1·38, the main product is the above 3 : 5-dinitro-derivative.

With nitric acid, D 1·52, between 0° and 5°, the product consists of a mixture of the 2 : 5-dinitro- and the 2 : 3 : 6-trinitro-derivatives; at higher temperatures decomposition occurs; if the nitration with acid of this strength is performed at 5—10° in an emulsion in acetic acid,

a *mononitro*-derivative is obtained (yellow needles, m. p. 127°), which on hydrolysis gives 3-nitro-4-aminoanisole.

With nitric acid, D 1·38, the above-mentioned nitrotoluenesulphonyl-*p*-aniside at 36° yields a *mononitro*-derivative (prismatic crystals, m. p. 132°), the constitution of which is shown by its hydrolysis to 3-nitro-*p*-anisidine. At higher temperatures, the *nitrotoluenesulphonyl* derivatives of 3:5-dinitro- and 2:3:6-trinitro-*p*-anisidine are obtained (m. p. 125—140° and 184—185° respectively); the former of these is also the product of nitrating a solution in acetic acid.

With nitric acid, D 1·52, at 5—10°, the product contains the *nitro-toluenesulphonyl* derivatives of 2:3-dinitro-*p*-anisidine and 2:5-dinitro-*p*-anisidine (m. p. of acyl derivatives, 180° and 154° respectively); on nitrating in acetic acid in the cold, the above-mentioned nitrotoluenesulphonyl derivatives of 3-nitro-*p*-anisidine and 2:5-dinitro-*p*-anisidine are obtained, the latter preponderating.

D. F. T.

**Decomposition of Mixed Phenyl Oxides in Presence of Nickel and Hydrogen.** ALPHONSE MAILHE and M. MURAT (*Bull. Soc. chim.*, 1912, [iv], 11, 122—123).—It is shown that all phenyl alkyl oxides when passed over heated nickel in a current of hydrogen are decomposed in accordance with the equations (1)  $C_6H_5 \cdot O \cdot R + H_2 = C_6H_5 \cdot OH + RH$ , and (2)  $C_6H_5 \cdot O \cdot R + H_2 = C_6H_6 + R \cdot OH$ , the alcohol and the paraffinic hydrocarbon formed being destroyed by the further action of the nickel. Anisole is most readily attacked, and yields 52% of the possible weight of phenol, whilst phenyl *isoamyl* oxide yields only 22%. Diphenyl oxide is attacked with great difficulty, and gives only 6% of the possible weight of phenol. Veratrole at 205° yields 16% of the possible weight of guaiacol, and the latter, on further treatment at 205°, yields a mixture of phenol and catechol.

T. A. H.

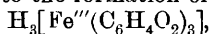
[Preparation of *p*-Aminophenyl Methyl Mercaptole.] AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 239310).—*p*-Aminophenyl methyl mercaptole, a colourless oil, comparing favourably with phenacetin in therapeutical action, is obtained by reducing *p*-nitrophenyl methyl mercaptole (Blanksma, *Abstr.*, 1902, i, 281); the salts are colourless and crystalline, and the *acetyl* derivative forms colourless needles, m. p. 127—128°.

F. M. G. M.

**Preparation of 4-Chloro- $\alpha$ -naphthol.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 240038).—It is found that 4-chloro- $\alpha$ -naphthol can be prepared by treating  $\alpha$ -naphthol arylsulphonyl ethers with chlorinating agents.  $\alpha$ -Naphthyl *p*-toluenesulphonate, colourless needles, m. p. 83—84°, prepared by the action of *p*-toluenesulphonyl chloride on sodium  $\alpha$ -naphthoxide in alcoholic solution, was dissolved in carbon tetrachloride and treated with chlorine, when a satisfactory yield of 4-chloro- $\alpha$ -naphthol (m. p. 116°) was obtained.

F. M. G. M.

The Red Coloration Produced in the Ferric Chloride Reaction with Catechol in Alkaline Solution. I. RUDOLF FRIEDRICH WEINLAND and KARL BINDER (*Ber.*, 1912, 45, 148—154).—The green coloration of an aqueous catechol solution produced by ferric chloride is changed to deep red on the addition of sodium, potassium, ammonium, barium, calcium, and magnesium hydroxides. The red coloration is due to the formation of salts of an acid,



analogous to the ferricyanides or ferrioxalates.

The *potassium* salt,  $\text{K}_3[\text{Fe}'''(\text{C}_6\text{H}_4\text{O}_2)_3] \cdot 2\text{H}_2\text{O}$ , is obtained as a lustrous, crystalline, brownish-black to dark bronze-red powder, consisting of microscopic triangular prisms, by the addition of ferric acetate to a solution of catechol in strong aqueous potassium hydroxide. It readily dissolves in water to deep red solutions, which are decolorised by excess of acid with the liberation of catechol. When heated with sodium sulphide or potassium cyanide in aqueous solution, the potassium salt is decomposed, yielding ferrous sulphide and potassium ferrocyanide respectively, although in the presence of potassium hydroxide the aqueous solutions may be heated with the substances without undergoing change.

The tendency to form salts of the above acid is so pronounced, that freshly precipitated ferric hydroxide in the presence of aqueous alkalis or ammonia dissolves on the addition of catechol, forming the corresponding alkali or ammonium salt.

The *ammonium* salt,  $(\text{NH}_4)_3[\text{Fe}'''(\text{C}_6\text{H}_4\text{O}_2)_3] \cdot \text{H}_2\text{O}$ , prepared in a similar manner to the sodium salt, is a brownish-black powder, consisting of microscopic, flat, violet-red needles.

The *sodium* salt,  $\text{Na}_3[\text{Fe}'''(\text{C}_6\text{H}_4\text{O}_2)_3] \cdot 10\text{H}_2\text{O}$ , forms microscopic, red, hexagonal columns, capped with truncated pyramids.

The *lead* salt is precipitated quantitatively on the addition of lead acetate to an aqueous solution of an alkali salt. The *morphine* and *strychnine* salts are crystalline; the *quinine* and *brucine* salts are amorphous.

Similar complex salts, stable towards alkalis, are obtained from catechol and aluminium, cupric, nickel, cobalt, and manganous salts, and also from pyrogallol, salicylic, gallic or protocatechuic acids, and ferric salts in alkaline solution.

F. B.

Derivatives of 4-Amino-orceinol (2-Amino-3:5-dihydroxy-toluene). FERDINAND HENRICH, G. TAUBERT, and H. BIRKNER (*Ber.*, 1912, 45, 303—314. Compare *Abstr.*, 1903, i, 413).—2-Amino-orceinol has now been isolated in the free condition by the addition of sodium hydroxide to a cold aqueous solution of the hydrochloride in quantity just insufficient for complete decomposition. It crystallises from ethyl acetate in lustrous, silvery-white leaflets, decomposing at 188—190°, with previous darkening at 160—180°. Its hydrochloride is oxidised by chromic acid in aqueous solution to 4-chloro-3-hydroxytoluquinone,  $\text{CO} \begin{array}{c} \text{CCl:C(OH)} \\ \text{CH=CMe} \end{array} \text{CO}$ , which forms intensely yellow crystals, m. p. 181—182°, volatile in ether vapour, dissolves in alkalis, yielding intensely red solutions, and is reduced by

sulphur dioxide in aqueous solution to 4-chloro-2 : 3 : 5-trihydroxytoluene,  $C_7H_7O_3Cl$ , colourless needles, m. p.  $137.5^\circ$ . Acidification of the solutions of the quinone in aqueous ammonia or sodium carbonate results in formation of a *substance* having the same composition as the original quinone. This substance separates from benzene or chloroform in yellow crystals, darkening at  $220^\circ$ , dissolves in water less readily than the original quinone, and is not volatile in ether vapour; but whether these differences are to be referred to isomerism or polymerism has not yet been determined.

That the quinone has the above constitution and not that of the isomeric 6-chloro-3-hydroxytoluquinone,  $CO < \begin{smallmatrix} CH:C(OH) \\ CCl=CMe \end{smallmatrix} > CO$ , has been established by the synthesis of the latter compound from 2-amino-*orcinol* hydrochloride. This is converted by amyl nitrite in alcoholic solution into *orcinol-2-diazonium chloride*, a yellowish-white powder, which forms, with cuprous chloride, a red, crystalline *additive* compound,  $C_6H_2Me(OH)_2 \cdot N_2Cl, Cu_2Cl_2$ . When heated under diminished pressure the additive compound melts at  $80-90^\circ$ , and decomposes at a higher temperature into 2-chloro-*orcinol*,  $C_7H_7O_2Cl$ , m. p.  $138-139^\circ$ , with previous sintering at  $115^\circ$ .

The last-named compound reacts with amyl nitrite and potassium hydroxide in alcoholic solution to form the *potassium* salt of 2-chloro-6-nitroso-*orcinol*, from which the free nitroso-compound is obtained by acidification with dilute sulphuric acid.

2-Chloro-6-nitroso-*orcinol*,  $C_7H_6O_3NCl$ , exists in two modifications: a stable, yellow, crystalline form, melting at  $159-160^\circ$  with previous darkening, and a brown modification, which passes into the yellow variety when heated.

2-Chloro-6-amino-*orcinol hydrochloride* is obtained in slender, white needles by reducing the preceding nitroso-compound with stannous chloride and hydrochloric acid. It is oxidised by chromic acid in aqueous solution to 6-chloro-3-hydroxytoluene, ruby-red crystals, m. p.  $165-166^\circ$  (decomp.). F. B.

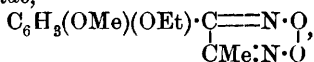
**Constitution of Diisoeugenol.** ERNESTO PUXEDDU (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 42-46. Compare Abstr., 1909, i, 225).—The paper deals with the action of light on *isoeugenol* and on its methyl, ethyl, and propyl ethers, as well as the action of light on *eugenol* and its ethers. The author has also examined the action of nitrous acid on *isoeugenol* ethyl ether and on *diisoeugenol* diethyl ether.

When a solution of 100 grams of *isoeugenol* in 200 c.c. of alcohol is treated with 25 c.c. of hydrochloric acid and exposed to light in a sealed tube, crystals of *diisoeugenol* are quickly deposited, and if the precipitate is collected after two days, the yield amounts to 60%. If the filtered solution is again exposed to light, a further quantity of the polymeride can be obtained. The mother liquors show a splendid blue fluorescence. Under the same conditions, sulphuric acid also acts feebly as a polymerising agent. *isoEugenol* methyl ether, *isoeugenol* ethyl ether, and *isoeugenol* propyl ether yield the analogous *polymerides* when treated in the same way. *isoEugenol propyl ether*,  $C_{13}H_{18}O_2$ ,

prepared from *isoeugenol* with sodium propoxide and propyl iodide, crystallises in long, prismatic needles, m. p. 54°. *Diisoeugenol dipropyl ether*,  $(C_{13}H_{18}O_2)_2$ , forms prismatic needles, m. p. 94°.

*Eugenol* and its methyl and ethyl ethers under the same conditions are not acted on by light.

When *isoeugenol* ethyl ether is treated with glacial acetic acid and potassium nitrite, a substance,  $C_{12}H_{14}O_4N_2$ , is obtained, which crystallises in yellow, tabular prisms, m. p. 85°. It is assigned the formula of the *peroxide*,



analogous to that from *isoeugenol* methyl ether (compare Malagnini, *Abstr.*, 1895, i, 35). *Diisoeugenol* diethyl ether does not react with nitrous acid, and therefore probably does not contain an unsaturated side-chain.

R. V. S.

**Action of Phorone on Catechol and Pyrogallol.** MARIO GHIGLIENO (*Atti R. Accad. Sci. Torino*, 1912, 47, 16—22).—Fabinyi and Széki (compare *Abstr.*, 1905, i, 591, 888) obtained products by heating acetone with catechol and with pyrogallol in a sealed tube at 145°. In the present paper it is shown that the formulæ ascribed to these substances are incorrect. Under the conditions of experiment the acetone is condensed to phorone, which reacts with the phenols, giving substances of the following constitutions, respectively :

$C(CH:CM_e)_2[C_6H_3(OH)_2]_2$   
and  $C(CH:CM_e)_2[C_6H_2(OH)_3]_2$ . This explains the existence of the tetrabromo- and dibromo-derivatives. In confirmation of this view, the authors have prepared the same substances, using phorone instead of acetone. It is not necessary to heat the mixture at 145°; the same products are obtained when phorone and the phenol are heated together in a sealed tube at 100°, or even in an open flask with condenser. In the case of the product from pyrogallol the somewhat discordant analyses of Fabinyi and Széki are explained by the fact that the substance contains 1 mol.  $H_2O$ , which it loses completely only at 130—140°, and which it re-absorbs very readily on exposure to air.

R. V. S.

**Action of Formic Acid on Triarylcarbinols.** ALFRED GUYOT and A. KOVACHE (*Compt. rend.*, 1912, 154, 121—122).—Triarylcarbinols are readily reduced when treated with twenty times their weight of crystallisable formic acid, giving the corresponding hydrocarbons with formation of water and evolution of carbon dioxide. The reaction may be made use of for accurately determining the number of hydroxyl groups in such carbinols, by weighing the carbon dioxide evolved from less than a gram of the substance. Quantitative results were obtained with triphenylcarbinol, phenyldi-*p*-tolylcarbinol, *o*-benzoyltriphenylcarbinol, and 9 : 10-diphenylanthranol, whilst 9-phenylanthranol and 9 : 10-dihydroxy-9 : 10 : 10-triphenyldihydroanthracene gave less than the calculated amount of carbon dioxide, although the yield of hydrocarbon was theoretical.

W. O. W.

**The Walden Inversion and Substitution Processes.** EMIL FISCHER (*Annalen*, 1912, 386, 374—386. Compare Abstr., 1911, i, 418).—An amplification of the author's view that the phenomena met with in the addition of halogens or halogen hydracids to stereoisomeric unsaturated compounds are probably of a similar type to the Walden inversion. Reactions such as that whereby both inactive dibromosuccinic acids result by the addition of bromine to maleic or to fumaric acid have been regarded by Werner and by van't Hoff as exceptional and due to a specific action of the halogen. Examples are given, however, to show that similar results may be obtained by the addition of groups or atoms other than halogens. It is true that the oxidation of cinnamamide by potassium permanganate yields only one *phenylglyceramide*,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 161—162° (corr.) (which yields the phenylglyceric acid, having m. p. 141°, by hydrolysis), and the oxidation of cinnamoylglycine gives only one *phenylglycerylglycine*,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p. 144—145° (corr.). However, Baeyer has shown that  $\Delta^1$ -tetrahydrophthalic acid yields two stereoisomeric hexahydrophthalic acids by reduction, whilst Fittig has obtained two dimethylsuccinic acids by the reduction of dimethylfumaric acid.

C. S.

**Spectrochemical Differentiation between Hydroaromatic Compounds with Endocyclic and with Semicyclic Double Linkings.** KARL AUWERS and PHILIPP ELLINGER (*Annalen*, 1912, 387, 200—239).—Unsaturated hydroaromatic hydrocarbons containing semicyclic double linkings exhibit a moderate exaltation of the specific refraction and a marked exaltation of the specific dispersion. Unsaturated hydroaromatic hydrocarbons containing endocyclic double linkings are optically normal. These statements are based, not only on the spectrometric examination of the many alkylidenecycloparaffins which have been prepared by Wallach, but also on a direct comparison of the alkylidenecyclohexanes (methylene-, ethylidene-, and isopropylidene-cyclohexanes) with the isomeric alkyl- $\Delta^1$ -cyclohexenes (methyl-, ethyl-, and isopropyl-cyclohexenes); the latter are optically normal, whilst the former exhibit an exaltation of 0.28—0.47 of  $\Sigma_D$ , and an exaltation of 6—10% of  $\Sigma_\gamma - \Sigma_a$ .

The spectrochemical method of differentiating between the two classes of isomerides has been utilised to show that Sabatier and Mailhe's alkylidenecyclohexane derivatives are really unsaturated endocyclic compounds, and that Zelinsky and Gutt's 3-methyl-1-ethylidenecyclohexane must be, on account of its optical normality, 3-methyl-1-ethyl- $\Delta^1$ -cyclohexene.

$\Delta^1$ -cycloHexenylacetic acid and its esters and their homologues containing a methyl group in position  $\alpha$ , 2, 3, or 4 are optically normal. cycloHexylidenecetic acid and its homologues containing a methyl group in position 2, 3, or 4 have too high m. p.'s to be suitable for spectrometric examination, but their methyl and ethyl esters show a marked exaltation, 0.79—1.05, of the specific refraction,  $\Sigma_D$ , and still more pronounced exaltation, 31—40%, of the specific dispersion,  $\Sigma_\gamma - \Sigma_a$ . These are due, not only to the semicyclic, but also to the conjugated, double linking. Esters of the acids contain-

ing a methyl group in the  $\alpha$ -position contain a disturbed conjugation, and therefore show smaller exaltations, but even in these cases the exaltations are so pronounced that there can be no uncertainty in distinguishing such esters from those of  $\alpha$ -substituted cyclohexenyl-acetic acids.

The authors regard the spectrometric method as far safer than any chemical process for the determination of the constitution of such easily changeable substances as cyclohexenyl- and the cyclohexylidene-acetic acids.

The following new compounds are described; they have been obtained by Wallach's methods as a rule. 1-isoPropylcyclohexanol,  $C_9H_{18}O$ , b. p.  $176.4-176.7^\circ$ ,  $D_4^{15.5}$  0.9142,  $n_a$  1.46064,  $n_D$  1.46419, and  $n_\gamma$  1.47387 at  $15.5^\circ$ ; ethyl  $\Delta^1$ -cyclohexenylacetate,  $C_8H_9 \cdot CH_2 \cdot CO_2Et$ , b. p.  $100^\circ/12$  mm.,  $D_4^{16.2}$  0.9829,  $n_a$  1.46422,  $n_D$  1.46906,  $n_\gamma$  1.48017 at  $16.2^\circ$ ; methyl  $\alpha$ -1-hydroxycyclohexylpropionate,

$OH \cdot C_6H_{10} \cdot CHMe \cdot CO_2Me$ ,  
b. p.  $132^\circ/18$  mm.,  $D_4^{20}$  1.0537; methyl  $\alpha$ - $\Delta^1$ -cyclohexenylpropionate,  $C_8H_9 \cdot CHMe \cdot CO_2Me$ , b. p.  $108-108.5^\circ/18$  mm.,  $D_4^{18.3}$  0.9864,  $n_a$  1.46373,  $n_D$  1.46648,  $n_\gamma$  1.47885 at  $18.3^\circ$ ; methyl 2-methylcyclohexylideneacetate,  $C_8H_9Me \cdot CH \cdot CO_2Me$  (prepared from methyl iodide and the silver salt of the acid, m. p.  $68^\circ$ ), b. p.  $119.9^\circ/15$  mm.,  $D_4^{14.2}$  0.9767,  $n_a$  1.47681,  $n_D$  1.48072,  $n_\gamma$  1.49802 at  $14.2^\circ$ ; the corresponding ethyl ester has b. p.  $128.2^\circ/13$  mm.,  $D_4^{14.8}$  0.9587,  $n_a$  1.47524,  $n_D$  1.47906, and  $n_\gamma$  1.49639 at  $14.8^\circ$ ; methyl 3-methylcyclohexylideneacetate,  $C_8H_9Me \cdot CH \cdot CO_2Me$ , b. p.  $117^\circ/13$  mm.,  $D_4^{15.5}$  0.9752,  $n_a$  1.47534,  $n_D$  1.47926,  $n_\gamma$  1.49668 at  $15.5^\circ$ ; the ethyl ester has b. p.  $131.4^\circ/18$  mm.,  $D_4^{15}$  0.9571,  $n_a$  1.47347,  $n_D$  1.47730,  $n_\gamma$  1.49464 at  $15^\circ$ .

C. S.

**Correlation of Ionisation and Structure. II. Negatively Substituted Benzoic Acids.** C. G. DERICK (*J. Amer. Chem. Soc.*, 1912, **34**, 74-82).—It was shown in an earlier paper (Abstr., 1911, ii, 713) that the free energy of ionisation for negatively substituted monobasic fatty acids in aqueous solution at  $25^\circ$  is the sum of the separate effects of each atom in the molecule. Hence it was demonstrated that the position of a negative atom or group in an acid can be determined if its  $\alpha$ -“place factor” and the ionisation constant of the substituted acid are known. In the present paper it is shown that the additive relationship in the free energy of ionisation is also true in the case of aromatic acids, and that it is therefore possible to determine the structure of substituted benzoic acids containing negative groups or atoms, if the ortho-, meta-, and para-“place factors” are known for each negative radicle.

The “place factors” have been determined for benzoic acid for the acetoxy-, carboxy-, chloro-, hydroxy-, and nitro-radicles for the ortho-, meta-, and para-positions; for the aldehydo-, benzoyl-, bromo-, carb-methoxy-, carbethoxy-, iodo-, and methoxy-radicles for the ortho-position; and for the cyano-, fluoro-, and iodo-radicles for the meta-position. From these numbers the ionisation constants for the substituted benzoic acids were calculated, and agreed closely with the experimental values in nearly all cases.

There is no simple relation between the "place factors" for the same radicle substituted in the ortho-, meta-, and para-positions in benzoic acid. Ionisation will not differentiate between 2:3- and 2:5-di-substituted benzoic acids, in which the substituting radicles in the 3- and 5-positions are the same and those in the 2-positions are also the same. The fact that the 3- and 5-positions are equivalent with respect to the 1-position has been proved in terms of the free energy of ionisation.

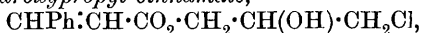
E. G.

**Barium Hippurate.** EYVIND BÖDTKER (*Chem. Zeit.*, 1912, 36, 105).—Analyses of this salt, prepared by neutralising hippuric acid with barium hydroxide, crystallising it from water, and drying the crystals between blotting paper, show that it contains  $5\text{H}_2\text{O}$ . The statement that it contains only  $1\text{H}_2\text{O}$  may be due to the salt having been dried over sulphuric acid before analysis, although the strontium salt, when similarly dried, does not lose water. Attempts to prepare ferric hippurate were not successful.

W. P. S.

**Preparation of Cinnamic Esters of Polyatomic Alcohols.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 239650. Compare Abstr., 1911, i, 858).— $\beta$ -Chloroethyl cinnamate,  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\cdot\text{C}_2\text{H}_4\text{Cl}$ , a colourless solid, m. p.  $31^\circ$ , b. p.  $188\text{--}191^\circ/20\text{ mm.}$ , is prepared by the interaction of chloroethyl alcohol and cinnamic acid in the presence of concentrated sulphuric acid; when heated at  $140^\circ$  with sodium acetate and dilute acetic acid, it furnishes *glycol cinnamate*, b. p.  $170\text{--}175^\circ/15\text{ mm.}$

$\gamma$ -Chloro- $\beta$ -hydroxypropyl cinnamate,

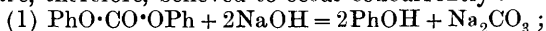


a yellowish, viscid liquid, b. p.  $210\text{--}218^\circ/20\text{ mm.}$ , prepared from monochlorohydrin and cinnamic acid, by similar treatment yields *glycerol cinnamate*. Other weak acids and their salts can replace acetic acid in this reaction.

F. M. G. M.

**Sodium Phenyl Carbonate as Intermediate Product of Kolbe's Synthesis for Salicylic Acid.** CARL H. SLUITER (*Ber.*, 1912, 45, 59—62).—It has been asserted (de Bruyn and Tymstra, Abstr., 1905, i, 209; Tymstra, Abstr., 1905, i, 439) that under the conditions of Kolbe's process, sodium phenyl carbonate cannot be an intermediate step on account of its dissociation into carbon dioxide and sodium phenoxide; in their opinion the carbon dioxide molecule inserts itself directly between the carbon and hydrogen atoms in the ortho-position of the sodium phenoxide, giving the phenolic sodium derivative of salicylic acid.

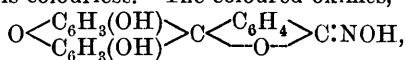
The author takes diphenyl carbonate (m. p.  $78\cdot2\text{--}78\cdot4^\circ$ ,  $D^{14}_D 1\cdot272$ ,  $D^{100}_D 1\cdot1032$ ), and examines carefully the reaction products obtained by heating to  $160^\circ$  with an equimolecular quantity of dry sodium hydroxide (compare Hentschel, Abstr., 1883, 588) in a current of nitrogen. The evolution of carbon dioxide ends after two to three minutes, and the residue contains sodium phenoxide, sodium carbonate, and sodium salicylate with some unchanged diphenyl carbonate. Two reactions are, therefore, believed to occur concurrently:



(2)  $\text{PhO}\cdot\text{CO}\cdot\text{OPh} + \text{NaOH} = \text{Ph}\cdot\text{OH} + \text{PhO}\cdot\text{CO}\cdot\text{ONa}$ ; the sodium phenyl carbonate then partly dissociates into carbon dioxide and sodium phenoxide, and partly is rearranged into sodium salicylate. The alternative explanation given above for the formation of the last substance cannot hold in this case, as the pressure of carbon dioxide would be quite insufficient for reaction with the sodium phenoxide. It appears, therefore, that under the conditions of Kolbe's synthesis, sodium phenyl carbonate can undergo rearrangement into sodium salicylate.

D. F. T.

**Two Phthaloximes and Some of Their Derivatives.** WILLIAM R. ORNDORFF and DAVID S. PRATT (*Amer. Chem. J.*, 1912, 47, 89—125).—It has been shown by R. Meyer (Abstr., 1905, i, 440; 1909, i, 652) that quinolphthalein yields three oximes, of which two are coloured, whilst the other is colourless. The coloured oximes,



were regarded as *cis*- and *trans*-stereoisomerides, and the group  $\text{C}:\text{NOH}$  was considered to be the chromophore. In order to ascertain whether this group behaves as a chromophore when present in a five-membered ring, a study has been made of phthalylhydroxylamine, first described by Lassar-Cohn (Abstr., 1881, 585), which the authors prefer to term phthaloxime.

The compound was prepared by Lach's method (Abstr., 1883, 1104), which consists of heating a mixture of phthalic anhydride, hydroxylamine hydrochloride, sodium carbonate, and water for an hour at  $60^\circ$ . As the reaction product cooled, colourless crystals of phthaloxime separated, in quantity equivalent to a 70% yield. When the mother liquor was heated at  $100^\circ$  for one and a-half hours and then left to cool, lemon-yellow crystals of an isomeric phthaloxime appeared.

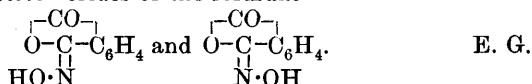
These oximes,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C}(\text{NOH}) \\ \diagdown \text{CO} \end{array} > \text{O}$ , both melt at  $220$ — $226^\circ$ , and are slowly decomposed when heated at  $110^\circ$ . Both forms dissolve in alkali hydroxides with the production of red solutions, which gradually become colourless, owing to the formation of salts of the hydroxamic acid. If the colourless oxime is heated with a solvent containing a hydroxyl group, it is partly converted into the yellow isomeride, and, if boiled for an hour with glacial acetic acid, it is quantitatively transformed into the yellow form. The yellow oxime can be quantitatively changed into the colourless variety by boiling it with acetic anhydride, the same colourless *acetate*, m. p.  $183$ — $185^\circ$ , being obtained in this case as when the colourless isomeride itself is acetylated. When the colourless acetate is treated with a solution of ammonia and afterwards acidified, the white oxime is precipitated. A yellow *acetate*, also of m. p.  $183$ — $185^\circ$ , can be obtained from the yellow oxime by the action of acetic anhydride at the ordinary temperature.

Both oximes yield red *ammonium*, *sodium*, *sodium hydrogen*, *potassium hydrogen*, and *silver* salts, from which the original oxime is regenerated in each case on treatment with acids. When the silver salts are treated with ethyl iodide, that of the colourless oxime yields

a colourless *ethyl ether*, and that of the yellow oxime, a lemon-yellow *ethyl ether*, both melting at 95–100°.

Each oxime has been submitted to a crystallographic examination. The colourless oxime forms monoclinic needles, elongated in the direction of the *b*-axis, and usually flattened parallel to a pair of faces in the ortho-zone; the crystals have  $n_D$  1.522 in a direction parallel to the elongation. The optical properties of the yellow oxime closely resemble those of the colourless form except in respect of colour. The colour of the yellow variety is due mostly, if not entirely, to fluorescence. A crystallographic study has also been made of the salts, acetates, and ethyl ethers.

The constitution of these oximes is discussed, and evidence is adduced to show that in all probability they are not structural isomerides, but stereoisomerides of the formulæ



*iso*Phthalanil. RUDOLF PUMMERER and GUSTAV DORFMÜLLER (*Ber.*, 1912, 45, 292–294).—The transformation of *isophthalanil* into

phthalanil,  $\begin{array}{c} \text{CO}\cdot\text{O} \\ | \\ \text{C}_6\text{H}_4 \end{array} > \text{C}\cdot\text{NPh} \rightarrow \text{C}_6\text{H}_4 < \begin{array}{c} \text{CO} \\ \text{CO} \end{array} > \text{NPh}$ , takes place slowly at the ordinary temperature, as indicated by the rise in m. p. of a specimen of the former compound from 116° to 150° after being kept for six months, and also by the isolation of phthalanil from the product. When shaken with concentrated aqueous sodium carbonate at the ordinary temperature, *isophthalanil* undergoes complete transformation in the course of five hours. With dilute sodium carbonate it is converted, after several days, mainly into phthalanilic acid, only traces of phthalanil being produced; phthalanil undergoes no change when subjected to the same treatment. The transformation has also been effected by boiling solutions of *isophthalanil* in pyridine, quinoline, and nitrobenzene; with water and light petroleum no change occurs.

*iso*Phthalanil reacts with benzene in the presence of aluminium chloride, yielding *o*-benzoylbenzanilide. F. B.

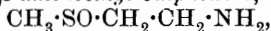
**Simple Fatty Amines containing Sulphur.** WILHELM SCHNEIDER (*Annalen*, 1912, 386, 332–350).—The possibility that derivatives of aminosulphones, other than cheirolin (methyl- $\gamma$ -thiocarbimidopropylsulphone) (*Abstr.*, 1910, i, 658), may occur in nature has led the author to prepare aliphatic aminosulphones and the corresponding thiocarbimides, aliphatic aminosulphides, and aminosulphoxides.

[With MAX MÜLLER and WILHELM BECK.]— $\beta$ -Phthalimidoethyl methyl sulphide,  $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CO} \\ \text{CO} \end{array} > \text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SMe}$ , m. p. 89°, prepared from sodium methyl mercaptide and  $\beta$ -bromoethylphthalimide, yields by hydrolysis methyl  $\beta$ -aminoethyl sulphide,  $\text{NH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SMe}$ , b. p. 146–148°, a colourless liquid having the odour of piperidine and strongly basic properties (*hydrochloride*, m. p. about 120°; *picrate*, m. p. 119°; *picrolonate*, decomp. 187°; *oxalate*, m. p. 197°; *benzoyl*

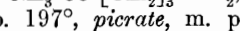
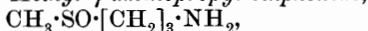
derivative, m. p. 57°). By treatment with alkali and an excess of methyl iodide, it yields, not an *NS*-dimethiodide, as does methyl- $\gamma$ -aminopropyl sulphide (*loc. cit.*), but the *methiodide* of methyl  $\beta$ -dimethylaminoethyl sulphide,  $\text{SMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_2$ , decomp. 220·5°, colourless leaflets, which is decomposed by warm alkalis with evolution of trimethylamine.

*$\beta$ -Phthalimidodiethyl sulphide*,  $\text{C}_6\text{H}_4\begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix} \text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SEt}$ , m. p. 39°, yields by hydrolysis  *$\beta$ -aminodiethyl sulphide*,  $\text{C}_4\text{H}_{11}\text{NS}$ , b. p. 163° (*hydrochloride*, m. p. 147°; *hydrogen oxalate*, m. p. 145·5°; *picrate*, m. p. 148°; *picrolonate*, decomp. 184°; *benzoyl derivative*, b. p. 221—222°/40 mm. [decomp.]). The *methiodide* of  $\beta$ -dimethylaminodiethyl sulphide decomposes at 216·5°.

By oxidising its hydrochloride with hydrogen peroxide and treating the product with alcoholic sodium ethoxide, methyl  $\beta$ -aminoethyl sulphide yields *methyl  $\beta$ -aminoethyl sulphoxide*,

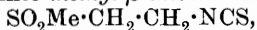


which cannot be distilled, but is volatile with steam. It forms an *oxalate*, m. p. 165°, *picrate*, m. p. 158°, and *picrolonate*, decomp. 205°, and is decomposed when treated with methyl iodide.  *$\beta$ -Aminodiethyl sulphoxide*, prepared in a similar manner, forms an *oxalate*, m. p. 176°, *picrate*, m. p. 138°, *picrolonate*, decomp. 190°, and, when heated with the calculated quantities of methyl-alcoholic methyl iodide and sodium carbonate, is converted into the *methiodide* of  $\beta$ -dimethylaminodiethyl sulphoxide, m. p. 168°.



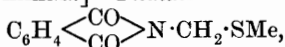
forms an *oxalate*, m. p. 197°, *picrate*, m. p. 143°, and *picrolonate*, decomp. 210°.

*Methyl- $\beta$ -aminoethylsulphone*, obtained in the form of the *hydrochloride*,  $\text{CH}_3\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2\cdot\text{HCl}$ , m. p. 169°, by oxidising the hydrochloride of the sulphide by potassium permanganate, forms a *picrate*, m. p. 167°, *picrolonate*, decomp. 225°, *platinichloride*, decomp. 227°, and *benzoyl derivative*, m. p. 134°, yields the *methiodide* of methyl- $\beta$ -dimethylaminoethylsulphone, m. p. 220°, with methyl-alcoholic methyl iodide at 120°, and is converted into *di- $\beta$ -methylsulphonethylthiocarbamide*,  $\text{SC}(\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{SO}_2\text{Me})_2$ , m. p. 141°, by carbon disulphide, and into *methyl- $\beta$ -thiocarbimidoethylsulphone*,



m. p. 46—47°, by Hofmann's method with carbon disulphide.  *$\beta$ -Aminodiethylsulphone*, prepared as the *hydrochloride*, m. p. 101—102°, in a similar manner, forms a *picrate*, m. p. 163°, *picrolonate*, decomp. 210°, *platinichloride*, decomp. 227°, *aurichloride*, m. p. 197°, *benzoyl derivative*, m. p. 86°, and *thiocarbamide*, m. p. 141°; the thiocarbimide could not be isolated.

[With WILHELM LOHMANN.]—*Phthalimidodimethyl sulphide*,



m. p. 114°, is obtained from bromomethylphthalimide and sodium methyl mercaptide in alcoholic solution. It is oxidised by hot aqueous potassium permanganate to the *sulphone*,  $\text{C}_{10}\text{H}_9\text{O}_4\text{NS}$ , m. p. 203°. Both the sulphide and the sulphone decompose completely when hydrolysed.

C. S.

**Chemical Action of Light on Vanillin and its Ethers.** ERNESTO PUXEDDU (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 717—723).—When vanillin in solution in alcohol, benzene, or other solvents is exposed to light, dehydrovanillin is obtained in small quantity, and no other product can be detected except a viscous oil. Vanillin methyl and ethyl ethers behave differently when exposed to light in benzene solution, the corresponding methyl and ethyl ethers of vanillic acid being formed respectively. R. V. S.

**Reactivity of the Carbonyl Group.** HERMANN STAUDINGER (*Annalen*, 1912, 387, 254—255).—A note explaining more fully the pictorial representation of the unsaturation of an atom by the length of the dotted line representing its residual affinity (compare Staudinger and Kon, *Abstr.*, 1911, i, 876). C. S.

**Behaviour of Antimony Trichloride and Tribromide towards certain Oxygenated Organic Compounds.** BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1785—1804).—The concentration-temperature diagrams given by acetophenone or benzophenone with antimony trichloride or tribromide are all nearly identical, each system being characterised by the formation of one molecular compound, which contains 1 mol. of the ketone to 1 mol. of antimony salt, and melts unchanged. Each diagram consists of four branches, corresponding with (1) the lowering of the m. p. of the ketone by addition of antimony salt, (2) the solubility in the ketone of the molecular compound, (3) the lowering of the m. p. of this compound by the addition of  $\text{SbX}_3$ , and (4) the lowering of the m. p. of  $\text{SbX}_3$  on addition to it of the molecular compound. Each diagram exhibits two eutectic points. The melting points of the various compounds are:  $\text{SbCl}_3\cdot\text{COMePh}$ ,  $60\cdot5^\circ$ ;  $\text{SbBr}_3\cdot\text{COMePh}$ ,  $37\cdot5^\circ$ ;  $\text{SbCl}_3\cdot\text{COPh}_2$ ,  $76^\circ$ ;  $\text{SbBr}_3\cdot\text{COPh}_2$ ,  $48\cdot5^\circ$ . The eutectic temperatures and the corresponding numbers of ketone mols. ( $n$ ) per mol. of antimony salt are as follows:

System.	M. p. Ketone.	1st eutectic point.		2nd eutectic point.		M. p. $\text{SbX}_3$ .
		Temperature.	$n$ .	Temperature.	$n$ .	
$\text{SbCl}_3\text{—COMePh}$ .....	$19\cdot5^\circ$	$1^\circ$	4·05	$32^\circ$	0·36	$73^\circ$
$\text{SbBr}_3\text{—COMePh}$ .....	$19\cdot5$	$1\cdot5$	3·17	31	0·6	94
$\text{SbCl}_3\text{—COPh}_2$ .....	48	35	4·63	39	0·26	73
$\text{SbBr}_3\text{—COPh}_2$ .....	48	29	2·82	40	0·5	94

Benzoic acid (m. p.  $120^\circ$ ) forms a molecular compound with neither antimony trichloride nor tribromide, the concentration-temperature diagram consisting, in each case, of two branches meeting at the following eutectic points:  $\text{SbCl}_3\cdot 0\cdot52\text{Ph}\cdot\text{CO}_2\text{H}$ ,  $46^\circ$ ;  
 $\text{SbBr}_3\cdot 0\cdot42\text{Ph}\cdot\text{CO}_2\text{H}$ ,  $79^\circ$ .

The system  $\text{SbCl}_3\text{—CH}_3\cdot\text{CO}_2\text{H}$  gives a molecular compound which forms only with difficulty. The first branch of the curve terminates at the eutectic point  $-9^\circ$ , corresponding with the composition  $\text{SbCl}_3\cdot 3\cdot43\text{CH}_3\cdot\text{CO}_2\text{H}$ . Then begins the curve of solubility of the molecular compound in acetic acid, but this is observable only on seeding with the molecular compound; unless this is done, branch 1 is prolonged below the eutectic point, and probably meets branch 4 in

another eutectic point. Branch 1 shows no arrest corresponding with the eutectic point  $\text{CH}_3\cdot\text{CO}_2\text{H}-\text{SbCl}_3, \text{CH}_3\cdot\text{CO}_2\text{H}$ , as the compound is not formed on cooling the solution. Branch 3 cuts branch 4 (lowering of m. p. of  $\text{SbCl}_3$  on addition of  $\text{CH}_3\cdot\text{CO}_2\text{H}$ ) at the eutectic point, about  $19^\circ$ , corresponding approximately with  $\text{SbCl}_3, 0.94\text{CH}_3\cdot\text{CO}_2\text{H}$ ; branch 3 can be followed below this eutectic point, but then represents an unstable condition.

The system  $\text{SbBr}_5\text{-CH}_3\cdot\text{CO}_2\text{H}$  forms no molecular compound, the curve consisting of two branches meeting at the eutectic point  $4^\circ$ , which corresponds with  $\text{SbBr}_5, 4.34\text{CH}_3\cdot\text{CO}_2\text{H}$ .

Benzoyl chloride forms no molecular compound with antimony chloride or bromide, each curve showing a single eutectic point:  $\text{SbCl}_3, 1.95\text{Ph}\cdot\text{COCl}$ ,  $-33^\circ$ , and  $\text{SbBr}_3, 5.45\text{Ph}\cdot\text{COCl}$ ,  $-6^\circ$ . T. H. P.

**The Reduction of Poly-unsaturated Ketones with Crossed Double Linkings by Paal's Method.** WALTHER BORSCHKE (*Ber.*, 1912, 45, 46—53).—The author has already successfully applied Paal's reduction method to the preparation of saturated ketones from such unsaturated ketones as cinnamylideneacetone (*Abstr.*, 1911, i, 880), and now extends the investigation to ketones in which each of the two carbon atoms adjacent to the carbonyl group has a double linking. The results indicate that where there is only one double bond on each side of the carbonyl group, the reduction proceeds smoothly, but that in other cases there is considerable formation of resinous substances as by-products.

The reduction of distyryl ketone yields di- $\beta$ -phenylethyl ketone, b. p.  $224^\circ/18$  mm.; the oxime melts at  $95-96^\circ$  (compare Dünschmann and von Pechmann, *Abstr.*, 1891, 674); a small quantity of a substance,  $\text{C}_{34}\text{H}_{34}\text{O}_2$ , m. p.  $126^\circ$ , was also obtained. Di-*p*-methoxystyryl ketone is reduced to *ae-di-p-methoxyphenylpentan- $\gamma$ -one*, which crystallises in needles, m. p.  $52^\circ$ .

Di-*o*-hydroxystyryl ketone gives *ae-di-o-hydroxyphenylpentan- $\gamma$ -one*, a viscid mass, which, when heated, loses water with the formation of *tetrahydrodibenzospiropyran* (compare Decker and Felser, *Abstr.*, 1908, i, 906), which crystallises in needles, m. p.  $110^\circ$ , b. p.  $217^\circ/16$  mm.

1 : 3-Dibenzylidenecyclopentan-2-one gives 1 : 3-dibenzylcyclopentan-2-one as an oil, b. p.  $232-233^\circ$ , which slowly crystallises in needles, m. p.  $47^\circ$ . In a similar manner, 1 : 3-dibenzylidenecyclohexan-2-one and 1 : 3-dibenzylidenecycloheptan-2-one give the corresponding 1 : 3-dibenzylcyclohexan-2-one, m. p.  $114^\circ$ , and 1 : 3-dibenzylcycloheptan-2-one, b. p.  $261-262^\circ/28$  mm.

Phenyl cinnamylidenemethyl ketone produces *phenyl  $\delta$ -phenylbutyl ketone*, b. p.  $225-226^\circ$ ; the oxime forms prismatic crystals, m. p.  $81-82^\circ$ , and by the Beckmann rearrangement changes into the anilide of  *$\delta$ -phenylvaleric acid*, m. p.  $89-90^\circ$ .

Styryl cinnamylidenemethyl ketone gives *an-diphenylheptan- $\gamma$ -one*, b. p.  $239^\circ/14$  mm.; the semicarbazone is an oil, whilst the hydrazone phenylcarbamate,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{C}(\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh})\cdot[\text{CH}_2]_3\cdot\text{CH}_2\text{Ph}$ , has m. p.  $122-123^\circ$ .

Dicinnamylideneacetone gives *ai-diphenylnonan- $\epsilon$ -one* ( *$\delta$ -phenylbutyl ketone*), an oil, b. p.  $258-260^\circ/13$  mm., which solidifies in a freezing

mixture; the *oxime* and *semicarbazone* are liquids, whilst the *hydrazone phenylcarbamate* forms silky needles, m. p. 129—130°.

2:6-Di-cinnamylidenecyclohexanone gives 2:6-di- $\omega$ -phenylpropyl-cyclohexanone as a viscous oil, b. p. 276—278°. D. F. T.

**Synthesis of Butin.** A. GÖSCHKE and JOSEF TAMBOR (*Ber.*, 1912, 45, 186—188. Compare Abstr., 1912, 1, 30).—The authors have succeeded in transforming synthetic butein into butin (compare Perkin and Hummel, *Trans.*, 1904, 85, 1459), thus completing the synthesis of both these natural products. *Butin triacetate* has m. p. 123°.

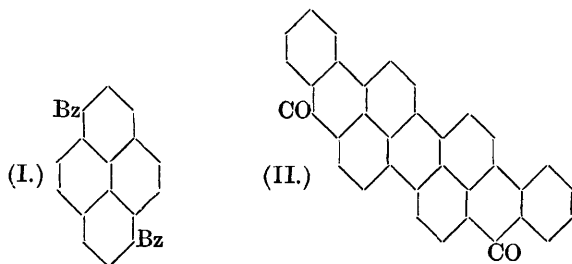
By the action of 3:4-dimethoxybenzaldehyde on resacetophenone and resacetophenone dimethyl ether respectively, they have prepared the 3':4'-dimethyl ether of *butein* (m. p. 203°) and *butein tetramethyl ether* (m. p. 89°).

2':4':2-Trihydroxychalkone, prepared by condensation of salicylaldehyde with resacetophenone, crystallises in orange needles + 1H<sub>2</sub>O, and has m. p. 185°. Its transformation into 3:2'-dihydroxyflavanone appears to be difficult. H. W.

**Preparation of Benzanthrone and its Derivatives.** ROLAND SCHOLL (D.R.-P. 239761).—When aromatic mono- or poly-ketones containing a free peri-position with regard to the carbonyl group are heated at about 140—150° with either aluminium chloride or bromide, or ferric chloride, condensation occurs, yielding benzanthrone or pyranthrone derivatives.

The following compounds have been prepared: Benzanthrone from phenyl  $\alpha$ -naphthyl ketone. *Naphthabenzanthrone* from 1:1'-dinaphthyl ketone, which can be prepared by the interaction of naphthoic acid with naphthalene in the presence of aluminium chloride.

*Dibenzoylpyrene* (I), m. p. 155°, and *tribenzoylpyrene*, m. p. 235—237°, are prepared by the action of benzoyl chloride on pyrene in the



presence of aluminium chloride and separated by fractional crystallisation from acetic acid; when the former is heated at 160° with aluminium chloride, it yields pyranthrone (Abstr., 1910, i, 271).

*Tri- $\alpha$ -naphthoylpyrene*, m. p. 218—219°, prepared from pyrene and  $\alpha$ -naphthoyl chloride, furnishes *naphthapyranthrone*.

*Dibenzoyl-1:1'-dinaphthyl*, obtained from 1:1'-dinaphthyl and benzoyl chloride, furnishes *violanthren* (II), a violet powder, whilst

*naphthylanthraquinonyl ketone* (from anthraquinone-2-carbonyl chloride and naphthalene) gives *phthaloylbenzanthrone*, and *m*-tolyl-1-naphthyl ketone yields *methylbenzanthrone*, brownish-yellow needles, m. p. 164—165°. F. M. G. M.

**Ketones Derived from *iso*Myristicin.** EVERARDO SCANDOLA (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 47—54).—The author has prepared the  $\alpha$ - and  $\beta$ -keto-derivatives of *isomyristicin*, and has attempted to obtain the dimeric form of *isomyristicin*.

The  $\alpha$ -ketone is prepared by heating together for some hours the dibromo-derivative of *isomyristicin* (Thoms, *Abstr.*, 1904, i, 47) and sodium methoxide, removing the excess of methyl alcohol, and distilling the residue with steam. After fractionation in a vacuum of the oil which passes over, the pure  $\alpha$ -keto-derivative of *isomyristicin*,  $C_{11}H_{12}O_4$ , is preferably obtained by way of the semicarbazide or oxime. It crystallises in small, silky needles, m. p. 93°. It yields a crystalline *bisulphite* compound, which does not melt below 230°. The *oxime*,  $C_{11}H_{13}O_4N$ , crystallises in very small prisms, m. p. 124°. The *semicarbazone*,  $C_{12}H_{15}O_4N_3$ , has m. p. 180°. The ketone does not give an hydroxamic acid with Piloty's acid.

The  $\beta$ -ketone of *isomyristicin* was prepared by Hoering's method (*Abstr.*, 1905, i, 902). When the dibromo-derivative of *isomyristicin* is heated with water and acetone in the presence of calcium carbonate (marble) for two hours, the acetone solution separated, and heated for a further two hours and then distilled,  $\beta$ -bromo- $\alpha$ -hydroxydihydroisomyristicin,  $C_{11}H_{13}O_4Br$ , is obtained. It is a very dense, yellowish-brown oil, with a pungent odour, and it cannot be crystallised or distilled in a vacuum. On treatment of this substance with alcoholic potassium hydroxide, a glycol,  $OH \cdot CHR \cdot CHMe \cdot OH$ , should be produced, from which the oxide,  $Ar \cdot CH \cdot CHMe$ , and finally its



isomeride, the  $\beta$ -ketone,  $Ar \cdot CH_2 \cdot COMe$ , could be obtained. Actually, the raw product of the reaction does not combine with bisulphite, and it gives analytical figures intermediate between those required by the glycol,  $C_{11}H_{14}O_6$ , and the oxide,  $C_{11}H_{12}O_4$ , but when it is distilled in a vacuum, most of it passes over at 230—240°/30 mm.; the distillate readily crystallises, and has m. p. 44—45°. After recrystallisation, it forms long, silky needles, m. p. 54—55°, and gives on analysis numbers corresponding with the formula  $C_{11}H_{12}O_4$ . This substance gives a bisulphite compound, and is evidently the  $\beta$ -ketone. The isomerisation of the oxide is best effected by heating the substance in glacial acetic acid with a few drops of concentrated sulphuric acid, and purifying the product by way of the bisulphite compound. The *semicarbazone*,  $C_{12}H_{15}O_4N_3$ , has m. p. 143—144°. The *oxime*,  $C_{11}H_{13}O_4N$ , crystallises in tufts of prisms, m. p. 111—112°. The  $\beta$ -ketone was also prepared by reduction of  $\beta$ -nitroisomyristicin and hydrolysis of the oxime produced.

Numerous attempts were made by various methods to polymerise *isomyristicin*. In only one case was any new product obtained. When *isomyristicin* is heated for five to ten minutes in glacial acetic acid solution with a trace of concentrated sulphuric acid, a substance

is obtained, which crystallises in small prisms, m. p. 232—233°, and may be the dimeric form of *isomyristicin*. The yield is less than 2%.

R. V. S.

**Constitution of Chrysophanic Acid.** EUGÈNE LÉGER (*Compt. rend.*, 1912, 154, 281—283. Compare Robinson and Simonsen, *Trans.*, 1909, 95, 1085; Oesterle, *Abstr.*, 1911, i, 887).—In order to determine the position of the methyl group in chrysophanic acid, the tetra-nitro-derivative was oxidised with nitric acid (D 1·5). 2 : 4 : 6-Trinitro-3-hydroxybenzoic acid was isolated from the products, but chrysammic acid could not be detected. It follows that the nitro- and hydroxy-groups in tetranitrochrysophanic acid occupy the same positions as they do in tetranitroaloe-emodin, and therefore that the methyl group in chrysophanic acid can only occupy the position assigned to it by Fischer, Falco, and Gross (*Abstr.*, 1911, i, 309). Chrysophanic acid is therefore 1 : 8-dihydroxy-3-methylanthraquinone. This conclusion is confirmed by fusing the acid with potassium hydroxide, when 5-hydroxy-*isophthalic* acid is formed, together with a much smaller amount of 4-hydroxy-*isophthalic* acid and other substances.

W. O. W.

**Preparation of Anthraquinone Derivatives Containing Sulphur.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 239762).—When diazotised aminoanthraquinones are treated with thio-carbamides, intermediate compounds are formed, which evolve ammonia on treatment with potassium hydroxide, and furnish the corresponding mercaptan. *Carbamylthiolanthraquinone*,  $C_{14}H_7O_2 \cdot S \cdot CO \cdot NH_2$ , orange, yellow crystals, was prepared from  $\alpha$ -aminoanthraquinone and thio-carbamide, whilst with phenylthiocarbamide a similar compound was produced.

F. M. G. M.

[Preparation of Benzoylaminoanthraquinone Derivatives.] FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 240079).—The preparation of benzoylaminoanthraquinones and their condensation products has previously been described; it is now found that more valuable colouring matters are produced by employing nitrobenzoyl chlorides, subsequently reducing the nitro-group and combining with another molecule of benzoyl chloride before condensing to form the dye.

*Benzoyl-p-aminobenzoyl-1-aminoanthraquinone*, yellow crystals, m. p. 315°, is prepared by benzoylating *p*-aminobenzoyl-1-aminoanthraquinone in nitrobenzene solution; *benzoyl-p-aminobenzoyl-2-aminoanthraquinone* has similar properties.

The tinctorial properties of the following final condensation products are tabulated in the original; *p*-aminobenzoyl-1-aminoanthraquinone with succinic acid, m. p. above 300°, with anthraquinonecarbonyl chloride, m. p. 280°, and with 2-anthraquinonylcarbonyl chloride, m. p. above 300°.

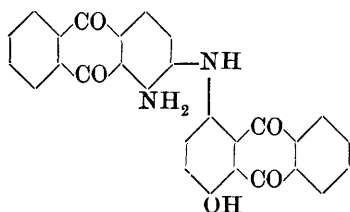
*p*-Aminobenzoyl-2-aminoanthraquinone with 2-anthraquinonylcarbonyl chloride.

*m*-Aminobenzoyl-1-aminoanthraquinone with 2-anthraquinonylcarbonyl chloride, m. p. 285°.

3:5-Diaminobenzoyl-1-aminoanthraquinone with 2-anthraquinonyl-carbamyl chloride (2 mols.), m. p. 235°.

*Benzoylaminoanthraquinonecarboxy-1-aminoanthraquinone* has m. p. above 300°. F. M. G. M.

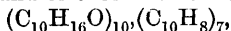
**Preparation of *o*-Aminodianthraquinonylamine Types of Compounds.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 240276).—The *product* (annexed formula), dark blue needles, was



prepared by boiling together 1-amino-4-hydroxyanthraquinone (10 parts), naphthalene (100 parts), anhydrous sodium acetate (5 parts), copper powder (0.2 part), and slowly adding 2-bromo-1-aminoanthraquinone (5 parts); when the latter component is replaced by 2-bromo-1-methylaminoanthraquinone a similar *compound* is

obtained, likewise from  $\alpha$ -amino-4-hydroxyanthraquinone with 1:3-dibromo-2-aminoanthraquinone, and from  $\alpha$ -aminoanthraquinone with 2-bromo-1-aminoanthraquinone. F. M. G. M.

**A Supposed Compound of Camphor and Naphthalene.** JOUNIAUX (*Bull. Soc. chim.*, 1912, [iv], 11, 129—132).—When naphthalene containing increasing quantities of camphor is melted and allowed to cool, the temperature at which solidification begins falls steadily from 80° to 32.5°, at which point the mixture contains 58 mols. of camphor to 42 mols. of naphthalene; a similar fall, reaching the same point at the same composition, occurs when increasing quantities of naphthalene are added to camphor. For every mixture, the finishing point of solidification is 32.5°. In view of these facts Girard's supposed compound of these two substances,



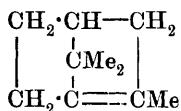
m. p. 32.6° (*J. Pharm. Chim.*, 1891, [v], 24, 105), appears to have been a eutectic mixture. T. A. H.

**Constitution of *iso*Fenchocamphoric Acid and of Some Compounds of the Fenchone Series.** OSSIAN ASCHAN [with W. SJÖSTRÖM and A. PETERSON] (*Annalen*, 1912, 387, 1—85).—The fractions obtained from a very large quantity of pinolene, b. p. below 150° (Abstr., 1907, i, 630), have been separately oxidised by 8% potassium permanganate at 60—80°, whereby carbonic, oxalic, and *dl*-camphoric acids are produced. From these facts and from the molecular refractions of the various fractions, the author deduces that pinolene contains at least three hydrocarbons: (i) *r*-bornylene, b. p. 148—149°, m. p. 40—42°, which yields *dl*-camphoric acid by oxidation; (ii)  $\alpha$ -pinolene, b. p. 144—146°, a dicyclic terpene, and (iii)  $\beta$ -pinolene (*cyclofenchene*),  $\text{C}_{10}\text{H}_{16}$ , a tricyclic terpene, which probably contains a trimethylene ring on account of its stability towards potassium permanganate.

$\beta$ -Pinolene (*cyclofenchene*), obtained from the pinolene fractions, b. p. 140—142° and 142—144°, by oxidation as above, has b. p.

141.5—143.5°,  $D_4^{20}$  0.8588,  $[\alpha]_D + 0.28^\circ$ , and  $n_D^{20}$  1.44769; its molecular refraction, therefore, exceeds by about 0.6 the value calculated for a tricyclic terpene, a fact which furnishes additional evidence for the presence of a trimethylene ring. By further prolonged oxidation with potassium permanganate,  $\beta$ -pinolene yields a very small quantity of *isophthalic acid*. This may be due to the presence of a little  $\alpha$ -pinolene; its formation, however, shows that the pinolene hydrocarbons can be converted into benzene derivatives of the meta-series.  $\beta$ -Pinolene in dry ether at  $-15^\circ$  forms an unstable, crystalline *hydrochloride*,  $C_{10}H_{16}\cdot HCl$ , m. p. 27.5—29°.

$\alpha$ -Pinolene hydrochloride, m. p. 38°, has been previously described as pinolene hydrochloride (*loc. cit.*).  $\alpha$ -Pinolene probably has the annexed formula; the halogen atom in its hydrochloride is attached to the CMe group.

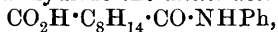


$\beta$ -Pinolene is unchanged by eight hours' boiling with 20% sulphuric acid, but when heated for four hours with 96% alcohol and 96% sulphuric acid yields a dicyclic *ether*,  $C_{10}H_{17}\cdot OEt$ , b. p. 197—200°,  $D_4^{20}$  0.8904,  $n_D^{20}$  1.45217.

Fractions, b. p. 144.5—146° and 146—148° respectively, of unoxidised pinolene, purified  $\beta$ -pinolene, and also *isopinene*, have been separately treated at 60—70° with glacial acetic and 50% sulphuric acids by Bertram and Walbaum's method, and the resulting acetates have been hydrolysed. In each case the main product is *dl-isofenchyl alcohol* (m. p. 43—44°), identified as the phenylurethane, m. p. 95—96°. In the case of the fraction, b. p. 146—148°, a little *isoborneol* is obtained (produced probably from the *r*-bornylene), whilst from the purified  $\beta$ -pinolene a mixture of *dl-isofenchyl* and *dl-fenchyl alcohols* is formed. By oxidation with potassium permanganate, therefore, the mixture yields *dl-isofenchone* and *dl-fenchone*, in addition to the chief product, *dl-isofenchocamphoric acid* (Wallach, *Abstr.*, 1908, i, 809). These facts prove that *dl-isofenchyl alcohol* is the chief product of the hydration of the mixture of fenchenes (consisting mainly of *isopinene*) obtained from  $\alpha$ - and  $\beta$ -pinolenes. A diagrammatic representation of the transformations is given.

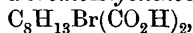
A description is given of the preparation in quantity and the purification of *dl-isofenchocamphoric acid*. It is best obtained from the pinolene fraction, b. p. 140—150°, which is converted into *iso-fenchyl alcohol* as above; the alcohol is then oxidised by alkaline 5% potassium permanganate without warming.

The constitution,  $\text{CH}_2 < \begin{array}{l} \text{CH}(\text{CO}_2\text{H}) - \text{CMe}_2 \\ \text{CMe}(\text{CO}_2\text{H}) \cdot \text{CH}_2 \end{array}$ , is ascribed to *isofenchocamphoric acid* on the following grounds. The saturated dibasic acid readily forms an *anhydride*, m. p. 94—95°, by distillation or by treatment with acetyl chloride; the acid, therefore, has the *cis*-configuration. From the anhydride the *anilic acid*,



m. p. 191—192°, *ethyl ester*,  $\text{C}_8\text{H}_{14}(\text{CO}_2\text{Et})_2$ , b. p. 267—268°,  $D_4^{20}$  1.0054,  $n_D^{21}$  1.44626, *methyl hydrogen ester*, m. p. 72—74°, and *ethyl hydrogen ester*, b. p. 289—292° (decomp.), are prepared. The distillation of the

calcium salt,  $C_{10}H_{14}O_4Ca$ , does not produce a cyclic ketone, indicating that the acid is a substituted succinic or glutaric acid. When heated with acetic and hydrochloric acids at  $180^\circ$  for ten hours, *dl-cis-isofenchocamphoric* acid is transformed into the less soluble *trans-isomeride*, m. p.  $169-170.5^\circ$ ; hence, one of the carboxyl groups is attached directly to a ring carbon atom. When *dl-cis-isofenchocamphoric* acid is treated with phosphorus pentachloride and the product is brominated as in the case of camphenic acid (Abstr., 1910, i, 709), two stereoisomeric  *$\alpha$ -bromoisofenchocamphoric acids*,

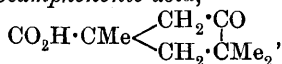


m. p.  $208-210^\circ$  and  $160-162^\circ$  respectively, are obtained. (The author's explanation of the production of the two stereoisomerides is given below.) The former acid, which is the main product, yields an *anhydride*, m. p.  $97^\circ$ , and an *ethyl ester*, b. p.  $155-156^\circ/5$  mm.,  $D_{15}^{25} 1.2425$ , and by reduction with zinc and acetic acid regenerates *dl-cis-isofenchocamphoric* acid. The introduction of only one bromine atom, even when an excess of the halogen is employed, indicates that there is only one hydrogen atom in the  $\alpha$ -position to a carboxyl group, whilst the formation of the two stereoisomerides is regarded as evidence that the carbon atom, to which this hydrogen atom is attached, forms part of the alicyclic ring. Other facts in harmony with the preceding constitution of *isofenchocamphoric* acid are the following. When heated with aqueous sodium carbonate or barium hydroxide, the  $\alpha$ -bromo-acid, m. p.  $208-210^\circ$ , yields *isofencholauronic*

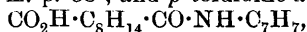
*acid*,  $CO_2H \cdot CMe \begin{smallmatrix} CH=CH \\ CH_2 \cdot CMe_2 \end{smallmatrix}$ , m. p.  $44-45^\circ$ ,  *$\alpha$ -hydroxyisofenchocamphoric acid*,  $C_8H_{13}(OH)(CO_2H)_2$ , m. p.  $185-186^\circ$  (decomp.), and *dehydroisofenchocamphoric acid*,  $C_8H_{12}(CO_2H)_2$ , m. p.  $189-190^\circ$ ; methods for the separation of these three acids are described. The same three acids are produced by the action of aqueous barium hydroxide on the  $\alpha$ -bromo-acid, m. p.  $160-162^\circ$ . When heated above its m. p. or warmed with 50% sulphuric acid,  *$\alpha$ -hydroxyisofenchocamphoric* acid is converted into the lactonic acid, *isofenchocamphanic*

*acid*,  $C_7H_{18} \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ C(CO_2H) \end{smallmatrix} O$ , m. p.  $177^\circ$ , which is also produced by heating the  $\alpha$ -bromo-acid, m. p.  $208-210^\circ$ , with quinoline at  $160^\circ$  (best method), and is re-converted into  *$\alpha$ -hydroxyisofenchocamphoric* acid by boiling 10% potassium hydroxide.

*$\alpha$ -Hydroxyisofenchocamphoric* acid is oxidised by lead dioxide and acetic acid to *isofenchocamphononic acid*,

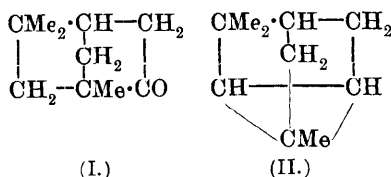


m. p.  $68-70^\circ$ , which forms a *semicarbazone*,  $C_{10}H_{17}O_3N_3$ , m. p.  $221^\circ$ . Finally, the fusion of  *$\alpha$ -hydroxyisofenchocamphoric* acid with potassium hydroxide at the lowest possible temperature yields formic acid and an *acid*,  $C_9H_{16}O_4$ , m. p.  $192-193^\circ$ , which is regarded as identical with Michailenko and Jaworski's  $\alpha\gamma\gamma$ -tetramethylglutaric acid, m. p.  $185-189^\circ$ , on account of its stability towards bromine and the formation of an anhydride, m. p.  $88^\circ$ , and *p*-toluidino-acid,

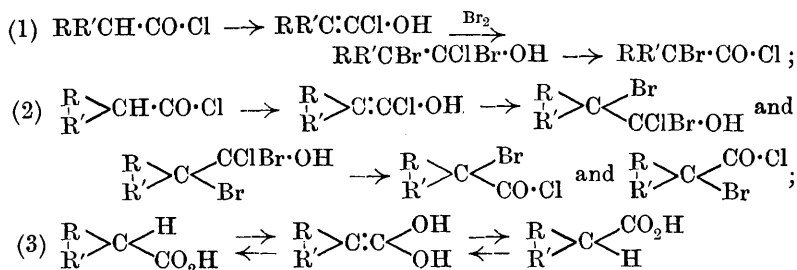


m. p.  $160-161^\circ$ .

From the preceding constitution of *isofenchocamphoric acid*, it follows that *isofenchone* and  $\beta$ -pinolene probably have the constitutions (I) and (II) respectively; the latter can produce fenchyl and *isofenchyl* alcohols by fission of the trimethylene ring and the addition of water in the two possible ways.



The author assumes the transformation  $>\text{CH} \cdot \text{CO} \cdot \rightarrow >\text{C}:\text{C}(\text{OH}) \cdot$  to account for the bromination of aliphatic acids (or, better, their chlorides), the formation of two stereoisomeric  $\alpha$ -bromo-acids by the bromination of alicyclic acids, and the transformation, without substitution, of geometric isomerides; thus:



Although this explanation is equally applicable to transformations of the maleic-fumaric acid type, the author prefers, in such cases, Wislicenus' explanation, because the additive capacity of an ethylenic linking so greatly exceeds that of the carbonyl group in a carboxylic group. C. S.

**Constitution of Camphene.** KARL AUWERS (*Annalen*, 1912, 387, 240—253).—See this vol., ii, 214.

**The Constituents of Ethereal Oils (Derivatives of Natural Cedrene).** FRIEDRICH W. SEMMLER and FELIX RISSE (*Ber.*, 1912, 45, 355—360. Compare Semmler and Hoffmann, *Abstr.*, 1907, i, 946).—Natural cedrene has been oxidised on a larger scale than previously by the action of ozone. The main neutral products are a ketone,  $\text{C}_{14}\text{H}_{24}\text{O}$  or  $\text{C}_{14}\text{H}_{22}\text{O}$ , b. p. 120—130°/13 mm. (semicarbazone, m. p. 218°), and the ketonic aldehyde,  $\text{C}_{15}\text{H}_{24}\text{O}_2$  (*loc. cit.*); the chief constituent of the acidic portion of the oxidation product is cedrene-ketonic acid (*loc. cit.*), b. p. 205—215°/10 mm. (methyl ester, b. p. 165—170°/10 mm.,  $D_{20}^{20}$  1.0509,  $n_D^{20}$  1.4882,  $\alpha_D - 32.4^\circ$  at 20°).

The ketonic acid is probably a methyl-ketonic acid, as it is oxidisable by sodium hypobromite to the dibasic acid, *cedrenedicarboxylic acid*, m. p. 182.5°; the methyl ester (*loc. cit.*) has b. p. 179—183°/13 mm.,  $D_{20}^{20}$  1.0778,  $n_D^{20}$  1.48084,  $\alpha_D - 31.6^\circ$ . D. F. T.

**Synthesis of an Aliphatic Terpene.** C. J. ENKLAAR (*Chem. Weekblad*, 1912, 9, 68—72. Compare *Abstr.*, 1909, i, 690).—A description of a method for the preparation of labile hydrocarbons of the

olefine series from tertiary alcohols, of the formation of an aliphatic terpene by the dehydration of linalool, and of the behaviour of this product on hydrogenation and ozonisation.

When linalool is brought into contact with active copper at 130—140° in a rapid current of carbon dioxide, the formation of a cyclic hydrocarbon is in large measure obviated, the main product being an aliphatic *hydrocarbon*. The copper was obtained in a very active condition by reducing copper oxide with hydrogen, the oxide being prepared by gentle ignition of copper nitrate. The excess of hydrogen was expelled by carbon dioxide at 170°. The hydrocarbon was separated from the unchanged linalool by repeated vacuum distillation, finally over sodium. It is a liquid,  $D^{15}_4$  0.804. Acetaldehyde, geraniol, and citral were by-products.

The same hydrocarbon was obtained by heating linalool with phenyl-carbimide:  $2\text{CO:NPh} + \text{C}_{10}\text{H}_{18}\text{O} = \text{CO(NHPh)}_2 + \text{C}_{10}\text{H}_{16} + \text{CO}_2$ . The yield is best with a slight excess of linalool and a temperature of 150—170°, a non-volatile brown oil being obtained as by-product. When the carbimide was in excess, the proportion of this oil was increased by 50%. The hydrocarbon had  $D^{15}_4$  0.811. The substance was not obtained quite pure, but the following physical constants are given:  $D^{15}_4$  0.802,  $n^{15}_D$  1.470, b. p. 62°/14 mm., hence it is probably myrcene.

Reduction with nickel and hydrogen at 130° and fractionation of the product yielded a decane, b. p. 159—160°/760 mm. (uncorr.),  $D^{15}_4$  0.739, identical with  $\beta\zeta$ -dimethyloctane obtained from ocimene (Abstr., 1908, i, 664). Reduction with sodium and alcohol yielded a hydrocarbon with the odour and b. p. (165—167°) of dihydromyrcene. This substance probably has the formula  $\text{C}_{10}\text{H}_{18}$ , because bromination by Baeyer and Villiger's method yielded a crystalline bromide, m. p. 88°, which produced no depression in the m. p. of dihydro-ocimene tetrabromide (compare *Rec. trav. chim.*, 1907, 26, 167, and 27, 448).

Ozonisation of the terpene by the method previously described (*ibid.*, 1908, 27, 422) precipitated an explosive *ozonide*, inflamed by concentrated sulphuric acid, and decomposed by water with formation of acetone, probably succinic acid, and other products not identified.

The impure hydrogenation product yielded an *ozonide* with similar properties. The liquid obtained by the action of water gave the pyrrole reaction distinctly, and probably contained acetone peroxide.

A. J. W.

**Reduction of Sabinene.** OTTO WALLACH (*Chem. Zentr.*, 1911, ii, 1802; from *Nachr. K. Ges. Wiss. Göttingen*, 1910, 544).—In the presence of metallic catalysts, sabinene takes up 2 atoms of hydrogen with the formation of *dihydrosabinene*,  $\text{CH}_2 \begin{array}{c} \text{CH}\cdot\text{CHMe} \\ | \\ \text{CPr}-\text{CH}_2 \end{array} \text{CH}_2$ , having b. p. 156—157°,  $D^{20}_4$  0.8120,  $n^{20}_D$  — 2°2'.

W. P. S.

**Leaf-Oil of the Washington Cedar (*Thuja plicata*).** ROBERT E. ROSE and CARL LIVINGSTON (*J. Amer. Chem. Soc.*, 1912, 34, 201—202).—As only a superficial examination of the oil obtained from the leaves of *Thuja plicata* (Brandel, *Pharm. Rev.*, 26, 248) has hitherto

been made [compare, however, Blasdale, Abstr., 1907, i, 630], a detailed study has now been carried out.

On distillation with steam, the leaves and twigs yielded about 1% of light yellow oil, which had a cedar-like odour,  $D_{20}^{20}$  0.913,  $n_D^{20}$  1.4552,  $[\alpha]_D^{20}$  -4.77°; acid number, 0.518; ester number, 2.28; saponification number, 2.8, and acetylation number, 8.8. The product was free from phenols, soluble in all proportions in 70% alcohol, and about 85% of it boiled at 100—110°/40 mm. The oil contains tanacetone 80—85%, pinene 3—5%, tanacetyl acetate 1—2%, and tanacetyl alcohol 1—3%.

E. G

**The Chemical Degradation of Chitin.** HUGO BRACH (*Biochem. Zeitsch.*, 1912, 38, 468—491).—A description is given of the preparation of the material from *Nephrops norvegicus*. The analyses showed that the substance had a composition corresponding with the formula  $C_{32}H_{54}O_{21}N_4$ . The estimation of the acetyl groups by a modification of Wenzel's method, which is described by the author, showed that for each nitrogen in the atom there exists an acetyl group. The results indicate that the simplest formula for chitin is one made up of a complex of four acetylglucosamine groups. Lenk's chitosan appears to be formed from chitin by the scission of half the acetyl groups. By the action of nitrous acid, the whole of the nitrogen in the molecule can be eliminated, a fact which the author shows does not contradict the assumption of the presence of acetylamino-groups. S. B. S.

**Constitution of Rhein.** OTTO A. OESTERLE (*Chem. Zentr.*, 1912, i, 142—143; from *Schweiz. Woch. Chem. Pharm.*, 1911, 49, 661—665).—Contrary to the view of the author and Riat (Abstr., 1909, i, 946) that aloë-emodin and its most nearly related derivatives are derived from 1:8-dihydroxyanthraquinone (chrysazin), Robinson and Simonsen (Trans., 1909, 95 1085) regard 1:6-dihydroxyanthraquinone (isochrysazin) as the parent substance of rhein. The author, therefore, has converted rhein through *rhein chloride*, yellow needles, and the *amide*, dark red needles, into an *aminodihydroxyanthraquinone*,  $C_{14}H_9O_4N$ , m. p. 255° or 258°, red needles, from which, by elimination of the amino-group, impure 1:8-dihydroxyanthraquinone, m. p. 182—183° instead of 191—192° (acetate, m. p. 232°), has been obtained. C. S.

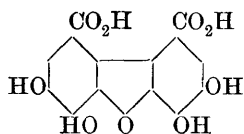
**Phylloxanthin.** LEON MARCHLEWSKI (*Ber.*, 1912, 45, 24—25).—The phylloxanthin described by Schunck (Abstr., 1885, 1241) is shown to be identical with *allochlorophyllan* (Marchlewski and Marszałek, Abstr., 1911, i, 735). Phylloxanthin yields 30.02% of phytol instead of 31.8%. On prolonged exposure to concentrated hydrochloric acid, phylloxanthin is converted into basic products, including a substance soluble in 20% hydrochloric acid.

A more recent preparation of phylloxanthin gave a solid substance instead of phytol on hydrolysis. E. F. A.

**Tannin. VIII.** MAXIMILIAN NIERENSTEIN (*Annalen*, 1912, 386, 318—332. Compare Abstr., 1910, i, 265).—Purpurotannin, the

amorphous, red oxidation product of penta-acetyl-leucotannin (Abstr., 1909, i, 402), has the composition  $C_{14}H_8O_9$ , forms a *quinoline* salt,  $C_{14}H_8O_9 \cdot 2C_9NH_7$ , dark red needles, and dissolves unchanged in boiling 2*N*-potassium hydroxide. It forms a *tetra-acetate*, m. p. 324—327°

(decomp.), *tetrabenzoate*, m. p. 279—281° (decomp.), and *tetramethyl ether*,  $C_{14}H_4O_5(OMe)_4 \cdot H_2O$ , m. p. 242—244° (decomp.), and yields diphenylene, not naphthalene, as stated (*loc. cit.*), by distillation with zinc dust. It is shown to be 1:2:7:8-*tetrahydroxydiphenyleneoxide* - 4:5-



*dicarboxylic acid* (annexed formula). When heated with piperidine (but not with quinoline) at 180°, it yields 1:2:7:8-*tetrahydroxydiphenylene oxide*,  $C_{12}H_8O_5$ , red needles, m. p. 334—338° (decomp.) (*tetra-acetate*, m. p. 247—251°), whilst by reduction with hydriodic acid and phosphorus at 180° it is converted into diphenylene oxide.

A course of formation of purpurotannin from leucotannin is suggested. The cause of its colour will be discussed later; apparently it is connected with the presence of hydroxyl groups in the periposition to the oxygen of the furan ring. C. S.

"Luteo-acid" (A Correction). MAXIMILIAN NIERENSTEIN (*Ber.*, 1912, 45, 365).—The analytical results for the composition of "luteo-acid" (pentahydroxydiphenylmethylolidecarboxylic acid) (Abstr., 1908, i, 897; 1909, i, 174; 1910, i, 265, 389) were low in the percentage of carbon; as the more carefully dried substance gives results agreeing well with the formula  $C_{14}H_8O_9$ , it is probable that the earlier discrepancies were due to occluded solvent. D. F. T.

Decomposition of Alkylidenehydrazines. Conversion of Furfuraldehyde into 2-Methylfuran. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1563—1565).—When heated in presence of a small quantity of potassium hydroxide, furfurylidenehydrazine decomposes, giving nitrogen and 2-methylfuran, a colourless liquid, b. p. 64°/757 mm.,  $D_4^{20}$  0.9159,  $n_D$  1.4344. The constants given for this compound by Atterberg (Abstr., 1880, 663) and by Harries (Abstr., 1898, i, 232) are inaccurate, doubtless on account of impure products being examined. T. H. P.

Coumarandione, the Oxygen Analogue of Isatin. KARL FRIES and W. PFAFFENDORF (*Ber.*, 1912, 45, 154—162. Compare Abstr., 1910, i, 186; also Stoermer, *ibid.*, 1909, i, 174, and following abstract).—Coumaran-1:2-dione,  $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown CO \end{smallmatrix} CO$ , is readily prepared by heating a solution of *o*-hydroxyphenylglyoxylic acid in light petroleum with phosphoric oxide, or by distilling the acid under diminished pressure. It crystallises in large, yellow, prismatic plates, m. p. 134°, b. p. 142°/17 mm., and dissolves in concentrated sulphuric acid, yielding a yellowish-red solution, which gradually becomes colourless owing to the loss of carbon monoxide and conversion of the diketone into salicylic acid.

With *o*-phenylenediamine it yields 2-hydroxy-3-hydroxyphenylquinoxaline (Marchlewski and Sosnowski, Abstr., 1901, i, 415). On exposure to air it takes up water with the formation of *o*-hydroxyphenylglyoxylic acid or its hydrate, m. p. 43°.

When heated at 220° under ordinary pressure, it loses carbon monoxide, yielding a ruby-red glassy mass, which sinters at 150°, forms a transparent, viscid liquid at 200°, and finally becomes mobile at 240°. The latter substance is hydrolysed by alkalis in alcoholic solution to salicylic acid, and gives a colloidal solution in chloroform. It probably consists of a polymeric *salicylide*, which, however, is different from the polymerides described previously.

*Ethyl o-hydroxyphenylglyoxylate*,  $C_{10}H_{10}O_4$ , prepared by boiling coumarandione in alcoholic solution, is a yellow oily liquid, which solidifies in a freezing mixture, m. p. 15°. It readily loses alcohol yielding the original ketone.

*Coumaran-1:2-dione-2-phenylhydrazone*,  $O\langle\begin{smallmatrix} C_6H_4 \\ CO \end{smallmatrix}\rangle C:N\cdot NPh$ ,

obtained from its components in glacial acetic acid solution, crystallises in lustrous, yellow plates, m. p. 185°, and is hydrolysed by alkalis in alcoholic solution to the *phenylhydrazone* of *o*-hydroxyphenylglyoxylic acid,  $C_{14}H_{12}O_3N_2$ . This crystallises in light yellow needles, m. p. 148° (decomp.), and is also obtained by heating *o*-hydroxyphenylglyoxylic acid with phenylhydrazine in aqueous solution. It readily loses water, yielding coumarandione-2-phenylhydrazone.

The *anil* of *o*-hydroxyphenylglyoxylic acid,  $C_{14}H_{11}O_3N$ , prepared by heating coumarandione with aniline in benzene or alcoholic solution, crystallises in pale yellow plates, m. p. 102°, and shows no tendency to form a lactone; the *acetyl* derivative has m. p. 138°.

The *p*-dimethylaminoanil,  $OH\cdot C_6H_4\cdot C(N\cdot C_6H_4\cdot NMe_2)\cdot CO_2H$ , crystallises in dark red needles of a metallic lustre, m. p. 153°; the *mono-sodium* salt and *monohydrochloride*, crystallising in yellow prisms, are mentioned. On treatment with phenylhydrazine, the *p*-dimethylaniline residue is eliminated with the formation of the phenylhydrazone of *o*-hydroxyphenylglyoxylic acid. With *o*-phenylenediamine it yields 2-hydroxy-3-hydroxyphenylquinoxaline.

When hydrolysed with aqueous alcoholic sodium hydroxide and the resulting solution neutralised with acetic acid, coumaran-1:2-dione-1-*p*-dimethylaminoanil (Fries and Hasselbach, Abstr., 1911, i, 151) is converted into *o*-hydroxyphenylglyoxyl-*p*-dimethylaminoanilide,  $OH\cdot C_6H_4\cdot CO\cdot CO\cdot NH\cdot C_6H_4\cdot NMe_2$ , which, however, could not be obtained in a pure condition, and was, therefore, characterised by means of its *benzoyl* derivative,  $C_{23}H_{20}O_4N_2$ , stout, red prisms, m. p. 138°.

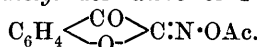
With excess of bromine in glacial acetic acid solution, coumarandione yields 3:5-dibromo-2-hydroxyphenylglyoxylic acid, which has m. p. 148° (decomp.) (compare Abstr., 1910, i, 332), and forms a *hydrate*,  $C_8H_4O_4Br_2\cdot H_2O$ , crystallising in slender, pale yellow needles, m. p. 110°.

1-Bromo-2-coumaranone,  $C_8H_5O_2Br$ , prismatic needles, m. p. 87°, and 1:1-dibromo-2-coumaranone,  $C_8H_4O_2Br_2$ , pale yellow needles, m. p. 142°, are obtained by brominating 2-coumaranone in carbon tetra-

chloride solution. When warmed with sulphuric acid, the dibromo-compound is converted into coumarandione, and finally into salicylic acid. On treatment with *o*-phenylenediamine it yields coumaro-phenazine. 1:1-Dichloro-2-coumaranone, prepared by chlorinating 2-coumaranone in glacial acetic acid solution, forms white, prismatic needles, m. p. 70°.

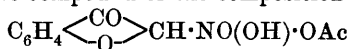
F. B.

**Coumarandione, the Analogue of Isatin in the Coumarone Series. A Correction.** RICHARD STOERMER (*Ber.*, 1912, 45, 162—163. Compare preceding abstract).—The compound described previously (*Abstr.*, 1909, i, 174) as the hydrate of coumarandione is now found to be the *acetyl* derivative of 1-oximino-2-coumaranone,



It is shown that the substance is formed by the action of acetic acid on *aci*-nitrocoumaranone, and not by the oxidation of "*leuco*-oxindigo," as previously supposed.

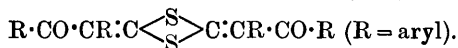
With respect to the mechanism of the reaction, the author imagines that an intermediate compound of the composition



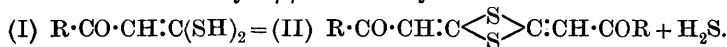
is first produced by the combination of acetic acid and *aci*-nitrocoumaranone, and that this is subsequently reduced by the nitrous acid formed by the spontaneous decomposition of the *aci*-nitro-compound, loss of 1 mol. of water taking place simultaneously.

F. B.

**Constitution of the Desaurins.** C. KELBER and A. SCHWARZ (*Ber.*, 1912, 45, 137—147).—By the interaction of carbon disulphide, potassium hydroxide, and ketones of the type  $\text{R} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{R}$ , Meyer (*Abstr.*, 1888, 484; 1890, 1144; 1892, 340, 1127) obtained a number of desaurins, to which he ascribed the constitution:



This formula has now been confirmed by the synthesis of similarly constituted desaurins (II) by the removal of hydrogen sulphide from 2 mols. of the aryl  $\beta\beta$ -dithiolvinyl ketones of the formula I:



A number of desaurins of the type  $\text{R} \cdot \text{CO} \cdot \text{CMe} : \text{C} \begin{array}{c} \diagup \text{S} \diagdown \\ \diagdown \text{S} \diagup \end{array} \text{C} : \text{CMe} \cdot \text{COR}$  have also been prepared by heating aryl ethyl ketones,  $\text{R} \cdot \text{COEt}$ , with carbon disulphide and finely-powdered potassium hydroxide.

The compound,  $\text{COPh} \cdot \text{CH} : \text{C} : \text{S}_2 : \text{C} : \text{CH} \cdot \text{COPh}$ , is obtained in small yield by heating phenyl  $\beta\beta$ -dithiolvinyl ketone (Kelber, *Abstr.*, 1910, i, 390) at 100°. It is also produced together with carbon oxysulphide, benzophenone, and benzoyl sulphide by rapidly heating the dibenzoyl derivative of the ketone (*loc. cit.*) either alone at 210°, or in solvents of high b. p., such as ethyl benzoate or acetophenone. It crystallises from ethylene dibromide in yellow, rectangular prisms, m. p. 212—214° (decomp.), and dissolves in strong sulphuric acid, yielding orange-red solutions having an intense green fluorescence.

The *lead* salt of phenyl  $\beta\beta$ -dithiolvinyl ketone,  $C_9H_9OS_2Pb$ , is a heavy, reddish-brown powder; the *mercuric* salt,  $C_{18}H_{14}O_2S_4Hg$ , is soluble in organic solvents, and crystallises from toluene in orange needles, which have m. p. 185—190° (decomp.), with previous darkening at 130—140°. When heated in solvents of high b. p., both the lead and mercuric salts are decomposed with the formation of metallic sulphide and the above-mentioned desaurin.

The *monothiourethane*,  $COPh \cdot C_2H_5S_2 \cdot CO \cdot NHPh$ , obtained from phenyl  $\beta\beta$ -dithiolvinyl ketone and phenylthiocarbimide in benzene solution, crystallises in slender needles, m. p. 94° (decomp.), and when carefully heated gives a small yield of the corresponding desaurin.

The *compound*,  $(C_4H_3S \cdot CO \cdot CH : C)_2S_2$ , may be prepared from  $\alpha$ -thienyl  $\beta\beta$ -dithiolvinyl ketone (Abstr., 1911, i, 740) by methods similar to those employed in the case of the preceding desaurin. It crystallises in moss-like aggregates of slender, yellow needles, which decompose at 260° with previous darkening, and yields with sulphuric acid deep red solutions having a green fluorescence.

The *mercuric* salt of  $\alpha$ -thienyl  $\beta\beta$ -dithiolvinyl ketone,  $C_7H_4OS_3Hg$ , is obtained from mercuric chloride and the ketone in alcoholic solution.

The *thiourethane*,  $C_4H_5S \cdot CO \cdot C_2H_5S_2 \cdot CO \cdot NHPh$ , prepared from the ketone and phenylthiocarbimide, decomposes at 80°.

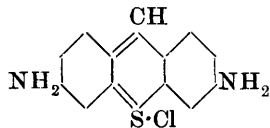
The *desaurin* from *p*-tolyl  $\beta\beta$ -dithiolvinyl ketone (*loc. cit.*) crystallises in yellow, rectangular prisms.

The *compound*,  $COPh \cdot CMe : C : S_2 : C : CMe \cdot COPh$ , prepared by heating phenyl ethyl ketone with carbon disulphide and potassium hydroxide, crystallises in lustrous, golden-yellow leaflets, m. p. 225°; the *compound*,  $(C_6H_4Me \cdot CO \cdot CMe : C)_2S_2$ , from *p*-(?)tolyl ethyl ketone in strongly refractive, yellow needles, m. p. 263—265°. The *compound*,

$(C_4H_3S \cdot CO \cdot CMe : C)_2S_2$ , from  $\alpha$ -thienyl ethyl ketone forms yellow needles, m. p. 258—260°; the *compound*,  $(C_{10}H_7 \cdot CO \cdot CMe : C)_2S_2$ , from  $\beta$ -naphthyl ethyl ketone crystallises in yellow leaflets, which have m. p. 264°, and decompose at 268—269°.

F. B.

**The Simplest Thiopyronine.** FRIEDRICH KEHRMANN and L. LÖWY (*Ber.*, 1912, 45, 290—292).—The chloride of the simplest thiopyronine, 3:6-diaminothiopyroninium chloride (annexed formula) is

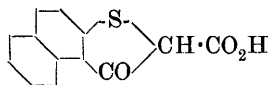


obtained in small yield by the addition of a glacial acetic acid solution of di-*p*-acetylaminodiphenylmethane to a solution of flowers of sulphur in fuming sulphuric acid at a temperature not exceeding 10°, and subsequent hydrolysis of the resulting 3:6-diacetylaminothiopyroninium sulphate (not isolated). It crystallises from alcohol in metallic green needles or prisms, which yield scarlet-red solutions having a greenish-yellow fluorescence. The *carbonate*, *acetate*, *iodide*, *dichromate*, and also the *nitrate*, crystallising in scarlet-red needles, are described; the *platinichloride*,  $(C_{13}H_{11}N_2S_2Cl)_2PtCl_4$ , was analysed.

Elimination of one of the amino-groups from the preceding chloride

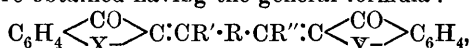
by successive treatment with nitrous acid (1 mol.) and alcohol results in the formation of apothiopyronine (3-aminothioxanthinium) chloride,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CH} \\ \text{S} \end{smallmatrix} \text{C}_6\text{H}_4$ , which was converted into a red, crystalline nitrate and platinichloride,  $(\text{C}_{13}\text{H}_{10}\text{NSCl})_2\text{PtCl}_4$ . F. B.

[Preparation of Ketonaphthathiophen.] KALLE & Co. (D.R.-P. 239093).—Derivatives of *o*-carboxynaphthylthiolacetic acids yield valuable dyes, and the following series of compounds have been prepared:  $\alpha$ -Naphthylamine-2-sulphonic acid is converted by diazotisation and subsequent treatment with copper sulphate and potassium cyanide into sodium 1-cyanonaphthalene-2-sulphonate, leaflets, which furnishes an acid chloride, long needles or prisms, m. p.  $143^\circ$ ; this when reduced with zinc dust in sulphuric acid solution and treated with chloroacetic acid yields a mixture of 1-cyanonaphthalene-2-thiolacetic acid and 1-carboxynaphthalene-2-thiolacetic acid, which can be separated by fractional crystallisation from water, when the acid is obtained in long, colourless needles, m. p.  $93^\circ$  and (when anhydrous)  $127\text{--}128^\circ$ .



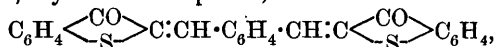
Ketonaphth thiophencarboxylic acid (annexed formula), colourless aggregates, is obtained by the fusion of the foregoing mixture with sodium hydroxide, and is converted by treatment with mineral acids into naphthoxythiophen, glistening, grey crystals, m. p.  $118\text{--}119^\circ$ . F. M. G. M.

[Preparation of Indigoid Compounds.] KALLE & Co. (D.R.-P. 239916).—When indoxyl, oxythionaphthens, or compounds of the same type (2 mols.) are condensed with a dialdehyde or diketone (1 mol.), substances are obtained having the general formula :



where R is a hydrocarbon; R', R'' hydrogen or hydrocarbon residues; X and Y alike or different atoms or groups, such as sulphur, oxygen or the imino-group.

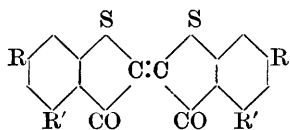
The yellow, crystalline compound,



was prepared from ketothionaphthen (2 mols.) and terephthalaldehyde (1 mol.), whilst the analogous compound obtained from the bisulphite derivative of glyoxal (1 mol.) forms brownish-yellow needles. The ketothionaphthens can be replaced by indoxyls in these reactions.

F. M. G. M.

[Preparation of "Dihalogendimethylthioindigos."] KALLE & Co. (D.R.-P. 239094).—The symmetrical "dihalogendimethylthioindigos" of the annexed general formula (where R is a halogen atom and R' a methyl group, or vice versa) are of technical value, and in this connexion the following compounds have been prepared.

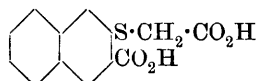
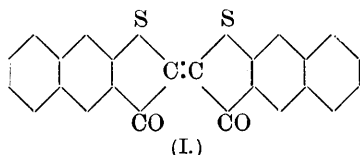


5-Chloro-3-amino-o-toluic acid, needles (prepared by the reduction of the corresponding chloronitrotoluic acid), when diazotised, xanthogenated, and treated with chloroacetic acid, yields 5-chlorophenyl-3-methyl-2-carboxyphenylthiolacetic acid, colourless needles, which on fusion with sodium hydroxide furnishes 6-chloro-3-hydroxy-4-methyl-(1)-thionaphthen-o-carboxylic acid, and subsequently on treatment with mineral acid, 6-chloro-3-hydroxy-4-methyl-(1)-thionaphthen, glistening, colourless needles.

The reaction is stated to be applicable to other halogenated nitro-toluic acids.

F. M. G. M.

[Preparation of "Naphthioindigo."] KALLE & Co. (D.R.-P. 240118).—"Naphthioindigo" (formula I) is prepared as follows:



2-amino-3-naphthoic acid is diazotised and converted successively into 2-thionaphthol-3-carboxylic acid, a yellow powder, m. p. 275—276°, and 3-carboxynaphthyl-2-thiolacetic acid (II), a colourless, crystalline powder, m. p. 203°; this when treated with alkali or acetic anhydride yields 3-keto-(1)-thioanthren, and by subsequent oxidation with potassium ferricyanide the foregoing "naphthioindigo."

F. M. G. M.

Bromo-derivatives of the Alkaloids of *Peganum harmala* and their Basic Derivatives. V. HASENFRATZ (*Compt. rend.*, 1912, 154, 215—217. Compare Fischer, *Abstr.*, 1889, 730; 1898, i, 160).—On treating harmaline, harmine, apoharmine, and methylapoharmine with bromine in acetic acid, the hydrobromides of the corresponding monobromo-derivatives are obtained. Bromoharmaline,  $C_{13}H_{13}ON_2Br$ , crystallises in colourless, slender needles, m. p. 195°; the hydrochloride and platinichloride are yellow. In the case of harmine, two isomeric compounds are formed, and may be separated by heating the hydrobromides at 50°, bromoharmine hydrobromide alone fusing at this temperature. Bromoharmine,  $C_{13}H_{11}ON_2Br$ , occurs in orthorhombic prisms, m. p. 275°; the salts crystallise from alcohol, but form jellies with water. isobromoharmine crystallises in long needles, m. p. 203°, and its salts crystallise from water; the platinichloride is orange-red. Bromoapoharmine,  $C_8H_7N_2Br$ , crystallises in long needles, m. p. 229°, and bromomethylapoharmine,  $C_9H_9N_2Br$ , in needles, m. p. 196°.

On brominating harmine in presence of sulphuric acid, and suspending the product, Fischer's supposed tetrabromide, in hot dilute alcohol, slender needles of dibromoharmine monohydrobromide are obtained; when treated with ammonia this gives dibromoharmine,  $C_{13}H_{10}ON_2Br_2$ , m. p. 209°. Fischer's compound appears to be the dihydrobromide of this base.

W. O. W.

Preparation of a Compound of Codeine with Diethylbarbituric Acid. KNOLL & Co. (D.R.-P. 239313).—Codeine

*diethylbarbiturate*, prisms, m. p.  $85^{\circ}$ , is readily prepared by mixing molecular proportions of codeine and diethylbarbituric acid (veronal) in aqueous or alcoholic solution, or by intimately mixing codeine hydrochloride with sodium diethylbarbiturate in the absence of solvents.

F. M. G. M.

**Degradation of Sparteine. Formation of a Hydrocarbon: Sparteilene.** CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1912, 154, 161—163. Compare Abstr., 1908, i, 43, 44, 563).—When methylhemisparteine is treated with methyl iodide, the product has the composition,  $C_{15}H_{22}N_2Me_2I$ , but appears to consist of a mixture of at least two isomerides. On treatment with silver oxide, it gives a quaternary ammonium base, which, on heating in a vacuum, yields inactive *dimethylhemisparteilene*,  $C_{15}H_{21}NMe_2$ , b. p.  $201-202^{\circ}/27.5$  mm. This substance forms a *methiodide* and a quaternary *hydroxide*; the latter decomposes at  $75^{\circ}$  in a vacuum, giving trimethylamine and *sparteilene*,  $C_{15}H_{20}$ . The new hydrocarbon is a colourless, odourless, optically inactive liquid, b. p.  $157-159^{\circ}/18$  mm., showing a molecular refraction corresponding with the existence of six ethylenic linkings. Its production with trimethylamine, taken in conjunction with the formation of methylsparteilene and trimethylamine from dimethylsparteine, is sufficient to establish the symmetrical character of the sparteine molecule. Oxidation of sparteilene by means of potassium permanganate leads to the formation of an *acid*,  $C_{10}H_{10}O_5$ , m. p.  $300-305^{\circ}$  on the Maquenne block.

W. O. W.

**Strychnos Alkaloids. XIV. Derivatives and Decomposition Products of Brucinolone. Decomposition of Dihydrobrucinonic Acid into *iso*Brucinolone and Glycollic Acid.** HERMANN LEUCHS and J. F. BREWSTER (*Ber.*, 1912, 45, 201—221. Compare Abstr., 1908, 1, 563; 1909, 1, 253, 954).—For the preparation of brucinolone, brucine, dissolved in acetone, was oxidised by potassium permanganate, whereby brucinonic and dihydrobrucinonic acids were obtained. The two acids are difficult to separate completely. Brucinolic acid was obtained by reduction of brucinonic acid (containing some dihydrobrucinonic acid). This latter acid appears to be formed even when the most carefully purified keto-acid is reduced, and the authors have come to the conclusion that it is stereoisomeric with brucinolic acid, since they were also able to show that the two acids are similarly affected by sodium hydroxide. Since dihydrobrucinonic acid is formed by the direct oxidation of brucine, it follows that the latter must contain a secondary alcoholic group.

For the conversion of brucinolic acid into brucinolone, the authors recommend the use of normal sodium hydroxide ( $1\frac{1}{4}$  mols. instead of  $1\frac{1}{2}$  mols. previously employed). The m. p. of brucinolone is now given as about  $270^{\circ}$ , and  $[\alpha]_D^{25} - 34.7^{\circ}$ . The latter value is somewhat dependent on concentration and source of light used.

By means of ice-cold nitric acid (D 1.4), brucinolone was converted into *nitrobisapomethyldehydrobrucinolone*, which forms orange-coloured leaflets.

*Bisapomethylbrucinolone* (bisdemethylbrucinolone of Abstr., 1909,

i, 954) was converted into the *triacetate* by treatment with acetic anhydride and sodium acetate. It crystallises in colourless leaflets, m. p. 260—261°.

In brucinolone hydrate I. (in which the  $\text{=N-CO-}$  of brucinolone is supposed to have been transformed into  $\text{=NH HO}_2\text{C-}$ ), the presence of the imino-group has been proved by the regeneration of brucinolone by the action of heat on the hydrate I., and by the formation of a *derivative* when treated with phenylcarbimide. The latter is a non-crystallisable, amorphous, white powder, m. p. 192° (decomp.) after previous softening. The presence of the carboxyl group is shown by the isolation of the *hydrochlorides* of the methyl ester, m. p. 189—190° (decomp.), and of the ethyl ester, m. p. 181° (decomp.).

The isolation of a by-product,  $\text{C}_{21}\text{H}_{24}\text{O}_6\text{N}_2$ , during the action of sodium hydroxide on brucinolic acid has been previously described (Abstr., 1909, i, 954). This substance when heated with 5*N*-hydrochloric acid yields a *hydrochloride*, which is completely melted at 255° after previous gas evolution. The free *base* obtained from this, which has been named brucinolone hydrate II., separates from water with varying amounts of water of crystallisation. It has m. p. 240° (decomp.), after softening at 190°. It differs from the hydrate I. in possessing less tendency to lose water. When the by-product,  $\text{C}_{21}\text{H}_{24}\text{O}_6\text{N}_2$ , is heated with sodium hydroxide, brucinolone is formed.

In order to gain further insight into the oxidation products of brucine, *brucinolone acetate* (m. p. 253—254°) was prepared by heating brucinolone with acetic anhydride and sodium acetate. This was oxidised in acetone solution by potassium permanganate. In this manner an *acid*,  $\text{C}_{23}\text{H}_{24}\text{O}_9\text{N}_2$ , was isolated, which gave a brownish-red coloration with alcoholic ferric chloride, and thus appears to be a keto-acid. When heated, it softens at 120°, melts at about 160° (decomp.), then solidifies, becoming yellow at 240°, and melting again at about 275°. When heated during ten minutes at 160—180°, it evolves carbon dioxide and leaves a neutral *substance*,  $\text{C}_{20}\text{H}_{24}\text{O}_7\text{N}_2$ , which has m. p. about 281°. During the oxidation, a neutral *product*,  $\text{C}_{23}\text{H}_{22}\text{O}_6\text{N}_2$  (m. p. about 312°), is also formed.

By the action of normal sodium hydroxide ( $1\frac{1}{2}$  mols.) on dihydrobrucinonic acid, glycollic acid was obtained together with *isobrucinolone*. The latter forms yellow crystals, m. p. 308° (decomp.), and has  $[\alpha]_D^{24} + 26.9^\circ$  in glacial acetic acid solution. H. W.

**Action of Acetic Anhydride on Some Benzylideneanthranilic Acids.** JOHN B. EKELEY and PAUL M. DEAN (*J. Amer. Chem. Soc.*, 1912, 34, 161—164).—The products of the condensation of anthranilic acid with aromatic aldehydes (compare Wolf, Abstr., 1911, i, 735) react with acetic anhydride to form a series of oxazines which are crystalline, very stable, and usually colourless.

Benzylideneanthranilic acid, m. p. 126°, yields 1-*keto*-4-*acetyl*-3-*phenyl*-dihydro-2 : 4-benzoxazine,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO-O} \\ \text{NAc} \cdot \text{CHPh} \end{smallmatrix}$ , m. p. 108°, which when heated with hydrochloric acid is decomposed into benzaldehyde and acetylanthranilic acid. *m*-Nitrobenzylideneanthranilic acid, m. p. 202°, and *p*-nitrobenzylideneanthranilic acid, m. p. 164°, yield 1-*keto*-

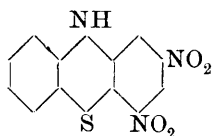
4-acetyl-3-m- and -p-nitrophenyldihydro-2:4-benzoxazines, m. p. 192° and 199° respectively. When p-hydroxybenzylideneanthranilic acid, m. p. 207°, is heated with acetic anhydride, 1-keto-4-acetyl-3-p-acetoxyphenyldihydro-2:4-benzoxazine, m. p. 148°, is produced. Salicylideneanthranilic acid, m. p. 195°, similarly gives 1-keto-4-acetyl-3-o-acetoxyphenyldihydro-2:4-benzoxazine, m. p. 162°. Vanillylideneanthranilic acid, m. p. 170°, crystallises in lemon-yellow needles, and when heated with acetic anhydride yields 1-keto-4-acetyl-3-p-hydroxy-m-methoxyphenyldihydro-2:4-benzoxazine, m. p. 184°, which forms pale straw-coloured needles.

E. G.

**Thiazines.** RICHARD MÖHLAU, HEINRICH BEYSCHLAG, and H. KÖHRES (*Ber.*, 1912, 45, 131—137. Compare Abstr., 1910, i, 337).—The authors have repeated the work of Kehrman and Steinberg (Abstr., 1911, i, 1034), and agree with them that the dinitrophen-thiazine, obtained by the interaction of picryl chloride and o-aminothiophenol, has the constitution originally ascribed to it by Kehrman and Schild (Abstr., 1900, i, 61). The synthesis of the isomeric 2:4-dinitrophen-thiazine is also described.

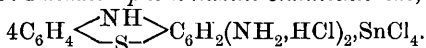
Di-o-aminodiphenyl disulphide is best prepared by reducing di-o-nitrodiphenyl disulphide (Blanksma, Abstr., 1901, i, 460) with hydrazine hydrate in alcoholic solution.

The *dibenzoyl* derivative,  $(\text{NHBz} \cdot \text{C}_6\text{H}_4)_2\text{S}_2$ , crystallises in pale yellow needles, m. p. 141°, and is reduced by aqueous sodium sulphide to o-benzoylaminophenyl mercaptan, which reacts with picryl chloride in the presence of sodium acetate, yielding trinitrophenyl o-benzoylaminophenyl sulphide,  $\text{NHBz} \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3$ . The latter compound crystallises in yellow prisms, m. p. 169°, and when boiled with sodium hydroxide in aqueous alcoholic solution is converted into 2:4-dinitrophen-thiazine (annexed formula), which crystallises



in almost black, lustrous prisms, m. p. 218° (appearing reddish-brown by transmitted light), dissolves in alcoholic sodium hydroxide, yielding bluish-violet solutions, and on reduction with stannous chloride and hydrochloric acid is

converted into 2:4-diaminophen-thiazine stannichloride,



This forms brownish-yellow needles, and is oxidised by ferric chloride in alcoholic solution in the presence of hydrochloric acid to 2:4-diaminophenazthionium chloride,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{S}^+\text{Cl} \end{array} \text{C}_6\text{H}_2(\text{NH}_2)_2$ . The ferrichloride,  $\text{C}_{12}\text{H}_{10}\text{N}_3\text{SCl}_4\text{Fe} \cdot \text{H}_2\text{O}$ , forms greenish-black, microscopic crystals, which lose their water of crystallisation at 110°; the platini-chloride, chromate, carbonate, and the thiazonium base itself are briefly mentioned.

Kehrman and Steinberg's 1:3-dinitrophen-thiazine has m. p. 187°.

F. B.

**Decomposition of Alkylidenehydrazines.** NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1554—1562).—The author has

been able to pass from carone through carylidenehydrazine to carane (compare Abstr., 1911, i, 1028), the hydrocarbon thus obtained being structurally identical with that prepared from pulegone, but exhibiting a lævo- instead of a dextro-rotation.

*Carylidenehydrazine*,  $\text{CMe}_2 \begin{array}{c} \text{CH} \cdot \text{C}(\text{N} \cdot \text{NH}_2) \cdot \text{CHMe} \\ \text{CH} \text{---} \text{CH}_2 \text{---} \text{CH}_2 \end{array}$ , obtained by the action of hydrazine hydrate on carone, is a viscous liquid, b. p.  $131^\circ/20$  mm.,  $D_0^{20}$  0.9683,  $n_D$  1.5082,  $[\alpha]_D + 375.7$ — $378.8^\circ$  (absolute alcohol). Its *thioureide*,  $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{N} \cdot \text{C}_{10}\text{H}_{16}$ , forms hexagonal plates, m. p.  $100$ — $101^\circ$ . Hydrolysis of carylidenehydrazine by either boiling dilute sulphuric acid or hydrochloric acid at the ordinary temperature yields a product showing all the physical properties of carvenone with the exception of a slight lævo-rotation, apparently due to admixture of a small quantity of an intermediate compound in the hydrolysis.

1-*Carane*,  $\text{C}_{10}\text{H}_{18}$ , has b. p.  $169$ — $169.5^\circ/761$  mm.,  $D_0^{20}$  0.8411,  $n_D$  1.4569,  $[\alpha]_D - 47.06^\circ$ , is very stable towards permanganate, and combines, with generation of heat, with halogen hydracids and bromine. The *bromo-derivative*,  $\text{C}_{10}\text{H}_{17}\text{Br}$ , obtained by the action of hydrobromic acid, has  $D_0^{20}$  1.1774,  $n_D$  1.4910,  $[\alpha]_D - 6.40^\circ$ , and yields  $\Delta^{(9)}$ -*m*-menthene and  $\Delta^{(8)}$ -*m*-menthene in the same way as *d*-carane (*loc. cit.*).  
T. H. P.

**Refutation of Bülow's Views Concerning Pyrazoline-carboxylic Acids.** EDUARD BUCHNER (*Ber.*, 1912, 45, 117—121).—Many arguments are advanced to disprove Bülow's view (this vol., i, 134) that a mixed azine,  $\text{CHX} \cdot \text{N} \cdot \text{N} \cdot \text{CX} \cdot \text{CH}_2\text{X}$ , not a pyrazoline derivative,  $\text{N} \begin{array}{c} \text{CX} \cdot \text{CHX} \\ \text{NH} \cdot \text{CHX} \end{array}$ , is produced by the action of ethyl diazoacetate on an unsaturated ester of the type  $\text{CHX} \cdot \text{CHX}$  ( $\text{X} = \text{CO}_2\text{Et}$ ).  
C. S.

**Derivatives and Decomposition Products of Methyl Methoxybenzoylacetates.** ANDRÉ WAHL and C. SILBERZWEIG (*Bull. Soc. Chim.*, 1912, [iv], 11, 61—69).—The methoxybenzoylacetates are convertible into  $\alpha\beta$ -diketonic esters, and, as these may react with various reagents giving compounds identical with those obtainable from the initial  $\beta$ -ketonic esters, the following compounds have been prepared and characterised so that they may be readily identified.

*Methyl  $\alpha$ -oximino-o-methoxybenzoylacetate*,  
 $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}(\text{NOH}) \cdot \text{CO}_2\text{Me}$ ,  
m. p.  $146$ — $147^\circ$ , produced by the action of nitrous acid on the  $\beta$ -ketonic ester in acetic acid, crystallises from ether. The original ester reacts with phenylhydrazine to form Tahara's 1-phenyl-3-o-methoxyphenyl-5-pyrazolone,  $\text{PhN} \begin{array}{c} \text{N} = \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{OMe} \\ \text{CO} \cdot \text{CH}_2 \end{array}$ , m. p.  $133$ — $134^\circ$ , yellow needles, and with *p*-nitrophenylhydrazine to form 1-*p*-nitrophenyl-3-o-methoxyphenyl-5-pyrazolone, m. p.  $217$ — $218^\circ$ , brown needles.

*Methyl  $\alpha$ -phenylhydrazonoazo-o-methoxybenzoylacetate*,  
 $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}(\text{N} \cdot \text{NHPh}) \cdot \text{CO}_2\text{Me}$ ,

m. p. 138—139°, obtained by the action of benzenediazonium chloride on the ester in the cold, forms yellow crystals from alcohol, and reacts with phenylhydrazine to form 4-phenylhydrazono-1-phenyl-3-o-methoxyphenyl-5-pyrazolone, m. p. 139°, orange crystals, and with *p*-nitrophenylhydrazine to form 4-phenylhydrazono-1-*p*-nitrophenyl-3-o-methoxyphenyl-5-pyrazolone, m. p. 200°, red crystals, from pyridine.

*Methyl p-nitrophenylhydrazono-o-methoxybenzoylacetate*, m. p. 170°, obtained by the action of the sodium derivative of *p*-nitrophenyl nitrosoamine on the  $\beta$ -ketonic ester, forms yellow crystals, and reacts with phenylhydrazine to give 4-*p*-nitrophenylhydrazono-1-phenyl-3-o-methoxyphenyl-5-pyrazolone, m. p. 267°, red crystals.

*Methyl oximino-m-methoxybenzoylacetate*, m. p. 115—116°, forms colourless needles from ether and light petroleum, and on treatment with phenylhydrazine gives 4-oximino-1-phenyl-3-m-methoxyphenyl-5-pyrazolone, m. p. 157°, which forms red crystals from acetic acid.

*Methyl phenylhydrazono-m-methoxybenzoylacetate*, m. p. 72—73°, forms yellow crystals; the free acid, m. p. 118—120°, forms yellow needles. *Methyl p-nitrophenylhydrazono-m-methoxybenzoylacetate*, m. p. 155—156°, crystallises in yellow needles. 1-Phenyl-3-m-methoxyphenyl-5-pyrazolone, m. p. 124°, forms pale yellow crystals. 4-Phenylhydrazono-1-phenyl-3-m-methoxyphenyl-5-pyrazolone, m. p. 137°, and the corresponding 4-*p*-nitrophenylhydrazono, m. p. 235°, both form red crystals.

*Methyl oximinooanisoylacetate*, m. p. 154°, forms colourless crystals from boiling methyl alcohol.

*Methyl phenylhydrazonoanisoylacetate*, m. p. 121—122°, forms orange crystals; the free acid, m. p. 149—150°, is yellow. The acetyl derivative of the ester has m. p. 116°, crystallises in colourless needles, and on reduction furnishes some acetanilide, whence it is believed to have the constitution  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}(\text{N}\cdot\text{NPhAc})\cdot\text{CO}_2\text{Me}$  (compare Auwers, Abstr., 1909, i, 222).

*Methyl p-nitrophenylhydrazonoanisoylacetate*, m. p. 175°, forms yellow crystals; the free acid, m. p. 236—238°, is also yellow, but dissolves in alkalis with an intense red colour.

1-Phenyl-3-*p*-methoxyphenyl-5-pyrazolone has m. p. 137—138°; the 4-oximino-derivative, m. p. 244°, forms red crystals. *p*-Nitrophenyl-3-*p*-methoxyphenyl-5-pyrazolone, m. p. 204—205°, is brown. 4-Phenylhydrazono-1-phenyl-3-*p*-methoxyphenyl-5-pyrazolone, m. p. 177°, is red; the corresponding *p*-nitrophenylhydrazono, m. p. 213—214°, separates from acetic acid in violet crystals, and the isomeric 4-phenylhydrazono-1-*p*-nitrophenyl-3-*p*-methoxyphenyl-5-pyrazolone, m. p. 239°, is red.

The methoxybenzoyl acetic esters are hydrolysed by boiling with 20% sulphuric acid into the corresponding *o*-, *m*-, and *p*-methoxyacetophenones. The semicarbazone of *m*-methoxyacetophenone has m. p. 195—197° (compare Klages, Abstr., 1904, i, 45) and that of the *p*-compound melts at 197°. T. A. H.

**Quinazolines. XXVIII. 4-Quinazolone-2-phthalones and Certain of their Derivatives.** MARSTON T. BOGERT and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1912, 34, 183—201).—An account is given of certain phthalones obtained by the action of

phthalic anhydride on 2-methyl-4-quinazolone (2-methyl-4-hydroxy-quinazoline) and its derivatives. These compounds, like the quino-phthalones, behave as yellow dyes, but are inferior to the latter in tinctorial power.

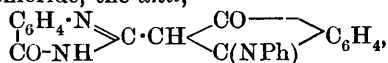
4-Quinazolone-2-phthalone [4-hydroxyquinazoline-2-phthalone, 2-indandionyl-4-quinazolone, or  $\beta$ -(4'-quinazolonyl-2')-diketohydrindene],

$\text{C}_6\text{H}_4 \cdot \text{N} \begin{array}{c} \nearrow \\ \text{CO-NH} \end{array} \text{C} \cdot \text{CH} \begin{array}{c} \nwarrow \text{CO} \\ \searrow \text{CO} \end{array} \text{C}_6\text{H}_4$ , m. p.  $318^\circ$  (corr.), obtained by heating a

mixture of 2-methyl-4-quinazolone and phthalic anhydride to about  $200^\circ$ , forms pale yellow, prismatic needles or hexagonal plates, and when heated above  $200^\circ$  sublimes in woolly masses of minute needles. In one experiment in which a large excess of phthalic anhydride was used, on extracting the reaction product with hot water, 2-methyl-4-quinazolone phthalate was obtained, which crystallises in pale yellow, fluorescent needles with  $1\text{H}_2\text{O}$ ; the anhydrous salt has m. p.  $171^\circ$  (corr.). The di-sodium salt of the phthalone is orange-red, whilst the mono-sodium and silver salts are pale yellow. On reducing the phthalone with zinc dust and sodium hydroxide, 4-quinazolone-2-

hydrindone,  $\text{C}_6\text{H}_4 \begin{array}{c} \nwarrow \text{N}=\text{C}-\text{CH} \cdot \text{CH}_2 \\ \searrow \text{CO} : \text{NH} \text{CO}-\text{C}_6\text{H}_4 \end{array}$ , is obtained, which forms olive-

yellow, microscopic crystals, sublimes above  $160^\circ$ , and melts at about  $328^\circ$  (decomp.). When the phthalone is heated with aniline in presence of zinc chloride, the *anil*,



m. p.  $284-285^\circ$  (uncorr.), is produced, which crystallises in brilliant, scarlet needles; its sodium salt and compound with zinc chloride are described. From the product of this reaction, a small quantity of another *anil*, m. p.  $258^\circ$ , was obtained, which forms red crystals and appears to be a condensation product of 1 mol. of aniline with 2 mols. of the phthalone.

4-Quinazolone-2-phthalonemonophenylhydrazone, m. p. about  $225^\circ$  (uncorr.), was obtained as an orange-brown, micro-crystalline powder. 4-Quinazolone-2-phthalone-6-sulphonic acid, m. p. about  $355-360^\circ$  (uncorr.), crystallises in minute plates or needles; its mono- and di-sodium and barium salts are described. Solutions of the di-sodium salt dye wool or silk light yellow shades. By the action of bromine on the sulphonic acid, there were formed a di- and a penta-bromo-2-methyl-4-quinazolone, a bromo-2-methyl-4-quinazolone-sulphonic acid, phthalic acid, and sulphuric acid. Dibromo-2-methyl-4-quinazolone, m. p. about  $293^\circ$  (decomp.), forms masses of delicate, colourless needles. Pentabromo-2-methyl-4-quinazolone, m. p. about  $243.5^\circ$  (decomp.), crystallises in colourless, prismatic needles. Bromo-2-methyl-4-quinazolonesulphonic acid, m. p.  $285-286.5^\circ$  (uncorr.), forms a grey, amorphous solid containing  $1\text{H}_2\text{O}$ ; its barium salt crystallises with  $4\frac{1}{2}\text{H}_2\text{O}$ .

Attempts to prepare 4-quinazolone-2-phthalines by heating the ammonium salt of the phthalone with alcoholic ammonia in sealed tubes did not meet with success. Bis-(4-quinazolone-2)- $\beta$ -phthaline,

$\text{C}_8\text{H}_5\text{ON}_2 \cdot \text{CH} : \text{C} \begin{array}{c} \nwarrow \text{NH} \\ \searrow \text{C}_6\text{H}_4 \end{array} \text{C} : \text{CH} \cdot \text{C}_8\text{H}_5\text{ON}_2$ , obtained by heating a

mixture of phthalimide and 2-methyl-4-quinazolone, is an orange-brown substance which darkens gradually when heated; its solution in dilute acetic acid acts as a powerful yellow dye. 4-*Quinazolone-2-β-phthaline*,  $C_8H_5ON_2 \cdot CH : C \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} C_6H_4$ , m. p. about  $349^\circ$  (decomp.), is also produced in this reaction, and forms orange-brown, microscopic prisms.

2-Methyl-4-quinazolone reacts with succinic anhydride with production of a tarry mass, from which a small quantity of a substance, m. p.  $274-277^\circ$  (decomp.), was isolated in the form of thin, colourless, lustrous plates.

6-Nitro-4-quinazolone-2-phthalone, obtained by heating 6-nitro-2-methyl-4-quinazolone with phthalic anhydride at about  $210^\circ$ , forms minute, yellow crystals and does not melt below  $355^\circ$ .

7-Acetylamino-4-quinazolone-2-phthalone, resulting from the action of phthalic anhydride on 7-acetylamino-2-methyl-4-quinazolone, crystallises in bright yellow, lustrous plates, and does not melt below  $356^\circ$ .

2-Methyl-3-ethyl-4-quinazolone,  $C_6H_4 \begin{smallmatrix} \text{N}=\text{CMe} \\ \text{CO} \cdot \text{NEt} \end{smallmatrix}$ , m. p.  $67^\circ$  (corr.), obtained by heating acetylanthranil with excess of an aqueous solution of ethylamine in presence of a little potassium hydroxide, forms colourless, slender needles; its *platinichloride* decomposes at about  $229^\circ$ . In one experiment in which potassium hydroxide was not added, *anthranilethylamide*,  $NH\text{Et} \cdot CO \cdot C_6H_4 \cdot NH\text{Ac}$ , m. p.  $139.5-140.5^\circ$  (corr.), was isolated in the form of transparent, prismatic plates.

3-Ethyl-4-quinazolone-2-phthalone, m. p.  $198.5^\circ$  (corr.), obtained from 2-methyl-3-ethyl-4-quinazolone and phthalic anhydride, forms bright yellow, lustrous, prismatic needles with a slight green fluorescence.

E. G.

**Formation of Pyrimidines by Use of Nitromalonaldehyde.** WILLIAM J. HALE and HARVEY C. BRILL (*J. Amer. Chem. Soc.*, 1912, 34, 82-94).—Hill and Torrey (Abstr., 1899, i, 788) have shown that nitromalonaldehyde reacts readily with primary amines. This work has now been extended to other amino-compounds.

When carbamide is allowed to react with the sodium derivative of nitromalonaldehyde in presence of a few drops of piperidine, the mono-ureide and 5-nitro-2-hydroxypyrimidine are produced.

*Nitromalonaldehyde mono-ureide*,  $NH_2 \cdot CO \cdot N : CH \cdot CH(NO_2) \cdot CHO$ , m. p.  $154^\circ$  (corr.), forms pale yellow crystals; its *sodium salt* crystallises with  $3H_2O$ . The *anil*,

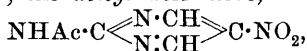
$NH_2 \cdot CO \cdot N : CH \cdot CH(NO_2) \cdot CH : NPh$ , m. p.  $211^\circ$  (corr.), crystallises in lustrous, red needles. The *oxime*,  $NH_2 \cdot CO \cdot N : CH \cdot CH(NO_2) \cdot CH : NOH$ , m. p.  $174-175^\circ$  (corr.), forms yellow leaflets.

5-Nitro-2-hydroxypyrimidine,  $OH \cdot C \begin{smallmatrix} \text{N} \cdot \text{CH} \\ \text{N} : \text{CH} \end{smallmatrix} C \cdot NO_2$ , m. p.  $203.5^\circ$  (corr.), crystallises in small, yellow plates; the *sodium*, *potassium*,

barium, and silver salts are described. The *methyl ether*, m. p. 168—169° (corr.), forms colourless plates.

5-Nitro-2-phenylpyrimidine,  $\text{CPh} \begin{smallmatrix} \text{N} \cdot \text{CH} \\ \text{N} : \text{CH} \end{smallmatrix} \text{C} \cdot \text{NO}_2$ , m. p. 219° (corr.), obtained by the interaction of benzamidine hydrochloride and sodium nitromalonaldehyde, crystallises in white plates.

5-Nitro-2-aminopyrimidine,  $\text{NH}_2 \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{CH} \\ \text{N} : \text{CH} \end{smallmatrix} \text{C} \cdot \text{NO}_2$ , m. p. 236° (corr.), prepared by the action of guanidine carbonate on sodium nitromalonaldehyde, forms colourless, slender needles, and when heated with solution of alkali hydroxide is converted into 5-nitro-2-hydroxypyrimidine; the *acetyl* derivative,



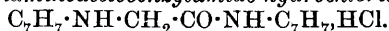
m. p. 172.5° (corr.), crystallises in long, colourless needles. When a small quantity of potassium hydroxide is added to a mixture of 5-nitro-2-aminopyrimidine and carbon disulphide at 60°, 5 : 5'-*di-nitro-2 : 2' - dipyrimidylthiocarbamide*,  $\text{CS}[\text{NH} \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{CH} \\ \text{N} : \text{CH} \end{smallmatrix} \text{C} \cdot \text{NO}_2]_2$ , m. p. 230—231° (corr.), is produced, which forms a mass of glistening leaflets.

*Nitromalonaldehyde phenylureide*,  $\text{CHO} \cdot \text{CH}(\text{NO}_2) \cdot \text{CH} : \text{N} \cdot \text{CO} \cdot \text{NHPh}$ , m. p. 176—177° (corr.), was obtained by the condensation of nitromalonaldehyde with phenylcarbamide. The corresponding *benzylureide*, m. p. 150—151° (corr.), and *methylureide* were also prepared.

E. G.

**Chlorides of Amino-acids.** CARL MANNICH and R. KUPHAL (*Ber.*, 1912, 45, 314—322).—By the internal condensation of benzyl-aminoacetyl chloride and of similar amino-acid chlorides in the presence of aluminium chloride, the authors hoped to prepare derivatives of isoquinoline,  $\text{CH}_2\text{Ph} \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{COCl} \rightarrow \text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{NH} \\ \text{CO} - \text{CH}_2 \end{smallmatrix}$ . It was found, however, that the chlorides readily lost hydrogen chloride even in the absence of aluminium chloride with the formation of diketopiperazines.

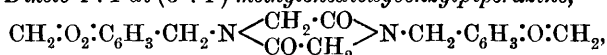
*Ethyl benzylaminoacetate*, prepared by the interaction of ethyl chloroacetate and benzylamine, is a colourless liquid of aromatic odour, b. p. 153—154°/13 mm., and is readily hydrolysed by hydrochloric acid to benzylaminoacetic acid (Mason and Winder, *Trans.*, 1894, 67, 187). It is accompanied by a substance, which crystallises from dilute alcohol in lustrous, white leaflets, m. p. 238—239°, consisting probably of *benzylaminoacetobenzylamide hydrochloride*,



The amino-acid is converted by the action of phosphorus pentachloride and acetyl chloride (Fischer, *Abstr.*, 1905, i, 263) into *benzylaminoacetyl chloride hydrochloride*,  $\text{C}_7\text{H}_7 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{COCl} \cdot \text{HCl}$ , which forms slender, white needles, and when heated in nitrobenzene solution yields 3 : 6-diketo-1 : 4-dibenzylpiperazine,  $\text{C}_7\text{H}_7 \cdot \text{N} \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix} \text{N} \cdot \text{C}_7\text{H}_7$ , crystallising in white needles, m. p. 172—173°.

**3:4-Methylenedioxybenzylamine**,  $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{NH}_2$ , prepared by reducing piperonaldoxime with sodium amalgam and alcohol, the solution being maintained continually acid by the addition of acetic acid, is a colourless liquid, b. p.  $138-139^\circ/13$  mm.; on exposure to air it forms a solid *carbonate*; the *hydrochloride*, lustrous, white leaflets, has m. p.  $227^\circ$ ; the *benzoyl* and *chloroacetyl* derivatives crystallise in slender, white needles, m. p.  $117-118^\circ$  and  $107-108^\circ$  respectively. It reacts with ethyl chloroacetate, yielding *ethyl 3:4-methylenedioxybenzylaminoacetate*,  $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , which forms a *hydrochloride*, white needles, m. p.  $157-158^\circ$ , and is hydrolysed by aqueous potassium hydroxide to the corresponding *acid*. This has m. p.  $206-207^\circ$ , and is converted by acetyl chloride and phosphorus pentachloride into *3:4-methylenedioxybenzylaminoacetylchloride hydrochloride*,  $\text{C}_{10}\text{H}_{11}\text{O}_3\text{NCl}_2$ .

**3:6-Diketo-1:4-di-(3':4')-methylenedioxybenzylpiperazine**,



prepared by heating the preceding chloride hydrochloride in nitrobenzene solution, forms white needles, m. p.  $234-235^\circ$ .

*Ethyl benzylmethylaminoacetate*,  $\text{C}_7\text{H}_7\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , obtained from ethyl chloroacetate and benzylmethylamine, has b. p.  $138^\circ/13$  mm.; the syrupy *hydrochloride*, the orange *platinichloride*, and the *picrate*, crystallising in stout, yellow needles, m. p.  $122-123^\circ$ , are described. When hydrolysed with concentrated hydrochloric acid, it yields the corresponding *acid*,  $\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}$ , which forms a *hydrochloride*, sintering at  $174^\circ$ , m. p.  $180-181^\circ$ , and a *chloride hydrochloride*,  $\text{C}_7\text{H}_7\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{COCl}\cdot\text{HCl}$ .

The latter compound reacts with aluminium chloride at  $100^\circ$ , yielding carbon monoxide, formaldehyde, and benzylmethylamine, together with *s-dibenzyl dimethylmethylenediamine*,  $\text{CH}_2(\text{NMe}\cdot\text{C}_7\text{H}_7)_2$ , a pale yellow oil, b. p.  $172-175^\circ/8$  mm. The constitution of the last-named compound has been established by its synthesis from benzylmethylamine and formaldehyde.

F. B.

**Preparation of Halogenated Dehydroindigotin Salts, their Nuclear Homologues and Substitution Products.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 239314).—Halogenated dehydroindigotin salts have previously been described, and the preparation of higher halogenated derivatives is now recorded.

*Trichlorodehydroindigotin acetate*, a canary-yellow powder, is prepared by passing chlorine into a cooled acetic acid solution of dehydroindigotin acetate until the product has completely separated; when nitrobenzene is employed as solvent, a *tetrachlorodehydroindigotin hydrochloride* is obtained, whilst under these conditions indigotin yields *trichlorodehydroindigotin hydrochloride* (isolated in the form of its *bisulphite* compound), and *5:5'-dibromoindigotin* in acetic acid solution furnishes *dichlorodibromodehydroindigotin hydrochloride*. Other solvents, such as acetyl chloride or carbon tetrachloride, can be employed, and the formation of other halogenated indigotins is discussed.

F. M. G. M.

**Action of Alkyl oxides and Amines on Benzoyl *iso*Cyanochloride [Benzoylcarbylamine Chloride].** TREAT B. JOHNSON and LEWIS H. CHERNOFF (*J. Amer. Chem. Soc.*, 1912, **34**, 164—170).—Benzoylcarbylamine chloride,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{N}\cdot\text{CCl}_2$ , obtained by Johnson and Menge (*Abstr.*, 1904, i, 949) by the action of chlorine on benzoyl thiocyanate, is decomposed by water with formation of hydrochloric acid, benzamide, and benzoic acid. It combines with sodium alkyl oxides to form compounds of a new class, the acylimidocarbonates, and reacts with amines with production of substituted guanidines, which yield stable salts with mineral acids and are hydrolysed by alkali hydroxide with formation of the free guanidines and benzoic acid.

*Diethyl benzoylimidocarbonate*,  $\text{NBz}\cdot\text{C}(\text{OEt})_2$ , b. p. 93—100°/20 mm. and 110—120°/32 mm., was prepared by the action of benzoylcarbylamine chloride on sodium ethoxide. *Dimethyl benzoylimidocarbonate*, b. p. 95—102°/20 mm., is a colourless oil.

*Benzoyl- $\alpha$ -diphenylguanidine*,  $\text{NBz}\cdot\text{C}(\text{NHPh})_2$ , m. p. 212° (decomp.), obtained by the action of benzoylcarbylamine chloride on a solution of aniline in benzene, forms colourless needles.  *$\beta$ -Benzoyl- $\alpha$ -di-o- and -m-tolylguanidines*,  $\text{NBz}\cdot\text{C}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$ , have m. p. 126° and 177—178° respectively. *Di-m-tolylguanidine*,  $\text{NH}\cdot\text{C}(\text{NH}\cdot\text{C}_6\text{H}_4\text{Me})_2$ , m. p. 108—109°, was obtained from the benzoyl compound by hydrolysis with potassium hydroxide.  *$\beta$ -Benzoyl- $\alpha$ -di-p-tolylguanidine*, m. p. 190°, yields a *hydrochloride*, m. p. 190—191° (decomp.). The following guanidines were also prepared: *benzoyltetraphenylguanidine*, m. p. 142—144°;  *$\beta$ -benzoyl- $\alpha$ -diphenyl- $\alpha$ -dimethylguanidine*, m. p. 135°;  *$\beta$ -benzoyl- $\alpha$ -di-p-anisylguanidine*, m. p. 128°, and *di-p-anisylguanidine*, m. p. 153°;  *$\beta$ -benzoyl- $\alpha$ -di- $\beta$ -naphthylguanidine*, m. p. 162°, and *di- $\beta$ -naphthylguanidine*, m. p. 197° (decomp.). E. G.

**Reduction of Semicarbazones.** SIDONIUS KESSLER and HANS RUPE (*Ber.*, 1912, **45**, 26—30).—Semicarbazones are readily reduced by sodium amalgam in dilute alcoholic solution at a slightly elevated temperature. In some instances, for example, those of cinnamaldehyde and styryl methyl ketone, the influence of the constitution of the semicarbazone prevents reduction to semicarbazide.

*Benzylsemicarbazide*,  $\text{CH}_2\text{Ph}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , from benzaldehyde-semicarbazone, crystallises in lustrous platelets, m. p. 155°. It is distinctly basic, dissolving in cold dilute acids, and reduces Fehling's solution on boiling. The *hydrochloride* forms silky, lustrous needles, m. p. 178—180°; the *sulphate* yields slender needles, m. p. 158°; the *picrate* gives slender, yellow needles, m. p. 161—162°, and the *oxalate* has m. p. 178—179° (decomp.). The *acetyl* derivative crystallises in beautiful, colourless plates, m. p. 207°; a diacetate could not be obtained; the *benzoyl* derivative forms colourless needles, m. p. 230°.

*Nitrosobenzylsemicarbazide*,  $\text{CH}_2\text{Ph}\cdot\text{N}(\text{NO})\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , prepared by the action of sodium nitrite and hydrochloric acid on benzylsemicarbazide, crystallises in long needles, m. p. 133° (decomp.).

*p-Methylbenzylsemicarbazide* crystallises in slender, colourless needles, m. p. 158°; the *hydrochloride* forms colourless needles, m. p. 138° (decomp.); the *sulphate* decomposes at 187°; the *picrate* yields yellow needles, m. p. 178° (decomp.), and the acid *oxalate* decomposes at

175°. The *acetyl* derivative crystallises in glistening, colourless platelets, m. p. 225° (not decomp.).

*Nitroso-p-methylbenzylsemicarbazide* separates in colourless platelets, and decomposes at 126—127°.

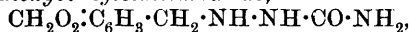
When cinnamaldehydesemicarbazone is reduced,  $\beta$ -phenylpropaldehydesemicarbazone, m. p. 128°, is the sole product.

Similarly, from the semicarbazone of styryl methyl ketone, the product is the semicarbazone of phenylethyl methyl ketone.

E. F. A.

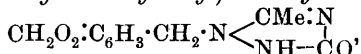
**Reduction of Semicarbazones and the Preparation of Some Hydroxytriazoles.** HANS RUPE and E. OESTREICHER (*Ber.*, 1912, 45, 30—38. Compare preceding abstract).—The property of semicarbazones of being reduced to semicarbazide is closely dependent on their constitution. A phenyl residue must be attached directly to the group C:N. Aliphatic hydrocyclic and compounds in which phenyl is replaced by benzyl cannot be reduced. The semicarbazones of benzoylpropionic acid and of *p*-benzoquinone could not be reduced. The semicarbazides vary considerably in their basic properties; those from benzophenone, acetophenone, and deoxybenzoin dissolve in dilute acids in the cold, whereas those from salicylaldehyde or piperonal dissolve only when boiled with acids.

3 : 4-Methylenedioxybenzylsemicarbazide,



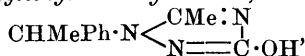
from piperonalsemicarbazone, forms transparent prisms, m. p. 184°. The *acetyl* derivative crystallises in slender, transparent needles, m. p. 203—204°; the *formyl* derivative forms long, transparent, rhombic plates, m. p. 204—205°.

3-Hydroxy-(mp-methylenedioxybenzyl)-5-methyl-1 : 2 : 4-triazole,



prepared by boiling the *acetyl* derivative with 30% sodium hydroxide and decomposing the sodium salt formed with hydrochloric acid, forms opaque, square crystals with stunted ends, m. p. 190°; it forms characteristic metallic salts. From the *formyl* derivative of the semicarbazide, 3-hydroxy-(mp-methylenedioxybenzyl)-1 : 2 : 4-triazole is obtained; it crystallises in stout, transparent plates, m. p. 246—247°. *α*-Phenylethylsemicarbazide,  $\text{CHMePh}\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , from acetophenonesemicarbazone, crystallises in four-edged, transparent prisms, m. p. 142—143°. The *acetyl* derivative forms platelets, m. p. 228—230°, the *formyl* derivative crystallises in slender, matted needles, m. p. 187°.

3-Hydroxy-1- $\alpha$ -phenylethyl-5-methyltriazole,



crystallises in short, well formed prisims, m. p. 146—147°.

3-Hydroxy-1- $\alpha$ -phenylethyltriazole is obtained in transparent, slender, intergrown prisms, m. p. 140°.

Diphenylmethylsemicarbazide,  $\text{CHPh}_2\cdot\text{NH}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , crystallises in long, lustrous, transparent needles, m. p. 164—165°; it gives an

intense yellow coloration with concentrated sulphuric acid. The *acetyl* derivative crystallises in small, transparent prisms, m. p. 237°; the *formyl* derivative yields small, colourless needles, m. p. 182°. The *nitrosoamine*,  $\text{CHPh}_2 \cdot \text{N}(\text{NO}) \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , forms slender, faintly yellow-coloured needles, m. p. 122°.

3-Hydroxy-1-diphenylmethyl-5-methyltriazole,  $\text{CHPh}_2 \cdot \text{N} \begin{matrix} \text{CMe:N} \\ \text{N}=\text{C:OH} \end{matrix}$ , crystallises in glistening needles, which appear under the microscope as prisms with two superposed pyramids.

3-Hydroxy-1-diphenylmethyltriazole forms slender, matted needles, m. p. 253°.

$\alpha\beta$ -Diphenylethylsemicarbazide, prepared from deoxybenzoinsemicarbazone, crystallises in long, slender, transparent needles grouped in stellar aggregates, m. p. 139°. The *acetyl* derivative forms slender, woolly needles, m. p. 196°; the *formyl* derivative gives small, transparent prisms, m. p. 194°.

*o*-Hydroxybenzylsemicarbazide, from salicylaldehydesemicarbazone, crystallises in four-edged prisms, m. p. 128°. The *acetyl* derivative separates in slender needles, m. p. 204°; the *formyl* derivative forms flat, transparent plates, m. p. 183—184°.

3-Hydroxy-1-*o*-hydroxybenzyl-5-methyltriazole forms crystals, m. p. 192°, and gives a reddish-violet coloration with sulphuric acid.

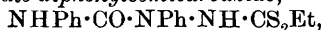
3-Hydroxy-1-*o*-hydroxybenzyltriazole forms platelets of silvery lustre, m. p. 211° (decomp.).

3-Hydroxy-5-benzyl-1-methyltriazole crystallises in transparent prisms, m. p. 168°.

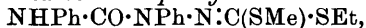
3-Hydroxy-1-benzyltriazole forms lustrous, nacreous platelets, m. p. 147—148°. E. F. A.

**Determination of Configuration of Stereoisomeric Hydrazones.** MAX BUSCH (*Ber.*, 1912, 45, 73—85).—Stereoisomeric diphenylsemicarbazones of unsymmetrical esters of dithiocarbonic acid,  $\text{NHPh} \cdot \text{CO} \cdot \text{NPh} \cdot \text{N} : \text{C}(\text{SR}) \cdot \text{SR}'$ , analogous to the stereoisomeric phenylhydrazones (*Abstr.*, 1911, i, 811) have been obtained.

*Ethyl dithiocarbonate-diphenylsemicarbazide*,



stout needles, m. p. 149—150°, obtained from equal molecular quantities of phenylcarbimide and ethyl phenyldithiocarbazinate in warm benzene, dissolves readily in aqueous alkalis, and is decomposed by prolonged boiling with alcoholic potassium hydroxide, yielding ethyl mercaptan and, after acidifying, 3-thiol-1:4-diphenyltriazolone (*Abstr.*, 1911, i, 689). By treating its alcoholic solution with equivalent quantities of potassium hydroxide and methyl iodide, it yields (a) *methyl ethyl dithiocarbonate-diphenylsemicarbazone*,



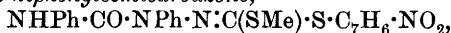
m. p. 93—94°, rhombic needles. The stereoisomeric (b) *methyl ethyl dithiocarbonate-diphenylsemicarbazone*, m. p. 87—88°, monoclinic needles or prisms, is prepared in a similar manner from methyl dithiocarbonate-diphenylsemicarbazide, ethyl iodide, and potassium hydroxide. These

two stereoisomeric semicarbazones behave very similarly. However, when warmed at 50—60° with alcoholic potassium hydroxide, the former yields ethyl mercaptan and the methyl thio-ether of 3-thiol-1:4-diphenyltriazolone, whilst the latter yields methyl mercaptan and the *ethyl* thio-ether, m. p. 111—112°, of the same triazolone; in both cases the alkyl group, which was introduced first, is eliminated as a mercaptan.

Another pair of stereoisomeric semicarbazones are described. *p*-Nitrobenzyl phenyldithiocarbazinate and phenylcarbimide in benzene yield *p*-nitrobenzyl dithiocarbonate-diphenylsemicarbazide,



m. p. 119—120°, colourless needles, which is converted by alcoholic potassium hydroxide and methyl iodide into (a) *p*-nitrobenzyl methyl dithiocarbonate-diphenylsemicarbazone,



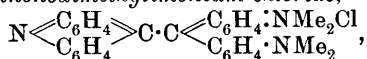
m. p. 126°, stout, yellow needles. The stereoisomeric (b) *p*-nitrobenzyl methyl dithiocarbonate-diphenylsemicarbazone, m. p. 147°, colourless plates, is prepared in a similar manner from methyl dithiocarbonate-diphenylsemicarbazide and *p*-nitrobenzyl chloride. Either of these semicarbazones is converted, when fused or heated in alcohol for one to two hours, into an equilibrium mixture of approximately equal quantities of both forms. When warmed with alcoholic potassium hydroxide, the yellow form yields the methyl thio-ether of 3-thiol-1:4-diphenyltriazolone, whilst the colourless form yields methyl mercaptan and the *p*-nitrobenzyl thio-ether, m. p. 178—179°, of the same triazolone; in both cases, again, the alkyl group which was first introduced is eliminated by the action of the alkali.

C. S.

**Influence of the Acridine Ring on the Colour of Certain Colouring Matters.** A. E. PORAI-KOSCHITZ, Y. I. AUSCHKAP, and N. K. AMSLER (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1587—1603).—In order to decide between the chromophore and dynamic theories (compare von Baeyer, Abstr., 1907, i, 757) of the colour of triphenylmethane colouring matters, the authors have prepared and studied acridylmalachite-green and acridylpyronine. The results obtained are distinctly in favour of the latter of the two hypotheses, since the absorption spectra of the two colouring matters scarcely differ from those of malachite-green and rosamine, the absorption bands being displaced towards the red end of the spectrum to an extent approximately such as is usually observed with any more or less considerable increase in the molecular weight. A further consequence of the replacement of the benzene ring by an acridine nucleus consists in a marked diminution in the “permanency” of the spectral bands, this being expressed in a decrease in the dyeing properties of the colouring matters. In the case of acridylmalachite-green, the quinonoid base was obtained in the pure state.

The action of 5-aldehydoacridine (compare Abstr., 1911, i, 688) on dimethylaniline in presence of zinc chloride and subsequent treatment with dilute hydrochloric acid, followed by oxidation of any leuco-compound with lead dioxide, yield a small quantity of a violet colour-

ing matter, which was not investigated further, and *dimethylaminophenyl-acridylmethylenequinonodimethyliminium chloride*,



which is a green colouring matter with a bronze lustre, dissolving slightly in water and readily in alcohol. It dyes cotton a somewhat bluer green than malachite-green, whilst wool is dyed only very faintly in neutral solution, but more strongly in presence of borax or ammonia. The first portions of wool immersed are coloured green with a slight blue tinge, but if successive portions are introduced into the same bath, the colour approaches more and more nearly to blue; this is found to be a result of the presence of alkali.

*Tetramethyldiaminodiphenylacridylmethane* (leuco-base of acridyl-malachite - green),  $\text{N} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{C} \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , forms yellow, acicular crystals, m. p. 171—172°, insoluble in water, but readily soluble in acids or organic solvents.

The *quinonoid base*,  $\text{N} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{C} \cdot \text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \cdot \text{NMe}_2 \cdot \text{OH} \\ \diagdown \text{C}_6\text{H}_4 \cdot \text{NMe}_2 \end{array}$ , forms greenish-golden plates.

In neutral aqueous solution the maximum intensity of the absorption band of acridylmalachite-green lies at  $\lambda = 642 \mu\mu$ , whilst, according to Formanek, that for malachite-green is at  $\lambda = 618.5 \mu\mu$ ; the displacement caused by the substitution of an acridine nucleus for a benzene ring is hence  $23.5 \mu\mu$ .

*Acridylpyronine*,  $\text{N} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{C} \cdot \text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_3(\text{NEt}_2) \\ \diagdown \text{C}_6\text{H}_3(\text{:NEt}_2 \cdot \text{OH}) \end{array} \text{O}$ , obtained by condensing 5-aldehydoacridine with *m*-diethylaminophenol in presence of sulphuric acid, dissolves in very dilute acids, giving a violet-red colour, changing to cherry-red on addition of concentrated acid. It dyes silk and wool reddish-violet, and cotton blue with a red tinge, no mordant being necessary. The absorption bands are almost identical in aqueous and in alcoholic solution, and in both cases little change is produced by acidification with nitric acid or addition of potassium hydroxide; this behaviour is characteristic of all colouring matters of the pyronine series. The absorption spectrum of acridine lies in the ultra-violet, close to the visible part of the spectrum, and the introduction of the pyronine residue results in the displacement of this absorption into the violet. The maximum intensities of the absorption bands lie at  $580 \mu\mu$  and  $534.8 \mu\mu$ , whilst Biehringer (Abstr., 1897, i, 73) found for tetra-ethylrosamine,  $563.5$  and  $527.5 \mu\mu$ ; the displacements caused by the replacement of the benzene ring by an acridine residue are hence  $16.5 \mu\mu$  and  $7.3 \mu\mu$ . T. H. P.

**Relation between Constitution and Phototropy.** MAURIZIO PADOA and F. BOVINI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 712—717. Compare Padoa and Graziani, Abstr., 1910, i, 778; Padoa and Santi, Abstr., 1911, i, 693, 1029).—The phototropy of the compounds described in the present paper follows the regularities previously discovered.

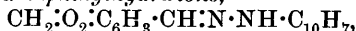
*$\beta$ -Benzil- $\alpha$ -naphthyllosazone*,  $\text{C}_2\text{Ph}_2(\text{:N} \cdot \text{NH} \cdot \text{C}_{10}\text{H}_7)_2$ , obtained by

Purgotti's method (Abstr., 1893, i, 354), forms lemon-yellow crystals, m. p.  $175^{\circ}$ , and is not phototropic.

$\beta$ -*Piperil- $\alpha$ -naphthyllosazone*,  $C_2(C_6H_3:O_2:CH_2)_2(:N\cdot NH\cdot C_{10}H_7)_2$ , prepared by MacNair's method (Abstr., 1890, 1245), crystallises in yellow needles, m. p.  $189^{\circ}$ , and is prototropic.

$\beta$ -*Anisil- $\alpha$ -naphthyllosazone*,  $C_2(C_6H_4\cdot OMe)_2(:N\cdot NH\cdot C_{10}H_7)_2$ , prepared like the preceding compound, crystallises in golden-yellow needles, m. p.  $155^{\circ}$ , and is prototropic.

*Piperonaldehyde- $\alpha$ -naphthylhydrazone*,



crystallises in greenish-yellow needles, m. p.  $147^{\circ}$ , and is not phototropic.

*Salicylaldehyde- $\alpha$ -naphthylhydrazone*,  $HO\cdot C_6H_4\cdot CH:N\cdot NH\cdot C_{10}H_7$ , forms lustrous, golden-yellow needles, m. p.  $134^{\circ}$ , and is not phototropic.

*Vanillin- $\alpha$ -naphthylhydrazone*,  $OMe\cdot C_6H_3(OH)\cdot CH:N\cdot NH\cdot C_{10}H_7$ , is an unstable, yellow, crystalline powder, which is not phototropic.

*p-Tolualdehyde- $\alpha$ -naphthylhydrazone*,  $C_6H_4Me\cdot CH:N\cdot NH\cdot C_{10}H_7$ , crystallises in greenish-yellow needles, m. p.  $152^{\circ}$ , and is not phototropic.

$\beta$ -*Benzil-1:3:4-xyllylosazone*,  $C_2Ph_2(:N\cdot NH\cdot C_6H_3Me_2)_2$ , is an orange-yellow, crystalline substance, m. p.  $71-72^{\circ}$ , and is phototropic.

*Piperil-1:3:4-xyllylosazone*,  $C_2(C_6H_3:O_2:CH_2)_2(:N\cdot NH\cdot C_6H_3Me_2)_2$ , forms lemon-yellow prisms, m. p.  $187^{\circ}$ , and is phototropic.

*Anisil-1:3:4-xyllylosazone*,  $C_2(C_6H_3\cdot OMe)_2(:N\cdot NH\cdot C_6H_3Me_2)_2$ , is an orange-yellow, crystalline substance, m. p.  $75^{\circ}$ , and is phototropic.

*Cumini-1:3:4-xyllylosazone*,  $C_2(C_6H_4Pr^a)_2(:N\cdot NH\cdot C_6H_3Me_2)_2$ , is a yellow, crystalline substance, m. p.  $64-70^{\circ}$ , and is not phototropic.

R. V. S.

**Researches on Purines. IV. 2-Oxypurine and 2-Oxy-8-methylpurine.** CARL O. JOHNS (*J. Biol. Chem.*, 1912, 11, 67-72).—6-Oxypurine (hypoxanthine) was first isolated by Scherer in 1850, and nearly fifty years later was synthesised by Fischer. 8-Oxypurine was prepared by Fischer and Ach. 2-Oxypurine was prepared by Tafel and Ach from guanine, but they did not offer any proof of its structure. In the present research it was prepared from 5:6-diamino-2-pyrimidone, and the product agrees in all respects with that of Tafel and Ach. When 5:6-diamino-2-pyrimidone is heated with formic acid, a *monoformyl* derivative is obtained; this yields a potassium salt, which when heated gives off water, and changes to the potassium salt of 2-oxypurine; 2-oxypurine crystallises with  $1H_2O$ , and does not lose it until heated to  $120^{\circ}$ . The picrate, nitrate, and hydrochloride were prepared.

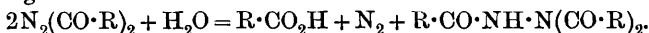
When 5:6-diamino-2-pyrimidone is boiled with acetic anhydride it forms chiefly a monoacetyl compound, together with some of the diacetyl compound. When the potassium salt of the former is heated, it yields the potassium salt of 2-oxy-8-methylpurine; this substance forms a *picrate*, decomp.  $250^{\circ}$ , and a *nitrate*, decomp.  $205^{\circ}$ , which may be used for its identification.

W. D. H.

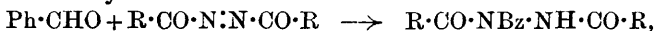
### Preparation and Reactions of Azo-acyl Compounds.

ROBERT STOLLÉ [with J. MAMPEL, J. HOLZAPFEL, and K. C. LEVERKUS] (*Ber.*, 1912, **45**, 273—289).—Azodiacyls of the type  $R \cdot CO \cdot N \cdot N \cdot CO \cdot R$  (where  $R = H, Me, CH_2Et, Ph, C_6H_4Cl$ , and  $\alpha\text{-C}_{10}H_7$ ) have been prepared by the action of iodine or bromine in ethereal solution on the mercury or silver salts of symmetrical diacylhydrazides,  
 $R \cdot CO \cdot NH \cdot NH \cdot COR$ .

The azodiacyls prepared from hydrazides of aromatic acids are comparatively stable, whilst those derived from aliphatic acids are unstable, and could only be obtained in ethereal solution or in an impure condition as red oils. They are converted by reducing agents, such as hydriodic acid, hydrogen sulphide, and phenylhydrazine, into the original hydrazides. When treated with water they yield triacylhydrazides, the decomposition taking place according to the following scheme:

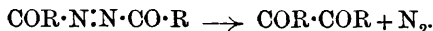


It is supposed that the first stage in the reaction consists in the partial hydrolysis of the azodiacyl to the compound (I), which instantly decomposes, thus: (I)  $NH \cdot N \cdot CO \cdot R \rightarrow H + N_2 + \cdot CO \cdot R$ ; this is followed by addition of  $H$  and  $\cdot COR$  to a second molecule of the azodiacyl with the formation of a triacylhydrazide. Evidence in support of this view is furnished by the production of triacylhydrazides by the reaction of azodibenzoyl and azodi- $\alpha$ -ethylbutyryl with benzaldehyde:

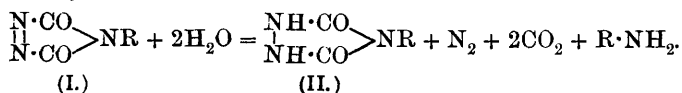


and also by the formation of benzoylhydrazobenzene,  $NPhBz \cdot NHPh$ , by heating azobenzene with benzaldehyde for fifteen hours at  $110^\circ$ .

The decomposition of the azodiacyls by heat has not yet been thoroughly investigated, but with azodibenzoyl and azodi- $\alpha$ -naphthoyl the decomposition occurs to a small extent as follows:

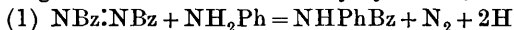


Azodicarboxylimide and several of its derivatives of the formula (I) below (where  $R = H, Ph, NH_2, N \cdot CHPh$ ) have also been prepared by the action of iodine in ethereal solution on the silver salts of the corresponding hydrazo-compounds (II); they are decomposed by water as follows:



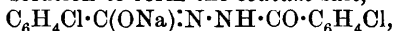
The mercury salt of *s*-dibenzoylhydrazide,  $CPh \langle \begin{array}{c} N - N \\ O \cdot Hg \cdot O \end{array} \rangle CPh$ , obtained by the action of mercuric chloride on the hydrazide and sodium ethoxide in alcoholic solution, is converted by bromine in ethereal solution into azodibenzoyl (Stollé and Benrath, *Abstr.*, 1900, i, 531; 1904, i, 935). When heated at  $270^\circ$  in an atmosphere of carbon dioxide, this decomposes, yielding small quantities of benzil and 2:5-diphenyl-1:3:4-oxadiazole. It combines with benzaldehyde at  $110^\circ$  to form tribenzoylhydrazide, a small amount of the above-

mentioned oxadiazole being produced simultaneously. It reacts with aniline, yielding benzanilide and *s*-dibenzoylhydrazide, thus:



and with dimethylaniline to form *s*-dibenzoylhydrazide, the dimethylaniline being oxidised to tetramethyldiphenylmethane and other products not yet investigated.

*s*-Di-*p*-chlorobenzoylhydrazide, prepared from hydrazine sulphate, *p*-chlorobenzoyl chloride, and aqueous sodium hydroxide, crystallises in felted needles, m. p. 289°, and reacts with sodium hydroxide in aqueous alcoholic solution to form the sodium salt,



which crystallises in lustrous, pale yellow leaflets, and is oxidised by iodine in ethereal solution to azodi-*p*-chlorobenzoyl,  $\text{N}_2(\text{CO}\cdot\text{C}_6\text{H}_4\text{Cl})_2$ , yellow needles, m. p. 147° (decomp.).

*s*-Di-*a*-naphthoylhydrazide, prepared in a similar manner, has m. p. 260°, and forms a silver salt,  $\text{C}_{10}\text{H}_7\cdot\text{C}(\text{OAg})\cdot\text{N}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_{10}\text{H}_7$ , which is oxidised to azodi-*a*-naphthoyl,  $\text{N}_2(\text{CO}\cdot\text{C}_{10}\text{H}_7)_2$ . This crystallises in orange-red needles, m. p. 148°, and when heated at 140–150° loses nitrogen, yielding di-*a*-naphthylldiketone,  $\text{C}_{10}\text{H}_7\cdot\text{CO}\cdot\text{CO}\cdot\text{C}_{10}\text{H}_7$ , m. p. 187°; it reacts with water to form *a*-naphthoic acid, *s*-di-*a*-naphthoylhydrazide, and tri-*a*-naphthoylhydrazide,  $\text{C}_{10}\text{H}_7\cdot\text{CO}\cdot\text{NH}\cdot\text{N}(\text{CO}\cdot\text{C}_{10}\text{H}_7)_2$ , which has m. p. 188°, and has also been prepared by the action of *a*-naphthoyl chloride on the silver salt of *s*-di-*a*-naphthoylhydrazide.

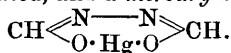
The sodium salt of *s*-benzoylacetylhydrazide,  $\text{C}_9\text{H}_9\text{O}_2\text{N}_2\text{Na}$ , is converted by mercuric chloride in alcoholic solution into the mercury salt,  $\text{C}_9\text{H}_9\text{O}_2\text{N}_2\text{Hg}$ .

Benzoylazoacetyl,  $\text{NAC}:\text{NBz}$ , obtained in an impure condition as a red oil by the interaction of iodine and the preceding mercury salt in ethereal solution, is decomposed by water, yielding benzoic acid, *s*-dibenzoylhydrazide, and dibenzoylacetylhydrazide,  $\text{NACBz}:\text{NHBz}$ , m. p. 171°.

2-Phenyl-5-methyl-1 : 3 : 4-oxadiazole,  $\text{CMe} \begin{smallmatrix} \text{N} \cdot \text{N} \\ \diagdown \quad \diagup \\ \text{O} \end{smallmatrix} \text{CPh}$ , prepared by heating *s*-benzoylacetylhydrazide with phosphoryl chloride, crystallises in lustrous plates, m. p. 67°; it forms with silver nitrate an additive compound crystallising in lustrous needles, m. p. 185°; an additive compound with mercuric chloride is also described.

Dibenzoyldiacetylhydrazide,  $\text{NACBz}:\text{NACBz}$ , prepared either from acetyl chloride and the mercury salt of *s*-dibenzoylhydrazide or from benzoyl chloride and the mercury salt of *s*-diacetylhydrazide, crystallises in leaflets, m. p. 109°.

*s*-Diformylhydrazide yields a crystalline silver salt,  $\text{C}_2\text{H}_2\text{O}_2\text{N}_2\text{Ag}_2$ , which explodes when heated, and a mercury salt,



Azodiformyl,  $\text{N}_2(\text{CHO})_2$ , prepared from the preceding mercury salt, could not be isolated on account of its instability; its ethereal solutions have a raspberry-red colour.

The mercury salt of *s*-diacetylhydrazide,  $\text{C}_4\text{H}_6\text{O}_2\text{N}_2\text{Hg}$ , prepared from

the hydrazide, sodium ethoxide, and aqueous mercuric chloride, reacts with iodine in ethereal solution in the presence of magnesium or barium oxides, yielding *azodiacetyl*,  $\text{NAc:NAc}$ , in an impure condition as a dark red oil.

*s-Di- $\alpha$ -ethylbutyrylhydrazide*,  $\text{N}_2\text{H}_2(\text{CO}\cdot\text{CHEt}_2)_2$ , prepared from the corresponding acid chloride and hydrazine hydrate in the presence of sodium carbonate, crystallises in white needles, m. p.  $230^\circ$ .

*Azodi- $\alpha$ -ethylbutyryl*,  $\text{N}_2(\text{CO}\cdot\text{CHEt}_2)_2$ , obtained from the mercury salt,  $\text{C}_{12}\text{H}_{22}\text{O}_2\text{N}_2\text{Hg}$ , of the preceding compound as a red oil, is decomposed by water into  $\alpha$ -ethylbutyric acid and *tri- $\alpha$ -ethylbutyrylhydrazide*,  $\text{CHEt}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{N}(\text{CO}\cdot\text{CHEt}_2)_2$ , which crystallises in colourless prisms, m. p.  $95^\circ$ , and has also been prepared by the interaction of  $\alpha$ -ethylbutyryl chloride and *s-a-diethylbutyrylhydrazide* in pyridine solution at  $100^\circ$ . It combines with benzaldehyde, yielding *benzoyldi- $\alpha$ -ethylbutyrylhydrazide*,  $\text{CHEt}_2\cdot\text{CO}\cdot\text{NBz}\cdot\text{NH}\cdot\text{CO}\cdot\text{CHEt}_2$ , crystallising in small prisms, m. p.  $123^\circ$ . The latter compound may also be prepared from benzoyl chloride and *s-di- $\alpha$ -ethylbutyrylhydrazide* in pyridine solution.

*Azodicarboxylimide* [*diketodihydro-1:3:4-triazole*],  $\begin{array}{c} \text{N}\cdot\text{CO} \\ || \\ \text{N}\cdot\text{CO} \end{array} \text{>NH}$ , obtained as a violet oil by the action of ethereal iodine on the silver salt of hydrazodicarboxylimide in the presence of barium and magnesium oxides, is instantly decomposed by water, yielding nitrogen, carbon dioxide, and hydrazodicarboxylimide.

Hydrazodicarboxylphenylimide yields the *silver* salts,  $\text{C}_8\text{H}_6\text{O}_2\text{N}_3\text{Ag}$  and  $\text{C}_8\text{H}_3\text{O}_2\text{N}_3\text{Ag}_2$ , of which the latter is converted in the usual manner into azodicarboxylphenylimide. This forms carmine-red crystals (compare Thiele and Stange, Abstr., 1895, i, 251), gives violet solutions in ether, and decomposes when heated into phenylcarbimide and

*hydrazotetracarboxyldiphenyldi-imide*,  $\text{NPh} \begin{array}{c} \text{CO}\cdot\text{N}\cdot\text{CO} \\ | \\ \text{CO}\cdot\text{N}\cdot\text{CO} \end{array} \text{NPh}$ , which crystallises from glacial acetic acid in lustrous, white leaflets, subliming in needles without melting.

*Azodicarboxylaminoimide* (*azodicarboxylhydrazide*) [*1-amino-2:5-diketodihydro-1:3:4-triazole*],  $\begin{array}{c} \text{N}\cdot\text{CO} \\ || \\ \text{N}\cdot\text{CO} \end{array} \text{>N}\cdot\text{NH}_2$ , prepared from the *silver* salt of aminourazole (Curtius and Heidenreich, Abstr., 1896, i, 143),  $\text{C}_2\text{H}_2\text{O}_2\text{N}_4\text{Ag}_2$ , is an unstable, violet powder; it explodes at  $72^\circ$ , and is slowly converted by water into aminourazole.

*Azodicarboxylbenzylidenehydrazide*,  $\begin{array}{c} \text{N}\cdot\text{CO} \\ || \\ \text{N}\cdot\text{CO} \end{array} \text{>N}\cdot\text{N}\cdot\text{CHPh}$ , obtained from the *silver* salt of benzylidenaminourazole (hydrazodicarboxylbenzylidenehydrazide),  $\text{C}_9\text{H}_6\text{O}_2\text{N}_4\text{Ag}_2$ , forms carmine-red crystals, which become colourless when heated (at  $135$ — $138^\circ$ ), owing to loss of nitrogen and conversion into *hydrazotetracarboxyldibenzylidenedihydrazide*,  $\text{CHPh}\cdot\text{N}\cdot\text{N} \begin{array}{c} \text{CO}\cdot\text{N}\cdot\text{CO} \\ | \\ \text{CO}\cdot\text{N}\cdot\text{CO} \end{array} \text{N}\cdot\text{N}\cdot\text{CHPh}$ , m. p.  $285^\circ$ .

The *mercury* salts of ethyl hydrazodicarboxylate yields, with iodine in ethereal solution, ethyl azodicarboxylate (Curtius and Heidenreich,

*loc. cit.*), and, when heated with benzoyl chloride in carbon tetrachloride solution at 100°, forms *ethyl dibenzoylhydrazodicarboxylate*,  $C_{20}H_{20}O_6N_2$ , which forms white crystals, m. p. 83°. F. B.

**Enzymic Decomposition of Hydrogen Peroxide. II.** PERCY WAENTIG and OTTO STECHE (*Zeitsch. physiol. Chem.*, 1912, **76**, 177—213. Compare Abstr., 1911, i, 759).—The behaviour of both animal and vegetable extracts in decomposing hydrogen peroxide is very similar, and in far closer agreement with Senter's hæmase than is generally stated. This is illustrated particularly by the influence of hydrogen and hydroxyl ions on the rate of reaction—any shift in equilibrium from that prevailing in distilled water, free from carbon dioxide, causes a retardation. The reaction is, however, less sensitive when relatively large amounts of impurity are present in the extracts; this may be due to the amphoteric character of the proteins in retaining acids or bases, or to a definite protective action of the impurities analogous to that of the so-called "protective colloids." This insensitive character is specially marked in catalase solutions prepared from the alcohol precipitate of an aqueous extract of germinating barley.

The enzyme extracts behave similarly at 0° and at 30°; at the higher temperature the hydrogen ion has less, the hydroxyl ion more, influence on the rate of change. The influence of temperature on the rate is very small. The course of change does not quite correspond with the simple mass-action law; the value of  $K$  falls off even in very dilute hydrogen peroxide solutions at 0°. Dialysis yields weaker extracts, but with these a more constant value of  $K$  is obtained. The amount of enzyme is roughly proportional to the rate of change.

Exposure to ultra-violet light weakens the enzyme activity; the effect is greater in alkaline than in neutral or acid solution.

Complete precipitation of the enzyme from extracts of liver, fat, barley, etc., requires an alcohol concentration of 55%. Animal extracts show a decline in activity when the concentration of hydrogen peroxide exceeds a certain point; this is not the case with plant extracts.

It would appear that the active substance which brings about the decomposition of hydrogen peroxide is the same irrespective of origin.

E. F. A.

**Preparation of Mercury *p*-Aminophenylarsinates.** AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 237787).—*Mercury hydrogen p-aminophenylarsinate*,  $[NH_2 \cdot C_6H_4 \cdot AsO(OH) \cdot O]_2Hg$ , a colourless powder, sparingly soluble in water, is prepared by stirring together an aqueous paste of *p*-aminophenylarsinic acid (2 mols.) and mercuric oxide (1 mol.). The *basic salt*,  $NH_2 \cdot C_6H_4 \cdot AsO(OH) \cdot O \cdot Hg \cdot OH$ , is obtained when equimolecular proportions of the amino-acid and mercuric chloride in the presence of alkali (2 mols.) are employed.

F. M. G. M.

## Organic Chemistry.

**The Autoxidation of Organic Compounds.** HERMANN STAUDINGER (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 216—219).—The autoxidation of compounds containing a double linking involves the formation of two oxides, one of which is symmetrical, as in the case of diphenylethylene,  $\begin{array}{c} \text{CPh}_2 \cdot \text{O} \\ | \\ \text{CH}_2 - \text{O} \end{array}$ , and the other unsymmetrical, as with trichloroethylene,  $\begin{array}{c} \text{CCl}_3 \\ | \\ \text{CHCl} \end{array} \text{---} \text{O} \cdot \text{O}$ , which then breaks up into  $\begin{array}{c} \text{CCl}_2 \\ | \\ \text{CHCl} \end{array} \text{---} \text{O}$  and oxygen. It is assumed that the first product is always the unsymmetrical compound, which may then undergo rearrangement. C. H. D.

**Action of the Grignard Reagent on Methyl ethylacetaldehyde and the Preparation of Some Diolefines, Olefines, and Saturated Secondary Alcohols.** E. BJELOUSS (*Ber.*, 1912, 45, 625—632. Compare *Abstr.*, 1910, i, 706).— $\delta$ -Methyl- $\Delta^7$ -octen- $\epsilon$ -ol,  $\text{CH}_2\text{Me} \cdot \text{CH} \cdot \text{CMe} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2\text{Me}$ , prepared from propyl chloride and methyl ethylacetaldehyde, is a colourless, mobile, strongly smelling liquid, m. p.  $79-81^\circ/10$  mm.,  $D_4^{25}$  0.8468,  $n_D^{25}$  1.4445. The *acetate* is a colourless, mobile liquid, b. p.  $87-89^\circ/14$  mm.; the *chloride* has b. p.  $59-62^\circ/11$  mm.

$\gamma$ -Methyl- $\Delta^7$ -hexadiene,  $\text{CH}_2\text{Me} \cdot \text{CH} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CH}_2$ , is a very mobile, colourless liquid, b. p.  $101-103^\circ$ ,  $D_4^{25}$  0.7407,  $n_D^{25}$  1.452.

$\delta$ -Methyl- $\Delta^7$ -octadiene,  $\text{CH}_2\text{Me} \cdot \text{CH} \cdot \text{CMe} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2\text{Me}$ , is a colourless liquid of characteristic odour, b. p.  $148-151^\circ$ ,  $D_4^{25}$  0.764,  $n_D^{25}$  1.4628.

$\gamma$ -Methylhexan- $\beta$ -ol,  $\text{CH}_2\text{Me} \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CHMe} \cdot \text{OH}$ , is a colourless, mobile liquid with an odour of peppermint, b. p.  $79-81^\circ/52$  mm.,  $D_4^{25}$  0.822,  $n_D^{25}$  1.4207; the *acetate* is a pleasant smelling liquid, b. p.  $84-87^\circ$ ; the *chloride* has b. p.  $53-58^\circ/36$  mm.

$\delta$ -Methylheptan- $\gamma$ -ol,  $\text{CH}_2\text{Me} \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2\text{Me}$ , is an agreeable smelling liquid, b. p.  $98-99^\circ/75$  mm.,  $D_4^{25}$  0.8263,  $n_D^{25}$  1.4261; the *acetate* has b. p.  $103-104^\circ/75$  mm.; the *chloride*, b. p.  $83-86^\circ/79$  mm.

$\delta$ -Methyloctan- $\epsilon$ -ol is a colourless, strongly smelling liquid, b. p.  $74-76^\circ/9$  mm.,  $D_4^{25}$  0.8156,  $n_D^{25}$  1.4262.

$\beta$ -Dimethyloctan- $\delta$ -ol,  $\text{CH}_2\text{Me} \cdot \text{CH}_2 \cdot \text{CHMe} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CHMe}_2$ , is similarly a colourless, mobile liquid, b. p.  $102-104^\circ/34$  mm.,  $D_4^{25}$  0.8125,  $n_D^{25}$  1.4259; the *phenylurethane* crystallises in bunches of needles, m. p.  $39-40^\circ$ .

$\beta$ -Dimethylnonan- $\epsilon$ -ol has b. p.  $98-99^\circ/11$  mm.,  $D_4^{25}$  0.8126,  $n_D^{25}$  1.4295; the crystalline *phenylurethane* has m. p.  $43-44^\circ$ .

$\gamma$ -Methyl- $\Delta^6$ -hexene,  $\text{CH}_2\text{Me} \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CHMe}$ , prepared by elimination of hydrogen bromide from methylhexanyl bromide, is an exceed-

ingly volatile liquid of pleasant odour, b. p. 85—90°,  $D_4^{25}$  0.7301,  $n_D^{25}$  1.4132.

$\delta$ -Methyl- $\Delta^7$ -heptene is very similar; it has b. p. 115—120°,  $D_4^{25}$  0.7411,  $n_D^{25}$  1.4171.

$\delta$ -Methyl- $\Delta^8$ -octene has a penetrating odour, b. p. 133—138°,  $D_4^{25}$  0.7388,  $n_D^{25}$  1.4178.

$\beta$ -Dimethyl- $\Delta^8$ -octene has b. p. 152—157°,  $D_4^{25}$  0.746,  $n_D^{25}$  1.4189.

$\delta\theta$ -Dimethyl- $\Delta^8$ -nonene has b. p. 165—169°,  $D_4^{25}$  0.753,  $n_D^{25}$  1.4278.

By the action of magnesium phenyl bromide on methylethylacraldehyde an alcohol is at first formed, but on distillation in a vacuum water is eliminated and a hydrocarbon,  $\alpha$ -phenyl- $\beta$ -methyl- $\Delta^{\alpha\gamma}$ -pentadiene (?), obtained; this is a yellow, mobile, strong smelling liquid, b. p. 228—231°/753 mm.,  $D_4^{25}$  0.8986,  $n_D^{25}$  1.5257.

$\alpha$ -Phenyl- $\beta$ -methylpentane, obtained on reducing phenylmethyl-pentenol, is a colourless, mobile, pleasant smelling liquid, b. p. 203—207°,  $D_4^{25}$  0.8584,  $n_D^{25}$  1.4827.

$\alpha$ -Naphthyl- $\beta$ -methyl- $\Delta^{\alpha\gamma}$ -pentadiene (?) is a yellow liquid of characteristic odour, b. p. 178—181°/12 mm.,  $D_4^{25}$  0.9801,  $n_D^{25}$  1.5697.

E. F. A.

**Compounds with Triple Linkings.** WILHELM MANCHOT [with JOHN C. WITHERS and HEINRICH OLTROGGE] (*Annalen*, 1912, **387**, 257—293).—Various observers have described additive compounds of acetylene and cuprous chloride, but have been unable to show that their substances are initial products of the reaction. The authors, using a modified form of the apparatus described previously (*Abstr.*, 1910, i, 85), now show that the initial product is the white substance,  $C_2H_2 \cdot CuCl$ . On account of its solubility and of the secondary reaction which occurs in concentrated solutions, this substance cannot be isolated from aqueous solutions; it is obtained, however, by working in absolute alcoholic solution at 0°. At 0° and atmospheric pressure, experiments with solutions containing 0.034 gram-molecule of cuprous chloride per litre and varying quantities of hydrochloric acid yield the following results. With 0.61 gram-molecule of hydrochloric acid per litre, a clear, colourless solution is obtained, and 22.44 litres of acetylene (per 1 gram atom of copper) are absorbed. With greater concentrations of hydrochloric acid, the absorption of acetylene diminishes owing to the concurrent reaction:  $CuCl + HCl = CuCl \cdot HCl$ . When the concentration of the hydrochloric acid is less than 0.61 mol. per litre, the absorption of acetylene also diminishes, owing to the formation of a dark violet substance,  $C_2Cu_2 \cdot CuCl \cdot H_2O$ .

When the concentration of the cuprous chloride in a solution of 0.61 mol. of hydrochloric acid per litre is increased, the absorption of acetylene diminishes, owing to the formation of a sparingly soluble white substance,  $2CuCl \cdot C_2H_2$ ; thus:  $2(CuCl \cdot C_2H_2) \rightleftharpoons C_2H_2 + 2CuCl \cdot C_2H_2$ . For example, the absorption of acetylene is 22.4 litres (per 1 gram atom of copper) when the concentration of the cuprous chloride is 0.00561 mol. of cuprous chloride, and only 11.43 litres when the concentration is increased to 0.5035 mol.

In its ability to form a compound of the type  $2CuCl \cdot C_2H_2$ , acetylene differs from carbon monoxide and ethylene, and resembles nitric oxide

which can form a compound  $2\text{FeSO}_4\cdot\text{NO}$  (Abstr., 1907, ii, 93 ; 1908, ii, 375 ; 1910, i, 85 ; ii, 414, 956). The additive capacity of acetylene towards cuprous chloride also differs from those of carbon monoxide and ethylene in the following respect. The latter two gases only form additive compounds in the presence of water, ammonia, or organic bases ; the presence of alcohol not only retards the addition, but causes decomposition of the additive compound when formed. In the case of acetylene the presence of water is unnecessary for the formation of the additive compound  $\text{CuCl}\cdot\text{C}_2\text{H}_2$  ; the additive compound is formed, as in the case of nitric oxide and ferrous chloride, in absolute alcohol.

Substituted acetylenes, such as phenylacetylene, *p*-anisylacetylene, methylenedioxyphenylacetylene, behave like acetylene itself towards cuprous chloride. By direct addition of the components, colourless additive compounds of the type  $\text{CR}:\text{CH}\cdot\text{CuCl}$  are obtained, which are converted by water or ammonia into coloured copper derivatives,  $\text{CR}:\text{CCu}$ . Hence the equation  $\text{CR}:\text{CH} + \text{CuCl} = \text{CR}:\text{CCu} + \text{HCl}$  expresses only the initial and the final states ; the first phase of the process, that is, the condition for the subsequent substitution, is the formation of an additive compound of the two components. These experiments, therefore, support the views on processes of substitution recently advanced by Werner and by E. Fischer.

The presence of the group  $:\text{CH}$  is not the condition for the formation of additive compounds of acetylenes and metallic salts, because, although many substances of the type  $\text{CR}:\text{CR}'$  do not form additive compounds, bromophenylacetylene, iodophenylacetylene, phenylpropionitrile, and phenylpropionamide react readily with cuprous chloride to form such substances.

The authors are of opinion that the degree of unsaturation of substances containing a triple linking varies from case to case with the nature of the groups attached to the  $\text{C}:\text{C}$  group. Even if a group R is itself unsaturated, it does not necessarily increase the unsaturation of the whole molecule  $\text{CR}:\text{CR}'$  ; thus, diphenyldiacetylene, di-*p*-anisyldiacetylene, and bis-3 : 4-methylenedioxyphenyldiacetylene do not form additive compounds with cuprous chloride.

The following new compounds are described : *p*-Anisylacetylene forms a canary-yellow copper derivative,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}:\text{CCu}$ , and a colourless additive compound,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}:\text{CH}\cdot\text{CuCl}$ , and yields by treatment in ether with sodium and subsequently with benzoyl chloride, benzoyl-*p*-anisylacetylene,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}:\text{CBz}$ , m. p.  $81^\circ$ , which does not react with cuprous chloride and forms a dibromide,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CBr}:\text{CBrBz}$ , m. p.  $90^\circ$ . Di-*p*-anisyldiacetylene,



m. p.  $144^\circ$ , white needles, is obtained almost quantitatively by shaking the copper derivative of *p*-anisylacetylene with alcoholic ammonia and oxygen for four days. Bis-3 : 4-methylenedioxyphenyldiacetylene,  $\text{C}_{18}\text{H}_{10}\text{O}_4$ , m. p.  $197^\circ$ , and diphenyldiacetylene are prepared in a similar manner.

C. S.

**Derivatives of Acetylene.** HUGO NOERDLINGER (*Kleine Mitt. Chem. Fabrik. Flörsheim*, No. 37).—The physical constants and properties of the following derivatives of acetylene are given : Heptinene (*n*-amyl-

acetylene, b. p. 108—110°/745 mm., 26°/10 mm., m. p. below -70°,  $D^{15}$  0.7546,  $D^{20}$  0.7470. Octinene (*n*-hexylacetylene), b. p. 130—132°/745 mm., 31°/8 mm., m. p. below -70°,  $D^{15}$  0.7680. Noninene (*n*-heptylacetylene), b. p. 160°/745 mm., 51°/8 mm., m. p. -65°,  $D^{15}$  0.7799. Decinene (*n*-octylacetylene), b. p. 181—182°/745 mm., 69—70°/10 mm., m. p. -36°,  $D^{15}$  0.7924. Undecinene (*n*-nonylacetylene), b. p. 202—204°/745 mm., 91°/8 mm., m. p. -33°,  $D^{15}$  0.8024.

All these compounds are colourless liquids, practically insoluble in water, soluble in organic solvents. They possess a high refractive index, and a characteristic odour which is particularly marked in the cases of heptinene and undecinene. With ammoniacal cuprous chloride and silver nitrate solutions, they yield yellow and white precipitates respectively. When dissolved in ether and treated with sodium, they evolve hydrogen and form highly reactive sodium compounds. H. W.

**Density and Thermal Expansion of Ethyl Alcohol and its Mixtures with Water.** N. S. OSBORNE, E. C. MCKELVY, and H. W. BEARCE (*J. Washington Acad. Sci.*, 1912, 2, 95—98).—The densities of twelve mixtures of ethyl alcohol and water were determined at 10°, 15°, 20°, 25°, 30°, 35°, and 40° by the method of hydrostatic weighing. For each mixture the constants  $\alpha$ ,  $\beta$ , and  $\gamma$  in the equation  $D_t = D_{25} + \alpha(t - 25) + \beta(t - 25)^2 + \gamma(t - 25)^3$ , and these values are tabulated together with  $D^{25}$ .

The values of  $\alpha$ ,  $\beta$ , and  $\gamma$  for each integral % of alcohol between 0 and 100 have been obtained by interpolation. The mean of fifteen determinations of the density of the purest alcohol at 25° was found to be 0.78506. H. M. D.

**Action of the Chlorides of  $\alpha$ -Alkyloxy-acids on Organo-metallic Derivatives of Zinc.** EDMOND E. BLAISE and L. PICARD (*Ann. Chim. Phys.*, 1912, [viii], 25, 253—276).—For the most part a résumé of work already published (*Abstr.*, 1911, i, 175, 260). The following new data are recorded regarding substances obtained in the general reaction.

*Ethyl n-amyl ether*, b. p. 119—120°, is a mobile, pleasant smelling liquid, insoluble in water, which on heating with hydriodic acid yields *n*-amyl iodide, from which *n*-amyl ether, b. p. 70°/12 mm., and *n*-amyl alcohol were prepared. The *phenylurethane* of the latter has m. p. 46°, and crystallises in tablets, and the *benzoate* boils at 137—138°/15 mm. *Ethoxymethyl n-butyl ketone*,  $\text{OEt} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_4\text{H}_9$ , b. p. 79°/18 mm., is a pleasant-smelling liquid; the *oxime*, b. p. 125°/17 mm., is a colourless liquid; the *semicarbazone*, m. p. 99°, forms brilliant, colourless spangles.

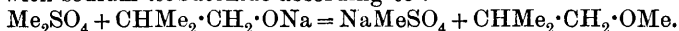
Condensation of ethoxyacetyl chloride with zinc *isoamyl* iodide furnished *ethyl isohexyl ether*,  $\text{OEt} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{Pr}^\beta$ , b. p. 68°/67 mm., or 137°/760 mm., and ethoxymethylhexanone (Sommelet, *Abstr.*, 1907, i, 107).

*p-Tolylethoxymethylethylcarbinol*,  $\text{OH} \cdot \text{CEt}(\text{CH}_2 \cdot \text{OEt}) \cdot \text{C}_6\text{H}_4\text{Me}$ , b. p. 130°/9 mm., obtained by the action of magnesium ethyl bromide on

*p*-tolylethoxymethyl ketone already described (Abstr., 1911, i, 175), gives by the application of Sommelet's method (*loc. cit.*),  $\beta$ -*p*-tolylbutaldehyde,  $C_6H_4Me \cdot CHEt \cdot CHO$ , b. p.  $104^\circ/8$  mm. The latter furnishes an *azine*, m. p.  $63^\circ$  (decomp.), a *semicarbazone*, *p*-nitrophenylhydrazone, m. p.  $104^\circ$ , and an *oxime*, m. p.  $70^\circ$ , all of which are crystalline.

T. A. H.

**Action of Alkyl oxides on Esters of Inorganic Acids.** I. L. RABTSEVITSCH-ZUBKOVSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 44, 151—154).—Methyl sulphate reacts with magnesium methoxide according to the equation:  $2Me_2SO_4 + Mg(OMe)_2 = 2Me_2O + Mg(SO_4Me)_2$ , and with sodium isobutoxide according to:



Magnesium methoxide and methyl phosphate yield methyl ether, and magnesium dimethyl phosphate:  $PO(OMe)_3 + Mg(OMe)_2 = 2Me_2O + Mg[O \cdot PO(OMe)_2]_2$ ; so that when alkyl oxides react with alkyl salts of polybasic inorganic acids, only one of the alkyloxy-groups of the salt is replaced by the metal of the alkyl oxide.

T. H. P.

**Preparation of Aminoethyl Alcohol from Egg Lecithin.** GEORG TRIER (*Zeitsch. physiol. Chem.*, 1912, 76, 496—498. Compare Abstr., 1911, i, 771).— $\beta$ -Aminoethyl alcohol is obtained as a product of the hydrolysis of egg lecithin by dilute sulphuric acid in not inconsiderable quantity, and identified by means of the aurichloride.

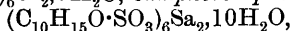
E. F. A.

**Should the Term Protagon be Retained?** WALDEMAR KOCH (*Proc. Amer. Soc. Biol. Chem.*, 1911, xl; *J. Biol. Chem.*, 11).—The term protagon has no longer any chemical significance; the substance so described contains at least three materials, namely, a phosphatide, which contains choline, a cerebroside, and a combination of a choline-free phosphatide and a cerebroside to which an ethereal sulphuric acid group is attached.

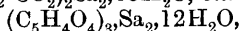
W. D. H.

**New Compounds of Samarium and Neodymium.** CHARLES JAMES, F. M. HOBEN, and C. H. ROBINSON (*J. Amer. Chem. Soc.*, 1912, 34, 276—281; *Chem. News*, 1912, 105, 121—122).—In the course of a search for salts which might be of value for fractionally separating the rare earths, the following compounds were prepared and are described.

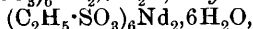
*Samarium ethylsulphonate*,  $(C_2H_5 \cdot SO_3)_6Sa_2, 6H_2O$ , *methylsulphonate*,  $(CH_3 \cdot SO_3)_6Sa_2, 7H_2O$ , *propylsulphonate*,  $(C_3H_7 \cdot SO_3)_6Sa_2, 9H_2O$ , *isobutylsulphonate*,  $(C_4H_9 \cdot SO_3)_6Sa_2, 7H_2O$ , *camphorsulphonate*,



*methanetrissulphonate*,  $[CH(SO_3)_3]_3Sa_2, 16H_2O$ , *m-xylene-4-sulphonate*,  $(C_6H_3Me_2 \cdot SO_3)_6Sa_2, 7H_2O$ , *glycollate*,  $(OH \cdot CH_2 \cdot CO_2)_6Sa_2$ , *cacodylate*,  $(Me_2AsO_2)_6Sa_2, 16H_2O$ , *ethanedisulphonate*,  $[C_2H_4(SO_3)_2]_3Sa_2, 4H_2O$ , *ethylglycollate*,  $(OEt \cdot CH_2 \cdot CO_2)_2Sa_2, 18H_2O$ , *citraconate*,



*sulphoacetate*,  $(C_2H_3O_5S)_3Sa_2$ , and *hydroxyethanesulphonate*. *Neodymium methylsulphonate*,  $(CH_3 \cdot SO_3)_6Nd_2, 7H_2O$ , *ethylsulphonate*,



propylsulphonate,  $(C_3H_7 \cdot SO_3)_6Nd_2 \cdot 6H_2O$ , isobutylsulphonate,  $(C_4H_9 \cdot SO_3)_6Nd_2 \cdot 8H_2O$ , ethanedisulphonate,  $[C_2H_4(SO_3)_2]_3Nd_2 \cdot 10H_2O$ , methanetrisulphonate,  $[CH(SO_3)_3]_2Nd_2 \cdot 14H_2O$ , camphorsulphonate,  $(C_{10}H_{15}O \cdot SO_3)_6Nd_2 \cdot 17H_2O$ , m-xylene-4-sulphonate,  $(C_6H_3Me_2 \cdot SO_3)_6Nd_2 \cdot 2H_2O$ , m-sulphobenzoate,  $(C_7H_4O_2S)_3Nd_2 \cdot 9H_2O$ , guinate,  $[C_6H_7(OH)_4 \cdot CO_2]_6Nd_2 \cdot 11H_2O$ , anisate,  $(OMe \cdot C_6H_4 \cdot CO_2)_6Nd_2$ , oxanilate,  $(NHPh \cdot CO \cdot CO_2)_6Nd_2 \cdot 5H_2O$ , cacodylate,  $(Me_2AsO)_6Nd_2$ , and hydroxyethanesulphonate. E. G.

Reduction of Higher Unsaturated Aliphatic Acids to Saturated Acids by the Action of Zinc and Water on their Halogen Derivatives; Grignard Reaction Applied to the Latter. SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 155—165).—Experiments with oleic, elaidic, erucic, undecenoic, ricinoleic, linoleic, and linolenic acids show that by addition of hydrogen bromide to these acids and treatment of the monobromosaturated acids thus obtained with zinc and water in a sealed tube, the corresponding saturated aliphatic acids themselves are obtained; for example,  $(C_{17}H_{34}Br \cdot CO_2)_2Zn + 2Zn + H_2O = (C_{17}H_{35} \cdot CO_2)_2Zn + (ZnBr_2 + ZnH)_2$ . Unsaturated hydroxy-acids may be converted into saturated hydroxy-acids in a similar manner. With monochloro-derivatives of saturated aliphatic acids, the reaction with zinc and water proceeds partly in the direction indicated by the above equation, but about one-third of the acid formed consists of the original unsaturated acid, from which the chloro-derivative of the saturated acid was obtained. As stated by Lewkowitsch ("Oils, Fats, and Waxes"), neither dichloro- nor dibromo-stearic acid gives the non-substituted stearic acid when heated with various metals in presence or absence of water or an organic solvent.

The following temperatures are those at which fused mixtures of oleic and stearic acid solidify: 10% stearic acid (90% oleic), 29.5°; 20%, 40.2°; 30%, 47.7°; 40%, 52.9°; 50%, 56.8°; 60%, 59.8°; 70%, 62.3°; 80%, 64.5°; 90%, 66.3°, and pure stearic acid, 68.0°.

T. H. P.

An Anomaly in the Reduction of Ethyl Acetoacetate. JULIUS TAFEL [with FRANZ ANDRE] (*Ber.*, 1912, 45, 437—452. Compare Tafel and Hahl, *Abstr.*, 1907, i, 765; Tafel and Jürgens, *Abstr.*, 1909, i, 545).—The electrolytic reduction of derivatives of acetoacetic esters has been interpreted to take place according to the scheme:  $CH_3 \cdot CO \cdot CHR \cdot CO_2Et \rightarrow CH_3 \cdot CH_2 \cdot CHR \cdot CH_3$ . Whilst, however, the range of the b. p. of the products obtained points to their uniformity, the actual b. p.'s do not in all cases agree with those recorded for the expected hydrocarbons, and in the cases where  $R = Et$ ,  $nPr$ , or  $nC_4H_9$ , lie close to those of the isomeric normal hydrocarbons; similarly, Tafel and Jürgens (*loc. cit.*) found for the reduction-product of ethyl isobutylacetoacetate a b. p. 7° higher than that given by Clarke (*Abstr.*, 1908, i, 593) for  $\beta\delta$ -dimethylhexane. The present work was undertaken with the object of explaining these differences,

and has led to the conclusion that the methyl group formed in the complete reduction of derivatives of acetoacetic esters is transposed and occurs, not as a side-chain, but as part of the main chain.

The reduction of ethyl *isobutyl*acetoacetate, whether with lead or cadmium electrodes, gave results precisely similar to those obtained by Tafel and Jürgens (*loc. cit.*) The product, which is now regarded as  $\beta$ -methylheptane or  $\gamma$ -methylheptane (instead of  $\beta\delta$ -dimethylhexane), appears to undergo slight decomposition when shaken with concentrated sulphuric acid according to the method previously used for its purification.

By the reduction of ethyl *sec.*-butylacetoacetate with lead electrodes, a hydrocarbon, b. p. 117·8—118·2°/746 mm., was obtained. This is regarded as  $\gamma$ -methylheptane or, possibly, a mixture of  $\delta$ -methylheptane and  $\gamma$ -ethylhexane.

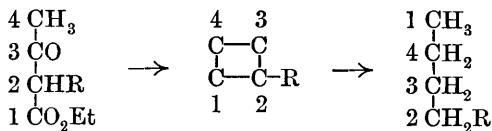
Methyl methylpropylacetoacetate, reduced at a cadmium electrode, yielded an octane of b. p. 116·1—118·2°/752 mm. This is probably  $\delta$ -methylheptane, possibly  $\gamma$ -methylheptane or  $\gamma$ -ethylhexane, or a mixture of the latter with  $\delta$ -methylheptane.

Methyl methyl*isopropyl*acetoacetate when similarly reduced gave an octane of b. p. 110—118°/756 mm., which is presumably a mixture of hydrocarbons.

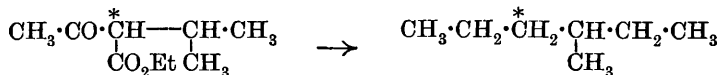
By the reduction of ethyl *isopropyl*acetoacetate, a heptane of b. p. 91—92·6°/747 mm., probably slightly impure  $\beta$ -methylhexane, or possibly  $\gamma$ -methylhexane, was obtained.

Ethyl ethylacetoacetate when reduced at cadmium or lead electrodes yielded a hydrocarbon which, after purification by means of concentrated sulphuric acid, had b. p. 68·2—69·1°/742 mm. This was unaffected by cold potassium permanganate, thereby differing from  $\gamma$ -methylheptane, which, according to Zelinsky and Zelikoff, is rapidly oxidised by this reagent—a statement, however, which the authors could not confirm experimentally.

An explanation of certain of these reactions may be found in the hypothesis that a tetramethylene ring is formed as an intermediate step in the reduction, and then broken in the manner indicated by the scheme :



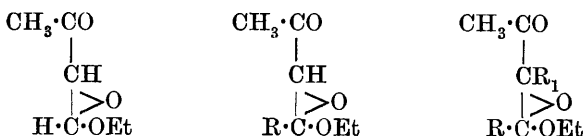
To explain the formation of  $\gamma$ -methyl derivatives from ethyl *iso*-butyl- and *isopropyl*-acetoacetates, it is necessary to assume that the carbon atom of the carbethoxy-group of the ester becomes detached from the  $\alpha$ -carbon atom (\*) and attached to a terminal C-atom of the alkyl group :



This leads to the same result as the above hypothesis in the cases of *n*-alkyl derivatives of ethyl acetoacetate and of ethyl diethylaceto-

acetate. In the cases of *sec.*-butyl, methylpropyl, and methylisopropyl derivatives, however, two products might be expected, whilst only one has been obtained, possibly owing to the proximity of their respective b. p.'s. On the whole, the second hypothesis explains the fact better than the first, but is advanced with caution on account of the difficulty of interpreting the mechanism involved.

A third possibility lies in the assumption of a new formulation for the substitution products of ethyl acetoacetate as shown in the following scheme :



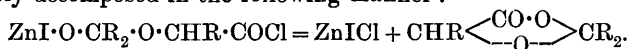
Possibly in ethyl acetoacetate this form may be in equilibrium with the forms generally assumed, and may also be the form mainly attacked during alkylation. According to this hypothesis, the same hydrocarbons should be obtained from monoalkyl derivatives of ethyl acetoacetate and from ethyl diethylacetoacetate as would be expected from the first hypothesis (see above). Ethyl methylpropylacetoacetate (from ethyl methylacetoacetate) should yield  $\gamma$ -ethylhexane, whilst ethyl methylisopropylacetoacetate (from ethyl methylacetoacetate) and ethyl methylbenzylacetoacetate (from ethyl benzylacetoacetate) should yield  $\beta$ -methyl- $\gamma$ -ethylpentane and  $\alpha$ -phenyl- $\gamma$ -methylpentane respectively.

H. W.

**A New Salt of  $\beta$ -Hydroxybutyric Acid.** PHILLIP A. SHAFFER (*Proc. Amer. Soc. Biol. Chem.*, 1911, xi; *J. Biol. Chem.*, 11).—If equivalent parts of zinc and calcium  $\beta$ -hydroxybutyrates (made by treating the free acid with zinc and calcium carbonate respectively) are poured together, a double salt,  $\text{ZnCa}(\text{C}_4\text{H}_7\text{O}_3)_4$ , is formed, which on the addition to the warmed solution of an equal volume of alcohol, crystallises out in needles or long, narrow plates. It is useful for the purification of the acid, which may be obtained from the double salt by removing the zinc with hydrogen sulphide, and the calcium with oxalic acid; or a solution of the salt acidified with sulphuric acid and dehydrated by plaster or anhydrous sodium sulphate may be extracted with dry ether. The salt prepared from the *l*-acid has a specific rotation,  $[\alpha]_D^{20} = -15.1^\circ$  (5% solution).

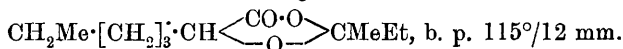
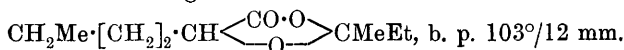
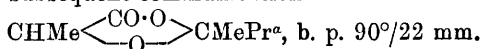
W. D. H.

**Syntheses by means of Mixed Organo-metallic Derivatives.**  
**Mixed *cyclo*Acetals.** EDMOND É. BLAISE (*Compt. rend.*, 1912, 154, 596—598. Compare Abstr., 1911, i, 175, 260).—The action of organo-zinc halides on acid chlorides of the type  $\text{COCl} \cdot \text{CHR} \cdot \text{O} \cdot \text{CO} \cdot \text{R}$  is abnormal, and leads to the production of cyclic compounds which the author proposes to term *cyclo*acetals. An intermediate compound is probably decomposed in the following manner :



The following new substances have been prepared; their use in the

synthesis of aldehydes,  $\alpha$ -ketonic acids, and  $\alpha$ -halogen ketones will be described in a subsequent communication.



Acetylsalicyl chloride gives the *compound*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \cdot \text{O} \\ \diagdown \quad \diagup \\ \text{O} \end{array} \text{CMeEt}$ , whilst acetyl *p*-hydroxybenzoyl chloride behaves normally.

W. O. W.

**Formation of Cork.** SIMON ZEISEL (*J. pr. Chem.*, 1912, [ii], 85, 226—230).—Polemical with Schmidt (this vol., i, 72). F. B.

**Oxidation Products of Sebacic Acid.** EYVIND BÖDTKER (*J. pr. Chem.*, 1912, [ii], 85, 221—225).—Succinic, glutaric, and adipic acids, together with a small quantity of  $\gamma$ -heptanone- $\alpha\gamma$ -dicarboxylic acid (Tönnies, Abstr., 1879, 915), are the only products formed when sebacic acid is boiled with concentrated nitric acid until it completely disappears. For details of the separation of the acids, the original should be consulted. F. B.

**Dissociation of Tartrates, Malates, and Camphorates of Amines as Revealed by their Rotatory Power.** JULES MINGUIN (*Ann. Chim. Phys.*, 1912, [viii], 25, 145—159).—The work on tartrates has been published already, and the general conclusions then drawn apply to the other salts now dealt with (Minguin and Wohlgemuth, Abstr., 1909, i, 11). The malates and camphorates of the aliphatic amines exist undissociated in solution, but in the case of the aromatic amines neutral malates are not formed and the hydrogen malates are dissociated in solution. Camphorates of the aromatic amines do not exist in solution. The hydrogen malates of aniline and of diethylaniline melt at  $132^\circ$  and  $67^\circ$  respectively. T. A. H.

**Lactonisation of  $\alpha$ -Ketonic Esters. Ethyl Pyruvate.** HENRI GAULT (*Compt. rend.*, 1912, 154, 439—441. Compare Abstr., 1911, i, 709; de Jong, Abstr., 1904, i, 550).—When the lactonisation of ethyl pyruvate is effected by saturating the ester with hydrogen chloride in the cold, the ethyl  $\alpha$ -keto- $\gamma$ -valerolactone- $\gamma$ -carboxylate first formed undergoes further change, and a neutral substance, b. p.  $176$ — $177^\circ/13$  mm., is obtained; this is probably the ethyl ether of the enolic form of the above ketone,  $\text{CO}_2\text{Et} \cdot \text{CMe} \begin{array}{c} \text{O} - \text{CO} \\ \diagdown \quad \diagup \\ \text{CH} : \text{C} \cdot \text{OEt} \end{array}$ , and appears to be identical with the compound prepared by Genvresse (Abstr., 1893, i, 552), which he supposed to be ethyl  $\alpha$ -keto- $\Delta^2$ -butene- $\alpha\gamma$ -dicarboxylate. It unites with hydrazine (2 mols.) to form a *compound*, m. p.  $180^\circ$  (decomp.), the constitution of which has not yet been elucidated.

W. O. W.

**Citrophosphate Solutions.** ANTONIO QUARTAROLI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 130—135).—The author criticises the work of Pratolongo (Abstr., 1911, ii, 865) on this subject. The supposed solutions of diammonium citrate used by that author are shown to have contained a mixture of diammonium and triammonium citrates with an excess of the latter. The differences between the cryoscopic depressions observed by Pratolongo and the calculated values are not due to hydrolysis, because they would require, for instance, that not only the diammonium citrate, but also three-quarters of the monoammonium citrate present should suffer hydrolysis. The present author's calculations (from the dissociation constants of ammonium hydroxide and citric acid) show that even triammonium citrate can be but little hydrolysed. The abnormal values obtained for  $i$  in the case of the ammonium citrates are therefore due, not to hydrolysis, but to electrolytic dissociation. It is further shown that the cryoscopic data do, in fact, support the hypothesis of the formation of complex salts, and exclude the possibility of the occurrence of double decomposition.

The paper records cryoscopic measurements for various solutions of citric acid, monoammonium citrate, triammonium citrate (and four intermediate solutions between the two last named), monopotassium citrate, dipotassium citrate, tripotassium citrate, monoammonium phosphate, diammonium phosphate, triammonium phosphate, triammonium citrate + calcium hydrogen phosphate, and triammonium citrate + barium hydrogen phosphate.

R. V. S.

**The Synthetic Application of Ethyl Methanetricarboxylate.** ROLAND SCHOLL (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 213—214).—The usual ethyl acetoacetate and ethyl malonate syntheses may be performed with ethyl methanetricarboxylate if alcohol is excluded. The reaction takes place at or above 100°, and a pure product is obtained. *Ethyl methanetetracarboxylate*, prepared from ethyl sodiomethanetricarboxylate and ethyl chloroformate, is a stable compound, b. p. above 290° undecomposed, and yielding malonic acid with dilute sulphuric acid.

C. H. D.

**New Method for the Catalytic Preparation of Aldehydes from Acids.** PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1912, 154, 561—564. Compare this vol., i, 156, 157).—The reduction of aliphatic acids by means of formic acid furnishes a convenient method for preparing the corresponding aldehydes with satisfactory yields. The vapour of the acid, mixed with excess of formic acid, is passed over titanium oxide at 250—300°. Under these conditions, no ketone is formed, but the formic acid decomposes into carbon monoxide and water, thus effecting reduction of the acid. The following acids readily give aldehydes, the numbers indicating the yield in percentages: acetic 50, phenylacetic 75, propionic 40, butyric 55, isobutyric 65, isovaleric 75,  $\gamma$ -methylvaleric 80, octoic 95, and nonoic acid 85%. In the last case, a small amount of the corresponding ketone, pelargone, is also formed. Crotonic acid gives the aldehyde.

When thoria is substituted for titanium oxide, the yields of aldehyde are lower.

W. O. W.

**Alfalfone, a Ketone of the Formula  $C_{21}H_{42}O$ , obtained from Alfalfa.** Alfalfa Investigation. II. C. A. JACOBSON (*J. Amer. Chem. Soc.*, 1912, 34, 300—302).—In an earlier paper (this vol., ii, 80) it was shown that myristone is present in alfalfa meal. Another ketone,  $C_{21}H_{42}O$ , m. p. 88·5—88·8°, has now been isolated in the form of a white, amorphous powder, and has been termed *alfalfone*. On reducing this ketone with sodium and alcohol, the corresponding carbinol,  $C_{21}H_{44}OH$ , m. p. 86·3—86·5°, is produced as a white, amorphous powder. E. G.

**New Anhydrides of Dextrose and Glucosides.** EMIL FISCHER and KARL ZACH (*Ber.*, 1912, 45, 456—465).—By the action of barium hydroxide on triacetylmethylglucoside bromohydrin (Fischer and Armstrong, *Abstr.*, 1902, i, 263), the authors have isolated a substance,  $C_7H_{12}O_5$ , which they provisionally name anhydromethylglucoside. It forms a crystalline hydrate, and is not converted into sugar by emulsin. Warm dilute acids convert it into *anhydrodextrose*,  $C_6H_{10}O_5$ , which strongly resembles the hexoses, differing from them, however, in its much greater ability to restore the colour to Schiff's reagent. It yields a *hydrazone* and an *osazone*.

The transformation of acetyldibromodextrose into *triacetyldextrose bromohydrin* and into *triacetylmentholglucoside bromohydrin* is also described together with the formation of *anhydromentholglucoside* from the latter substance.

*Anhydromethylglucoside* was prepared by warming triacetylmethylglucoside bromohydrin with barium hydroxide in aqueous alcoholic solution. After filtration and evaporation, the residue was distilled under a pressure of 0·2—0·3 mm., when the anhydride passed over between 160° and 165° (temp. of bath) as a colourless syrup. In aqueous solution it had  $[\alpha]_D^{25} - 136·95^\circ$ . Under suitable conditions it formed a hydrate which was not obtained free from syrup. At 56°/12 mm. it still retained water. When dried over phosphoric oxide at 100°/12 mm., it melted, lost all its water, and left a residue of anhydromethylglucoside.

Anhydrodextrose was formed by hydrolysing anhydromethylglucoside with 4·5% sulphuric acid. It crystallised in long needles, m. p. 118° (corr.) after slight softening. In aqueous solution it had  $[\alpha]_D^{20} + 53·89^\circ$ . It dissolved readily in water and alcohol, with difficulty in ethyl acetate.

Anhydrodextrosephenylhydrazone was best prepared by mixing anhydrodextrose with pure phenylhydrazine. The solid mass obtained by gently warming the mixture was washed with ether and crystallised from water, from which the phenylhydrazone separated in faintly yellow leaflets, m. p. 157—158° (corr.).

Anhydrodextrosephenylosazone, prepared in the same manner as dextrosephenylosazone, crystallised in slender needles. It darkened when heated, and had m. p. about 180° (corr. decomp.).

Triacetylmethyl-*d*-glucoside bromohydrin was formed when ethereal solutions of acetyldibromodextrose and menthol were shaken with silver carbonate. It separated from alcohol in long needles, m. p. 140° (corr.), and had  $[\alpha]_D^{20} - 49·62^\circ$  in chloroform solution. Treat-

ment with sodium hydroxide in alcoholic solution transformed it into anhydromentholglucoside, m. p.  $113^{\circ}$  (corr.),  $[\alpha]_D^{25} - 96.73^{\circ}$  in alcoholic solution.

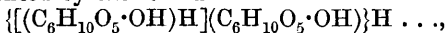
*Triacetylbenzylglucoside bromohydrin* was obtained in the same manner as the above menthol compound. It had m. p.  $141^{\circ}$  (corr.) after previous softening,  $[\alpha]_D^{20} - 46.76^{\circ}$  in chloroform solution.

Acetyldibromodextrose when shaken in acetone solution with silver carbonate yielded triacetyldextrose bromohydrin, m. p.  $119^{\circ}$  (corr.),  $[\alpha]_D^{20} + 23.33^{\circ}$  in acetone solution. Mutarotation has not yet been observed with this compound.

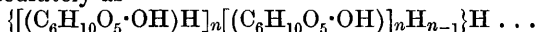
H. W.

**Dextrinisation of Starch by Desiccation.** GIOVANNI MALFITANO and (Mlle.) A. MOSCHKOFF (*Compt. rend.*, 1912, 154, 443—446).—The conversion of starch into dextrin is attributed to progressive dehydration of the substance, and not to the ordinary hydrolytic action of water. Starch was dehydrated over phosphoric oxide at the ordinary temperature and at higher temperatures up to  $150^{\circ}$ , the loss of water, percentage of carbon and hydrogen, and amount of soluble matter formed being determined from time to time. In a vacuum, at  $25^{\circ}$ , 28.1% of soluble matter was formed after twenty days; this rose to 90% when the material was heated for four hours at  $120^{\circ}$ . Some decomposition occurs, even at  $50^{\circ}$ , before dehydration is complete, as is shown by the starch turning brown. This, however, is not the cause of increased solubility, for at  $150^{\circ}$  solubility is less, and analysis shows that no oxidation has occurred.

These experiments lead to the suggestion that the starch micro-cells are composed of molecules of  $C_6H_{10}O_5$ , linked together by water, in a manner represented by the formula



or more accurately as



Soluble starch, amylopectin, erythropectin, etc., may be regarded as arising by successive removals of  $C_6H_{10}O_5$  groups. When dextrinisation occurs in the ordinary way by heating starch with water, the effect is the same, but the mechanism is different, water between the complexes being removed by ionisation.

W. O. W.

**Lintner Soluble Starch.** ERNEST D. CLARK (*Biochem. Bulletin*, 1911, 1, 194—206).—A study of the reducing power and erythropectin reaction with iodine on Lintner soluble starch prepared from potato starch. The product can only be purified with the greatest difficulty, if at all, from the dextrin to which these reactions are due.

W. D. H.

**Action of Tetrabromoethane on Organic Bases.** WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1912, 34, 286—290).—When tetrabromoethane is added to a solution of an organic base in dry ether, the hydrobromide of the base is precipitated and tribromoethylene is produced and remains in the solution. The reaction takes place more easily with aliphatic amines than with aromatic bases, and more easily with primary than with secondary or tertiary amines. It is

accelerated by direct sunlight. The hydrobromides of various amines have been obtained in the pure state by this method, and their mercuribromides and auribromides prepared.

When piperidine is added to an ethereal solution of tetrabromoethane, the hydrobromide is instantaneously and quantitatively precipitated, and this constitutes a convenient and inexpensive method for the preparation of tribromoethylene.

The following salts are described: *Ethylamine mercuribromide*,  $\text{NH}_2\text{Et}\cdot\text{HBr}\cdot\text{HgBr}_2$ , m. p.  $91^\circ$ . *Diethylamine hydrobromide*, m. p.  $205^\circ$ , *auribromide*,  $\text{NHEt}_2\cdot\text{HBr}\cdot\text{AuBr}_3$ , m. p.  $162^\circ$ , and *mercuribromide*, m. p.  $120^\circ$ . *Triethylamine auribromide*, m. p.  $140^\circ$ , and *mercuribromide*, m. p.  $109^\circ$ . *Dipropylamine hydrobromide*, m. p.  $271^\circ$ , *auribromide*, m. p.  $119^\circ$ , and *mercuribromide*, m. p.  $109^\circ$ . *Tripropylamine hydrobromide*, m. p.  $180^\circ$ , *auribromide*, m. p.  $149^\circ$ , and *mercuribromide*, m. p.  $104^\circ$ . *isobutylamine hydrobromide*, m. p.  $138^\circ$ , *auribromide*, m. p.  $154^\circ$ , and *mercuribromide*, m. p.  $164^\circ$ . *Di-isobutylamine hydrobromide*, m. p.  $313^\circ$ , *auribromide*, m. p.  $245^\circ$ , and *mercuribromide*, m. p.  $60^\circ$ . *Amylamine hydrobromide*, m. p.  $243^\circ$ , *auribromide*, m. p.  $105^\circ$ , and *mercuribromide*, m. p.  $213^\circ$ . *Di-isoamylamine hydrobromide*, m. p. about  $315^\circ$ , *auribromide*, m. p.  $220^\circ$ , and *mercuribromide*, m. p.  $97^\circ$ . *Allylamine hydrobromide*, m. p.  $91^\circ$ , and *mercuribromide*, m. p.  $115^\circ$ . *Benzylamine mercuribromide*, m. p.  $211^\circ$ . *Dibenzylamine auribromide*, m. p.  $165^\circ$ , and *mercuribromide*, m. p.  $145^\circ$ . *Pyridine mercuribromide*, m. p.  $152^\circ$ . *Picoline mercuribromide*, m. p.  $88^\circ$ . *Piperidine mercuribromide*, m. p.  $143^\circ$ . E. G.

**Hexabromoselenates [Selenibromides].** ALEXANDER GUTBIER and W. GRÜNEWALD (*J. pr. Chem.*, 1912, [ii], 85, 321—330).—An account of the preparation and properties of the selenibromides of the alkali metals and a number of aliphatic amines of the general formula  $\text{R}_3\text{SeBr}_6$ . The general method of preparation consists in the addition of an aqueous solution of the alkali bromide or of the amine in hydrobromic acid to an excess of a solution of the compound  $\text{H}_2\text{SeBr}_6$  in hydrobromic acid. The latter solution was prepared by adding bromine to a mixture of finely divided selenium and strong hydrobromic acid. The selenibromides are stable towards air, but are decomposed by water; those of the alkali metals crystallise in octahedra or cubes, belonging to the regular system [LENK.]. In addition to the selenibromides of sodium, potassium, caesium, rubidium, ammonium and of methylamine, dimethylamine, trimethylamine and ethylamine, all of which have been previously isolated (Muthmann and Schäfer, Abstr., 1893, ii, 318; Norris, Abstr., 1898, i, 510; Lenher, Abstr., 1899, ii, 18), the following new compounds are described: *Diethylammonium selenibromide*,  $(\text{NH}_2\text{Et}_2)_2\text{SeBr}_6$ , lustrous, brownish-red needles of monoclinic habit; the corresponding *propylamine* compound,  $(\text{NH}_3\text{Pr}^a)_2\text{SeBr}_6$ , ruby-red plates of a metallic lustre and rhombic habit; *butylammonium selenibromide*,  $(\text{NH}_3\cdot\text{C}_4\text{H}_9)_2\text{SeBr}_6$ , forms lustrous, orange-red leaflets; the *isobutylamine* compound, vivid red, hexagonal platelets. *Ethylenediammonium selenibromide*,  $(\text{C}_2\text{H}_{10}\text{N}_2)_2\text{SeBr}_6$ , forms garnet-red crystals of a metallic lustre, belonging to the

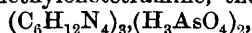
triclinic system; the *propylene* compound,  $(C_3H_{12}N_2)SeBr_6$ , garnet-red crystals of rhombic habit. F. B.

**Action of Tetraiodoethylene on Organic Bases.** WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1912, 34, 290—293).—In earlier papers (Dehn, *Abstr.*, 1911, i, 829; Dehn and Dewey, 1911, i, 914) it was stated that carbon tetrabromide and di-iodoacetylene combine with organic bases, dissolved in dry ether, to form molecular compounds. It is now shown that tetraiodoethylene behaves in a similar manner. Sunlight is generally necessary to promote the reactions. The compounds are decomposed by water; in the case of the diethylamine compound the main reaction is  $NH_2Et_2 \cdot C_2I_4 \rightarrow NH_2Et_2 + C_2I_4$ , but a large proportion decomposes, thus:  $3NH_2Et_2 \cdot C_2I_4 + 3H_2O \rightarrow 3NH_2Et_2 \cdot HI + 3C_2I_2 + 2HI + HIO_3$ . Although the normal course of the reaction between tetraiodoethylene and organic bases is that indicated, secondary reactions take place involving the production of di-iodoacetylene, thus:  $3NH_2Et_2 + 2C_2I_4 \rightarrow 2NH_2Et_2 \cdot HI + 2C_2I_2 + NH_2Et_2 \cdot I_2$ , and  $3NH_2Et_2 + 3C_2I_4 \rightarrow NH_2Et_2 \cdot HI + NH_2Et_2 \cdot I_2 + NH_2Et_2 \cdot HI \cdot I_2 + 3C_2I_2$ . The crystalline mass precipitated from the ethereal solution is, therefore, usually a mixture of two or more substances which are sometimes very difficult to separate. The following compounds are described.

The ethylamine compounds,  $NH_2Et \cdot C_2I_4$ , m. p.  $155^\circ$ , and  $NH_2Et \cdot 2C_2I_4$ , m. p.  $133^\circ$ ; ethylamine hydriodide, m. p.  $167^\circ$ , and mercuri-iodide, m. p.  $136^\circ$ . The diethylamine compound,  $NH_2Et_2 \cdot C_2I_4$ , m. p.  $158^\circ$ ; diethylamine hydriodide, m. p.  $165^\circ$ , and mercuri-iodide, m. p.  $115^\circ$ . The triethylamine compound,  $NEt_3 \cdot 2C_2I_4$ , m. p.  $132^\circ$ ; triethylamine hydriodide, m. p.  $173^\circ$  (decomp.), and mercuri-iodide, m. p.  $84^\circ$ . The isopropylamine compound,  $NH_2Pr^i \cdot 2C_2I_4$ , m. p.  $160^\circ$ . The dipropylamine compound,  $NHPr^a_2 \cdot 2C_2I_4$ , m. p.  $130^\circ$ ; dipropylamine hydriodide, m. p.  $229^\circ$  (decomp.), and mercuri-iodide, m. p.  $81^\circ$ . The di-isoamylamine compound,  $NH(C_5H_{11})_2 \cdot C_2I_4$ , m. p.  $150^\circ$ ; di-isoamylamine mercuri-iodide, m. p.  $110^\circ$ . The benzylamine compound,  $CH_2Ph \cdot NH_2 \cdot C_2I_4$ , m. p.  $115^\circ$ ; benzylamine hydriodide, m. p.  $162^\circ$ , and mercuri-iodide, m. p.  $134^\circ$ . The  $\omega$ -phenylethylamine compound,  $C_2H_4Ph \cdot NH_2 \cdot C_2I_4 \cdot C_2I_2$ , m. p.  $138^\circ$  (decomp.);  $\omega$ -phenylethylamine hydriodide, m. p.  $267^\circ$ , and mercuri-iodide, m. p.  $131^\circ$ . The piperidine compound,  $C_5H_{11}N \cdot 2C_2I_4$ , m. p.  $147^\circ$ ; piperidine hydriodide, softening at  $172^\circ$ , and mercuri-iodide, m. p.  $104^\circ$ . The quinoline compound,  $C_9H_7N \cdot C_2I_4$ , m. p.  $132^\circ$ . The acetamide compound,  $NH_2Ac \cdot C_2I_4 \cdot I$ , m. p.  $175^\circ$ .

Precipitates were also obtained with pyridine, triphenylphosphine, triethylstibine, *p*-phenylenediamine, collidine, and picoline. E. G.

**New Compound of Hexamethylenetetramine with Ortho-arsenic Acid.** GUIDO ROSSI (*Giorn. Farm. Chim.*, 1911, 60. Reprint 8 pp.).—On mixing saturated alcoholic solutions of ortho-arsenic acid and hexamethylenetetramine, the compound,



is obtained. It crystallises in transparent needles, m. p.  $173$ — $174^\circ$ , and (from experiments with a rabbit) is much less toxic than arsenic acid. R. V. S.

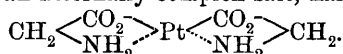
**Stereoisomerism of Internally Complex Salts: Stereoisomeric Cobaltic Salts of  $\alpha$ -Amino-acids.** HEINRICH LEY and H. WINKLER (*Ber.*, 1912, 45, 372—377).—The electrical conductivity of solutions of the stereoisomeric cobaltglycines (Abstr., 1909, i, 886) is extremely small, but still capable of being measured. The results show that the dissociation of these compounds is hardly appreciable. When dissolved in 0.01*N*-sulphuric acid the conductivity of the solution is practically identical with that of the pure acid, indicating that the amino-group is completely saturated by the internal complex formation.

Experiments in which the rate of dehydration of the red and violet isomeric cobaltglycines has been measured show that the violet isomeride loses its water of crystallisation the more readily.

Using a method similar to that described for the cobaltglycines (*loc. cit.*), isomeric *cobalti- $\alpha$ -alanines*,  $\text{Co}(\text{C}_3\text{H}_6\text{O}_2\text{N})_3$ , have been prepared from alanine and cobaltic hydroxide. The violet isomeride crystallises in prisms, whilst the red isomeride forms microscopic needles. Both forms are very stable, dissolving in acids, for example, in concentrated sulphuric acid, without decomposition. The absorption spectra of the solutions are practically identical with those of the cobaltglycines.

The isomeric dinitrotetramminecobaltic salts (flavo- and croceo-salts) cannot be transformed directly one into the other, as is also the case with the above complex compounds. The absorption spectra of dilute solutions of the chloride and nitrate are also practically identical, the only difference being that the croceo-salt gives an additional band in the extreme ultra-violet. T. S. P.

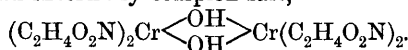
**Internally Complex Salts of Platinum and Chromium.** HEINRICH LEY and K. FICKEN (*Ber.*, 1912, 45, 377—382).—When a solution of potassium platinochloride is boiled with an excess of glycine, colourless crystals of *platinoglycine*,  $\text{Pt}(\text{C}_2\text{H}_4\text{O}_2\text{N})_2$ , are obtained; they are sparingly soluble in hot water, and soluble in concentrated sulphuric acid. The stability of this compound points to the formation of an internally complex salt, namely,



*Platino- $\alpha$ -alanine*,  $\text{Pt}(\text{C}_3\text{H}_6\text{O}_2\text{N})_2$ , is similarly prepared from alanine, and forms glistening, white leaflets. If, however, an excess of alanine is not used (1 mol. of potassium platinochloride to 2 mols. of alanine), a yellow solution is obtained after heating for several hours, which, on precipitation with alcohol, gives yellow needles of *potassium platino-chloroalanine*,  $\text{K} \left[ \begin{array}{c} \text{Cl} \\ \diagdown \end{array} \text{Pt} \begin{array}{c} \diagup \text{CO}_2 \\ \diagdown \text{NH}_2 \end{array} \text{C}_2\text{H}_4 \right]$ , which are fairly readily soluble in water. An analogous glycine compound can also be obtained.

If 1 mol. of the green or violet chromium chloride is heated in aqueous solution with 3 mols. of glycine, and 3 mols. of sodium hydroxide gradually added, a dark red solution is obtained, from which violet crystals of *chromiglycine*,  $\text{Cr}(\text{C}_2\text{H}_4\text{O}_2\text{N})_2 \cdot \text{OH} \cdot \frac{1}{2}\text{H}_2\text{O}$ , separate. If these are collected from the hot solution, and the filtrate concen-

trated in a vacuum over sulphuric acid, a further quantity of violet crystals is deposited, together with larger, red crystals, having the composition  $\text{Cr}(\text{C}_2\text{H}_4\text{O}_2\text{N})_3 \cdot \text{H}_2\text{O}$ . The red are heavier than the violet crystals, from which they are readily separated by levigation with alcohol. Chromium-pentammine chloride can be used instead of chromium chloride in the above preparation. Both the red and violet salts are sparingly soluble in water and the usual organic solvents. On prolonged boiling with water, the red salt apparently changes into the violet salt. With concentrated sulphuric acid, they give red solutions, which, in contradistinction to those of the cobaltglycines, gradually decompose with the formation of chromic sulphate. The violet salt is either an hydroxoquo-salt,  $\text{Cr}(\text{C}_2\text{H}_4\text{O}_2\text{N})_2 \cdot \text{OH} \cdot \text{OH}_2$ , or, more probably, an internally complex salt,

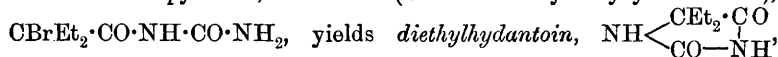


Similar compounds are obtained when  $\alpha$ -alanine is used in place of glycine, the *red* salt being  $\text{Cr}(\text{C}_3\text{H}_6\text{O}_2\text{N})_3$ , and the *violet* salt,  $\text{Cr}(\text{C}_3\text{H}_6\text{O}_2\text{N})_2 \cdot \text{OH} \cdot \text{H}_2\text{O}$ .

Other amino-acids give similar compounds, which are to be described in another paper.

T. S. P.

**Adaline.** KARL W. ROSENMUND and F. HERRMANN (*Ber. deut. pharm. Ges.*, 1912, 21, 96—103. Compare Abstr., 1911, i, 118; ii, 1120).—It is shown that, on treatment with boiling water, hot alkaline solution or pyridine, adaline ( $\alpha$ -bromo- $\alpha$ -ethylbutyrylcarbamide),



colourless crystals, m. p. 181—182°, and that when alkaline solutions are used some *ethylcrotonylcarbamide*,  $\text{CH}_3 \cdot \text{CH} : \text{CEt} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , m. p. 91°, is also formed, together with a high-boiling oil,  $\text{C}_{13}\text{H}_{20}\text{O}_6\text{N}_2$ , b. p. 283—286°, which probably contains two adaline residues.

T. A. H.

**Reduction of Aliphatic Amides and Esters by the Metal-Ammonias.** E. CHABLAY (*Compt. rend.*, 1912, 154, 364—366).—Aliphatic amides decolorise solutions of sodium in liquid ammonia at  $-50^\circ$ , forming a mixture of sodium alkylxide and the sodium derivative of the amide. A similar reaction occurs with esters, the same products being formed. The reaction in the latter case is represented by the equations (1)  $\text{R} \cdot \text{CO}_2\text{R}' + 2\text{Na}, \text{NH}_3 = \text{R} \cdot \text{CO} \cdot \text{NHNa} + \text{R}'\text{ONa} + \text{NH}_3 + \text{H}_2$ ; (2)  $\text{R} \cdot \text{CO} \cdot \text{OR}' + 2\text{Na}, \text{NH}_3 + \text{H}_2 = \text{R} \cdot \text{CH}_2 \cdot \text{ONa} + \text{R}'\text{ONa} + 2\text{HN}_3$ .

W. O. W.

**Ureabromin.** ARTHUR BILTZ (*Pharm. Zentr.-h.*, 1912, 53, 245—246).—This name is applied to a molecular combination of carbamide and calcium bromide,  $\text{CaBr}_2 \cdot 4\text{CO}(\text{NH}_2)_2$ , prepared by mixing the two components in solution. It is readily soluble in alcohol or water, insoluble in ether, light petroleum or benzene, and melts at  $186^\circ$ . It gives all the ordinary reactions of its components when dissolved in water. It is proposed to use it in medicine as a substitute for alkali bromides.

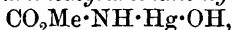
T. A. H.

**Reactions of Methylene. III. Diazomethane.** HERMANN STAUDINGER and OTTO KUPFER (*Ber.*, 1912, 45, 501—509. Compare Abstr., 1911, i, 702, 751).—During the course of some unsuccessful experiments for the preparation of cyano-isonitrile and of di-iso-cyanogen, diazomethane has been obtained in 25% yield by the slow addition of chloroform ( $1\frac{1}{4}$  mol.) in absolute alcohol to a hot alcoholic solution of potassium hydroxide (4 mols.) and hydrazine (1 mol.). A slow stream of nitrogen is passed through the apparatus during the preparation, whereby the diazomethane is removed and absorbed in ether. Methylhydrazine is a by-product of the reaction.

Pure diazomethane has b. p.  $-24^{\circ}$  to  $-23^{\circ}$  and m. p.  $-145^{\circ}$ , and is extremely dangerously explosive, spontaneously or by contact with iodine, grease, etc. In dilute ethereal solution, however, it can be ignited without exploding. When carbon monoxide is passed through ethereal diazomethane and the gaseous mixture is heated at  $400-500^{\circ}$  in a quartz tube, the methylene produced by the decomposition of the diazomethane reacts with the carbon monoxide to form keten, which is detected by passing the issuing gases into ethereal aniline, whereby acetanilide is produced.

Benzoylhydrazine, potassium hydroxide, and chloroform react in hot alcohol to form about 3% of diazomethane, the main product being benzoic acid, obtained from the intermediately formed phenylketen. Phenylhydrazine is scarcely attacked by potassium hydroxide and chloroform in hot alcohol, but *as*-diphenylhydrazine is converted into benzophenone in 60% yield. C. S.

**Urethane and Mercuric Acetate.** A. PIERONI (*Gazzetta*, 1911, 41, ii, 754—756).—*Mercurimethylurethane hydroxide*



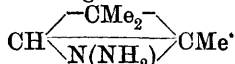
is obtained by treating an alcoholic solution of equimolecular quantities of methylurethane and mercuric acetate with a slight excess of alcoholic potassium hydroxide. *Mercurimethylurethane acetate*,  $\text{CO}_2\text{Me}\cdot\text{NH}\cdot\text{Hg}\cdot\text{C}_2\text{H}_3\text{O}_2$ , is prepared by dissolving equimolecular quantities of methylurethane and mercuric acetate in a little water at  $60^{\circ}$ . On keeping the solution over calcium oxide the substance separates out in crusts of microscopic needles. When treated with alcoholic potassium hydroxide, it decomposes almost quantitatively according to the equation:  $\text{CO}_2\text{Me}\cdot\text{NH}\cdot\text{Hg}\cdot\text{C}_2\text{H}_3\text{O}_2 + 2\text{KI} + \text{H}_2\text{O} = \text{HgI}_2 + \text{CO}_2\text{Me}\cdot\text{NH}_2 + \text{C}_2\text{H}_3\text{O}_2\text{K} + \text{KOH}$ .

*Mercuriethylurethane*,  $\text{CO}_2\text{Et}\cdot\text{NHg}$ , is deposited from a solution of ethylurethane and mercuric acetate in water; it forms crusts of microscopic needles, containing 1 mol.  $\text{H}_2\text{O}$ , which it loses in a vacuum over sulphuric acid.

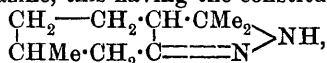
*Mercuri-isoamylurethane*,  $\text{CO}(\text{OC}_5\text{H}_{11})\cdot\text{NHg}$ , is obtained by keeping an alcoholic solution of equimolecular quantities of *isoamylurethane* and mercuric acetate; it forms crystalline crusts, m. p. about  $165^{\circ}$  (decomp.). With sodium iodide, it decomposes in the same way as mercurimethylurethane acetate. R. V. S.

**Decomposition of Pyrazoline Bases as a means of Obtaining Derivatives of cycloPropane.** NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 165—180).—The conversion into the

dicyclic hydrocarbon, carane, of the base obtained by the action of hydrazine on tanacetone (compare Abstr., 1911, i, 1028) seemed to indicate that the formation of the trimethylene ring was related to the formation of the base. Since mesityl oxide, a compound structurally very similar to pulegone, also reacts with hydrazine to form a compound which gives 1:1:2-trimethylcyclopropane on decomposition, it was at first thought that the product of the interaction of mesityl oxide and hydrazine was not a pyrazoline derivative, as Curtius supposed, but a compound having the structure:



Further investigation has shown, however, that this compound is really a pyrazoline derivative, as also is the base formed by pulegone with hydrazine, this having the constitution:



and not that previously given (*loc. cit.*). The decomposition of this compound into carane and nitrogen is exactly similar to that of 3:5:5-trimethylpyrazoline (from mesityl oxide and hydrazine) into 1:1:2-trimethylcyclopropane and nitrogen, the two nitrogen atoms being eliminated from the pyrazole nucleus and the residue closing up to a three carbon-atom ring. Similar decompositions take place with 1-methyl-1:2-diethylpyrazoline, which yields 1-methyl-1:2-diethylcyclopropane, and with esters of pyrazoline-3:4:5-tricarboxylic acid, which yield esters of cyclopropanetricarboxylic acids (compare Buchner, Abstr., 1888, 1274; 1890, 736).

The author intends to ascertain whether derivatives of cyclopropanone can be obtained in a similar manner from pyrazolone compounds.

1:1:2-Trimethylcyclopropane,  $\text{C}_6\text{H}_{12}$ , obtained by heating 3:5:5-trimethylpyrazoline in a sealed tube with potassium hydroxide and platinised porous tile, is a liquid, b. p.  $52.5^\circ/752$  mm.,  $52.6^\circ/753$  mm.,  $52.8^\circ/756$  mm.,  $D_0^{20}$  0.6949,  $n_D$  1.3866. The compound described under this name by Zelinsky and Zelikoff (Abstr., 1901, i, 657) was apparently not pure, the high value of the molecular refraction indicating considerable admixture of ethylene hydrocarbon. The action of alkaline permanganate on 1:1:2-trimethylcyclopropane is very slow, but much more rapid than with the dicyclic trimethylene hydrocarbons, thujane and carane, or with the 1-methyl-1:2-diethylcyclopropane described below. Fuming nitric acid readily reacts with the hydrocarbon with development of heat, whilst concentrated sulphuric acid polymerises it.

The action of bromine on 1:1:2-trimethylcyclopropane in acetic acid solution yields: (1) a small proportion of  $\beta$ -bromo- $\beta$ -methylpentane,  $\text{CMe}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Me}$ , b. p.  $135-138^\circ/752$  mm.,  $D_0^{20}$  1.1806,  $n_D$  1.4517, which is the result of a secondary reaction of the hydrogen bromide liberated on the hydrocarbon; (2)  $\beta\delta$ -dibromo- $\beta$ -methylpentane,  $\text{CMe}_2\text{Br} \cdot \text{CH}_2 \cdot \text{CHMeBr}$ , b. p.  $87-89^\circ/23$  mm.,  $D_0^{20}$  1.6242,  $D_0^{20}$  1.5979,  $n_D$  1.5097, which yields  $\beta$ -methylpentane when reduced with hydrogen

iodide; thus combination of bromine with 1:1:2-trimethylcyclopropane takes place at the least hydrogenated carbon atom.

Reduction of 1:1:2-trimethylcyclopropane by Sabatier's method gives  $\beta\beta$ -dimethylbutane, so that hydrogen combines with this hydrocarbon at the most highly hydrogenated carbon atom.

The action of fuming hydriodic acid on 1:1:2-trimethylcyclopropane yields: (1)  $\beta$ -iodo- $\beta\gamma$ -dimethylbutane,  $\text{CMe}_2\text{I}\cdot\text{CHMe}_2$ , b. p.  $83-84^\circ/77$  mm.,  $141^\circ/755$  mm. (slight decomp.),  $D_0^{20}$  1.4435,  $n_D$  1.5035, which seems to be accompanied by a small proportion of another iodo-compound, probably  $\beta$ -iodo- $\beta$ -methylpentane. The action of fuming hydrobromic acid on 1:1:2-trimethylcyclopropane yields  $\beta$ -bromo- $\beta$ -methylpentane (see above).

1-Methyl-1:2-diethylcyclopropane,  $\text{CH}_2\begin{matrix} \text{CHEt} \\ \text{CMeEt} \end{matrix}$ , obtained by heating 5-methyl-3:5-diethylpyrazoline (compare Curtius and Zinkeisen, Abstr., 1899, i, 165) in a sealed tube at  $240^\circ$ , has b. p.  $108-109^\circ/742$  mm.,  $D_0^{20}$  0.7382,  $n_D$  1.4102. It combines slowly with bromine, whilst with hydrobromic acid it gives  $\gamma$ -bromo- $\gamma$ -methylheptane (I), b. p.  $101-102^\circ/53$  mm.,  $D_0^{20}$  1.1406,  $n_D$  1.4613, which, when distilled with aniline, yields an unsaturated hydrocarbon,  $\text{C}_8\text{H}_{16}$ , b. p.  $117-119^\circ/742$  mm.,  $D_0^{17.5}$  0.7426,  $n_D$  1.4210, this forming a liquid bromide.

T. H. P.

Loschmidt's Graphic Formulæ: History of the Benzene Theory. RICHARD ANSCHÜTZ (*Ber.*, 1912, 45, 539-553).—Historical. The author gives an account of the graphic formula developed by Loschmidt in his "*Chemische Studien*" (Vienna, 1861). It is pointed out that the latter ascribed a ring structure to the benzene nucleus four years before Kekulé published his benzene theory. F. B.

Stereochemistry of the Aromatic Series. ROMÁN CASARES (*Anal. Fis. Quim.*, 1912, 10, 14-18).—The author proposes a three dimensional formula for benzene based on an alternate arrangement of tetrahedra, in such a way that the projection on a plane is a regular hexagon. The difference from Ladenburg's prism formula is slight, and the same difficulty would be experienced in explaining the mechanism of reduction. Naphthalene, anthracene, phenanthrene, and chrysene are formulated on the same principle. G. D. L.

Hydrogenation and Dehydrogenation. HEINRICH WIELAND (*Ber.*, 1912, 45, 484-493).—The researches of Sabatier, Ipatieff, Knoevenagel, and others show that the addition of hydrogen to an unsaturated organic compound in the presence of finely divided nickel, copper, palladium, etc., at a definite temperature is reversed at a higher temperature. It is to be anticipated, therefore, that Paal's method of reducing substances containing double linkings by hydrogen in the presence of colloidal palladium at the ordinary temperature is reversible, and that, under definite conditions, the same state of equilibrium must be reached whether the unsaturated or the hydrogenised substance is employed initially. The author finds that by shaking with palladium

black (carefully prepared free from oxygen), aqueous quinol is partly converted into *p*-benzoquinone and quinhydrone, hydrazobenzene dissolved in benzene is changed into azobenzene and aniline, dihydronaphthalene dissolved in benzene yields naphthalene and tetrahydronaphthalene, and dihydroanthracene in benzene is slowly transformed into anthracene; acenaphthene and bisdiphenylene-ethane are unchanged under the preceding conditions.

In these reactions the palladium plays the part, not of a catalyst, but of a substance of active mass; by increasing the amount of the metal, the equilibrium of the system is shifted in the direction whereby the yield of the dehydrogenised substance is increased.

Unsaturated substances which decolorise potassium permanganate can, in general, be catalytically hydrogenised, but are not necessarily attacked by nascent hydrogen; naphthalene is unaffected by hydrogen and palladium, but is reduced to dihydronaphthalene by sodium and alcohol, whereas dihydronaphthalene is unaffected by sodium and alcohol, but is easily converted into tetrahydronaphthalene by hydrogen and palladium. It appears, therefore, that the activation of hydrogen in the presence of a finely divided metal is not due to the production of nascent (atomic) hydrogen, but more probably to the formation of a metallic hydride which additionally reacts with the unsaturated substance:  $R \cdot R + PdH_2 \rightleftharpoons RH \cdot R \cdot PdH \rightleftharpoons RH \cdot RH + Pd$ . The probability of the formation of such intermediate additive compounds is supported by the facts that methyl or ethyl alcohol is absorbed by palladium black with development of heat, and the alcohol can only be recovered by long keeping in a vacuum; it then contains a certain amount of the aldehyde. Under such conditions, propyl alcohol is much more readily converted into propaldehyde, whilst benzyl alcohol yields benzaldehyde at once.

C. S.

**The Addition of Chlorine to Dichlorobenzenes.** T. VAN DER LINDEN (*Ber.*, 1912, 45, 411—418. Compare this vol., i, 174).—The author hoped by the removal of two molecules of hydrogen chloride from any dichlorobenzene hexachloride [octachlorocyclohexane] to obtain a substance of the composition  $C_6H_2Cl_6$  which might be considered as identical with the assumed intermediate product in the substitution of a chlorine atom into tetrachlorobenzene.

The additive compound of *p*-dichlorobenzene and chlorine was obtained by passing chlorine into a solution of the substance in carbon tetrachloride under strong sodium hydroxide solution in sunlight, also by exposing to sunlight a mixture of the theoretical quantities of *p*-dichlorobenzene and chlorine in a closed tube. The main product (from its resemblance to  $\beta$ -benzene hexachloride) is designated  $\beta$ -*p*-dichlorobenzene hexachloride, and after recrystallisation from nitrobenzene has m. p.  $262^\circ$ ; it has already been obtained by Jungfleisch (*Bull. Soc. chim.*, 1868, [2], 9, 352). On treatment with alcoholic potash, three molecules of hydrogen chloride are eliminated with formation of pentachlorobenzene; the same behaviour is exhibited by all the isomerides described below.

The carbon tetrachloride mother liquors of the above substance contained an isomeric hexachloride, which, on account of its low m. p.

and considerable solubility, is termed *α-p-dichlorobenzene hexachloride*; the m. p. is 89·6°. Indications of a third isomeride, m. p. 110—120°, were also observed. *o-Dichlorobenzene hexachloride*, obtained by the sealed tube method, has m. p. 147°.

*m-Dichlorobenzene hexachloride* was obtained by the action of chlorine on the dichloro-compound under a layer of dilute sodium hydroxide solution; it has m. p. 81·8°.

As the above substances, even when treated with an insufficiency of alcoholic potash, yield only pentachlorobenzene and unchanged substance, *α*- and *β*-chlorobenzene hexachlorides were prepared by the sealed tube method, but alcoholic potash again removes simultaneously three molecules of hydrogen chloride from each molecule of hexachloride.

D. F. T.

### Reduction of Nitrobenzene by means of Ferrous Hydroxide.

HERMAN CAMP ALLEN (*J. Physical Chem.*, 1912, 16, 131—169).—The products of reduction of nitrobenzene by ferrous sulphate with slight excess of sodium hydroxide depend on the temperature, concentration, and order of mixing of the reacting substances.

When nitrobenzene is run into a well stirred mixture of ferrous sulphate and sodium hydroxide solutions or when nitrobenzene and ferrous sulphate are stirred together and sodium hydroxide is slowly introduced, the reduction takes place in a neutral or slightly alkaline medium, and the product is mainly aniline. The yield of aniline varies from 100% at room temperature to 80% at the boiling point. A high yield of aniline is also obtained when the ferrous sulphate is added last, if it is run in quickly and in excess.

When, however, sodium hydroxide and nitrobenzene are stirred together, and ferrous sulphate is added very slowly, the reduction takes place in a strongly alkaline medium, and the product is mainly hydrazobenzene. At 75° the yields were: aniline 21%, hydrazobenzene 60%, azoxybenzene 14%. At the boiling point the yields were: aniline 33%, hydrazobenzene 58%. When the ferrous sulphate was restricted to the amount required to reduce to azoxybenzene only, the yields were: aniline 18%, azoxybenzene 76%.

Both azoxybenzene and azobenzene are reduced by excess of alkaline ferrous sulphate at the boiling point, the product being hydrazobenzene with some aniline. Aniline seems to be formed in this way in the alkaline reduction of nitrobenzene at 100°, whereas at the ordinary temperature it is formed by the nitrosobenzene-phenyl-hydroxylamine route. There is a minimum production of aniline at about 75°, and the utility of alcohol in the electrolytic production of hydrazobenzene and azobenzene is partly due to its solvent action, and partly to its favourable boiling point.

According to Haber's scheme for the reduction of nitrobenzene (*Abstr.*, 1900, i, 281), azoxybenzene is the immediate forerunner of hydrazobenzene, as the above results suggest, and the oxidation of hydrazobenzene by nitrobenzene gives azobenzene, the nitrobenzene being reduced to azoxybenzene at the same time. The author finds that the production of azobenzene from hydrazobenzene on boiling for twenty minutes with excess of nitrobenzene is almost quantitative, and

azoxybenzene is formed simultaneously, in accordance with Haber's view. In the Elbs method of electrolytic preparation of azobenzene, the intermediate stage is probably azoxybenzene, since with a low current density in well stirred solutions, azoxybenzene is the principal product.

In the author's experiments, 1.2 gram of nitrobenzene was reduced and the filtered liquid was extracted with benzene. It was assumed that the extract contained only aniline, hydrazobenzene, azobenzene, azoxybenzene, and unaltered nitrobenzene. The aniline was extracted with dilute sulphuric acid and titrated with bromate. The residue was estimated by evaporating until a more or less sharp bend in the time-weight curve indicated that the last traces of benzene had been removed. A similar procedure gave the residue after aniline and hydrazobenzene had been extracted together by 1:3 sulphuric acid; hence hydrazobenzene was calculated by difference. Azobenzene was estimated colorimetrically in the above residue, and nitrobenzene was reduced to aniline and titrated. Azoxybenzene was then calculated by difference. Phenylhydroxylamine was present in traces only.

In neutral or slightly alkaline reductions at the boiling point, about 15% of the nitrobenzene remained unaccounted for. It is suggested that decomposition of the intermediate product, phenylhydroxylamine, may have given rise to substances not extracted by benzene from the aqueous solution. In strongly alkaline reductions at the boiling point, the nitrobenzene could all be accounted for.

R. J. C.

**Fission of Phenylethyltrimethylammonium [Chloride].** HERMANN EMDE (*Apoth. Zeit.*, 1912, 27, 18—19).—The reduction of phenylethyltrimethylammonium chloride by means of sodium amalgam (compare Abstr., 1909, i, 708; this vol., i, 20) results in the formation of trimethylamine and styrene instead of ethylbenzene as previously assumed. In this case, the action of sodium amalgam is precisely similar to that of sodium hydroxide.

Explicit directions are given for the reduction of crude benzyl cyanide to phenylethylamine, and for the transformation of the latter into phenylethyltrimethylammonium chloride by means of methyl sulphate.

H. W.

**New Derivatives of Indene.** VICTOR GRIGNARD and CHARLES COURTOT (*Compt. rend.*, 1912, 154, 361—364. Compare Abstr., 1911, i, 193, 292).—The action of bromine on magnesium indenyl bromide gives rise to the formation of 1:2:3-tribromoindane,  $C_9H_7Br_3$ , m. p. 133—134°, together with an oily substance containing 1-bromoindene,  $C_9H_7Br$ . The latter is best prepared by adding the organo-magnesium derivative to cyanogen bromide, when it is obtained as a yellow liquid, b. p. 126°/22 mm. The compound resembles allyl bromide in its reactions. If cyanogen chloride is used instead of the bromide, 1-cyanoindene,  $C_{10}H_7N$ , b. p. 140—142°/14 mm., is formed. When treated by Pinner's method, this yields ethyl indene-1-carboxylate, b. p. 140°/8 mm. (compare Weissgerber, Abstr., 1911, i, 1442).

*Di-indenyl*,  $CH \begin{smallmatrix} \diagup C_6H_4 \diagdown \\ \diagdown CH \diagup \end{smallmatrix} CH \cdot CH \begin{smallmatrix} \diagup C_6H_4 \diagdown \\ \diagdown CH \diagup \end{smallmatrix} CH$ , prepared by the

action of iodine on magnesium indenyl bromide in toluene, occurs as colourless crystals, m. p. 99–100°; when treated with bromine it forms two *tetrabromides*. One of these is soluble in chloroform and has m. p. 138–139°, whilst the other is insoluble and has m. p. 222–224°. W. O. W.

**The Influence of the Nitro-group on the Sulphonation of Diphenylmethane.** ALFRED KIEGL (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 225–226).—Wedekind and Schenk (*Abstr.*, 1911, i, 190) found it impossible to sulphonate the methylene group of diphenylmethane with chlorosulphonic acid. An attempt has therefore been made to lessen the liability of the nuclei to sulphonation, and at the same time to increase the reactivity of the methylene group by the introduction of substituents. It is found, however, that nitro-groups increase the readiness with which diphenylmethane is sulphonated. In all three nitrodiphenylmethanesulphonic acids, the sulpho-group occupies the para-position in the un-nitrated nucleus. Triphenylmethane behaves in a similar manner, and *o*-nitrotriphenylmethane gives a disulphonic acid with concentrated sulphuric acid on the water-bath.

*p*-Aminodiphenylmethane-*p*-sulphonic acid yields a sparingly soluble diazosulphonic acid, which behaves as an internal salt, although the two salt-forming groups are attached to different nuclei. C. H. D.

**Sulphonation of  $\beta$ -Nitronaphthalene.** HANS KAPPELER (*Ber.*, 1912, 45, 633–635).—The sulphonation of  $\beta$ -nitronaphthalene with fuming sulphuric acid is completely analogous to that of  $\beta$ -naphthylamine. A mixture of two monosulphonic acids is obtained, which were identified by reduction to the corresponding  $\beta$ -naphthylaminesulphonic acids.

*2-Nitronaphthalene-5-sulphonyl chloride* forms large, pale yellow prisms, m. p. 127°; the corresponding *amide* crystallises in yellow, four- and six-sided plates, m. p. 223–224°.

*2-Nitronaphthalene-8-sulphonyl chloride* separates in tiny, almost colourless needles, m. p. 169–170°; the *amide* forms colourless, crystalline tablets, m. p. 261–262°.

The free *sulphonic acids* were obtained as colourless, microcrystalline precipitates. E. F. A.

**Action of Sulphurous Acid on Aldehydoaminic Bases.** MARIO MAYER (*Gazzetta*, 1912, 42, i, 50–56. Compare *Abstr.*, 1911, i, 223).—*Benzylideneaniline anhydrosulphite*,



is an orange-yellow powder, m. p. 115–120° (decomp.), which is obtained when dry sulphur dioxide acts on dry benzylideneaniline, and also (more easily) when a benzene solution of benzylideneaniline is saturated with sulphur dioxide. The substance loses sulphur dioxide when kept, leaving benzylideneaniline as the only product.

Aniline benzylideneaniline sulphite, already obtained by Knoevenagel, can also be prepared by saturating an ethereal solution of benzylideneaniline with sulphur dioxide. When it is heated in a

sealed tube for some hours at 105—110°, aniline and aniline sulphite are formed, and, in addition, *benzylideneaniline hydrogen sulphite*,  $C_{13}H_{13}O_3NS$ . This decomposition renders improbable Eibner's supposition (Abstr., 1901, i, 376) that the original compound is dianilinophenylmethane anhydrosulphite,  $CHPh(NHPh)_2SO_2$ . Benzylideneaniline hydrogen sulphite is best prepared by passing sulphur dioxide through a very dilute aqueous-alcoholic solution of benzylideneaniline; it forms tufts of acicular crystals, m. p. 145°. If the solution is more concentrated, the salt of m. p. 125° is obtained, but when this is removed, the liquid slightly warmed, and treated with more sulphur dioxide, a substance separates in the form of long, flat needles, m. p. 147°, which are identical in behaviour with those above mentioned, m. p. 145°. Benzylideneaniline hydrogen sulphite yields the above-mentioned salt of m. p. 125° when treated with aniline.

Speroni (Abstr., 1903, i, 246) obtained the neutral anhydrosulphite of aniline and benzaldehyde, giving the m. p. 138—140°. On repeating this preparation the author obtains a substance, m. p. 125°, which is identical with Knoevenagel's salt previously referred to. If, however, this compound is treated with warm alcohol, the greater part of it then has m. p. 140° (decomp.) and gives the same analytical figures as the salt of m. p. 125°, and it is suggested that the two substances are the aniline salts of two isomeric forms of the sulphurous acid. Speroni, by treating a neutral aqueous solution of aniline sulphite with benzaldehyde, obtained a substance, m. p. 130°, but the author, working under the same conditions, always obtains a product, m. p. 125—127°, identical with the salt of m. p. 125° already mentioned.

When the three compounds above described (of m. p. 115—120°, 145° and 125° respectively) are treated with a cold, saturated, alcoholic solution of picric acid, the first two yield benzylideneaniline picrate, whilst the third gives also aniline picrate.

In regard to the constitution of the sulphites described in this and in the earlier paper, the author rejects Eibner's view (*loc. cit.*) that all compounds formed from aldehydes, amines, and sulphurous acid are sulphites of aldehydoaminic bases. Such substances as the additive products from benzylideneaniline and sulphur dioxide or sulphurous acid do belong to that type, but the other compounds described in the present paper and the aldehydo- and keto-sulphites of the alkaloids do not. The aldehydoaminic bases which are obtained when some of these decompose are not present in the compounds themselves, but are formed by the interaction of the aldehyde and amine first formed in the decomposition.

R. V. S.

**Electrolysis of Phenylalkylhydroxyethylammonium Iodides and Some Derivatives of Choline.** BRUNO EMMERT (*Ber.*, 1912, 45, 430—433).—The electrolysis of quaternary phenylammonium salts at lead cathodes leads to the formation of tertiary aliphatic amines (Abstr., 1909, i, 376, 602). An attempt has been made to extend this method to those cases in which unsaturated aliphatic and

hydroxyalkyl groups are attached to the *N*-atom. By the electrolysis of phenyldimethylallylammonium iodide, however, propylene and dimethylaniline were obtained in good yield, the allyl instead of the phenyl group being eliminated. Electrolysis of phenyldimethylhydroxyethylammonium iodide and of phenylmethylethylhydroxyethylammonium iodide yielded dimethyl- $\beta$ -hydroxyethylamine and methylethyl- $\beta$ -hydroxyethylamine, whilst, at the same time, a certain amount of a tertiary aniline was formed, one aliphatic group being split off.

Dimethyl- $\beta$ -hydroxyethylamine was dried over potassium hydroxide and barium oxide, and, whilst still somewhat moist, had b. p. 129—133°. Ladenburg (Abstr., 1882, 166) found 130—134°, and Knorr (Abstr., 1889, 905) 128—130°. The *gold* salt was analysed.

Methylethyl- $\beta$ -hydroxyethylamine, isolated through its *hydrochloride*, had b. p. 149—150°. The *aurichloride* was analysed. When treated with methyl iodide in ethereal solution, it formed *dimethylethyl- $\beta$ -hydroxyethylammonium iodide*, which, on treatment with moist silver oxide, yielded the corresponding base. The latter was identified by conversion into its *aurichloride*, m. p. 276—277° (decomp.). Methylethyl- $\beta$ -hydroxyethylamine and ethyl iodide reacted to form an iodide, from which methyl-diethyl- $\beta$ -hydroxyethylammonium hydroxide was prepared. The *aurichloride* obtained from the latter had m. p. 246—247° (decomp.).

A similar series of compounds was obtained from methylethyl- $\beta$ -hydroxyethylamine and propyl iodide. In this case the corresponding *aurichloride* could not be obtained in a crystalline state. The *platinichloride*,  $C_{16}H_{40}O_2N_2Cl_6Pt$ , was analysed. H. W.

**Diphenylhydroxylamine.** HEINRICH WIELAND and ALEXANDER ROSEEU (*Ber.*, 1912, 45, 494—499).—The interaction of nitrosobenzene and magnesium phenyl bromide in ether at  $-15^\circ$  under carefully regulated conditions leads to the formation of  *$\beta\beta$ -diphenylhydroxylamine*,  $NPh_2\cdot OH$ , m. p.  $60^\circ$  (decomp.), colourless crystals. The substance, when pure, can be kept for eight days without decomposition, develops a deep blue coloration with concentrated sulphuric acid, is neutral in character, reduces ammoniacal silver solutions in the cold, and yields diphenylamine by reduction. It reacts with diphenylhydrazine hydrochloride (0.5 mol.) in slightly acidified alcohol to form the hydrochloride of quinoneanildiphenylhydrazone (Abstr., 1911, i, 82), the constitution of which is thus definitely settled. C. S.

**Action of Bromine in Presence of Aluminium Bromide on the Methylcyclohexanols.** FERNAND BODROUX and FELIX TABOURY (*Compt. rend.*, 1912, 154, 521. Compare Abstr., 1911, i, 779).—The three methylcyclohexanols behave similarly to cyclohexanol in their behaviour towards bromine in presence of aluminium bromide. In each case the solid pentabromotoluene is formed, together with a yellow oil. The latter is a mixture of bromo-derivatives, and is capable of undergoing further bromination, giving gummy products in the case of methylcyclohexan-2- and -4-ol. The third isomeride, however, gave a small quantity of *hexabromomethylcyclohexane*,  $C_7H_8Br_6$ , in the form of long, colourless needles, m. p.  $295^\circ$ . W. O. W.

**Halogen Derivatives of Phenolic Ethers.** ALPHONSE MAILHE and MARCEL MURAT (*Compt. rend.*, 1912, 154, 601—604 \*).—The catalytic method, in which thorium oxide is employed, is very advantageous for the preparation of diphenyl ether and its homologues, which are obtained with difficulty by the ordinary processes.

*p*-Chlorodiphenyl ether,  $\text{OPh}\cdot\text{C}_6\text{H}_4\text{Cl}$ , prepared by the action of chlorine in presence of iodine on diphenyl ether in carbon tetrachloride solution, has b. p.  $284^\circ/760$  mm.,  $D^{15}_D$  1.2026,  $n_D$  1.599; *di-p*-chlorodiphenyl ether,  $\text{O}(\text{C}_6\text{H}_4\text{Cl})_2$ , formed at the same time has b. p.  $312$ — $315^\circ$ . *p*-Bromodiphenyl ether has b. p.  $305^\circ$ , and the dibromo-derivative, m. p.  $54^\circ$ , b. p.  $338$ — $340^\circ$ . Di-*o*-tolyl ether gave the following compounds: a monochloro-derivative, b. p.  $308$ — $310^\circ$ , a dichloro-derivative, b. p.  $338$ — $340^\circ$ , a monobromo-derivative, b. p.  $330^\circ/670$  mm.,  $D^{10}_D$  1.4162. Di-*p*-tolyl ether gave a monochloro-derivative, b. p.  $315^\circ/760$  mm., a dichloro-derivative, b. p.  $240$ — $245^\circ/20$  mm.,  $D^{10}_D$  1.1800, a monobromo-derivative, b. p.  $330$ — $333^\circ/760$  mm.,  $D^{10}_D$  1.417, and a dibromo-derivative, m. p.  $131^\circ$ .  
W. O. W.

**Action of Bromine and Chlorine on Dehydrodicarvacrol.** HENRI COUSIN (*Compt. rend.*, 1912, 154, 441—443; *J. Pharm. Chim.*, 1912, [vii], 5, 236—240.† Compare Abstr., 1910, i, 476).—Dibromodehydrodicarvacrol,  $\text{C}_{20}\text{H}_{24}\text{O}_2\text{Br}_2$ , prepared by the action of bromine on dehydrodicarvacrol in chloroform solution, occurs in pale yellow prisms, m. p.  $179$ — $180^\circ$  (corr.). The corresponding dichloro-derivative, obtained by using the calculated amount of chlorine, crystallises in pale yellow prisms. When excess of chlorine is employed, dichlorodehydrodicarvacroquinone tetrachloride,  $\text{C}_{20}\text{H}_{22}\text{O}_2\text{Cl}_4$ , is formed as a yellow resin, slowly changing to crystals, m. p.  $155$ — $156^\circ$  (decomp.). When treated with reducing agents, this substance yields dichlorodehydrodicarvacrol; the corresponding quinone has not been isolated.  
W. O. W.

**Colour of Alkaline Solutions of Quinol and of Their Oxidation Products.** ROBERT LUTHER and A. LEUBNER (*J. pr. Chem.*, 1912, [ii], 85, 233—234).—On treatment with aqueous alkalis, quinone gives yellowish-green solutions, which become brownish-black on exposure to air. Addition of sodium sulphite to solutions of quinone produces an intensely greenish-blue coloration, which gradually changes to light yellow. When shaken with air, the yellow solutions become green and then light yellow. If the traces of oxidation-products formed by dissolving the quinone are destroyed by potassium hydrogen sulphite or quinol, the addition of sodium sulphite produces a brown coloration. The blue coloration is probably due to the formation of an alkali salt of an oxidation product of quinone.

According to Euler and Bolin (Abstr., 1909, ii, 374) quinol dissolves in alkalis, yielding yellow solutions, owing to the formation of quinonoid salts. The authors find, however, that solutions of potassium carbonate or potassium hydroxide and of quinol, to which small quantities of sodium hydrogen sulphite have been added in

\* and *Bull. Soc. chim.*, 1912, [iv], 11, 328—332.

† and *Bull. Soc. chim.*, 1912, [iv], 11, 332—336.

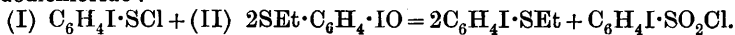
order to destroy dissolved oxygen and traces of quinone, do not yield yellow colorations when mixed, but gradually acquire a dark brown colour on exposure to air. From these observations the conclusion is drawn that salts of quinol, quinone, hydroxyquinol, and dihydroxyquinol are respectively colourless, yellow, bluish-green, and reddish-brown.

F. B.

**Isomerism Among the Ethers of Diisoeugenol.** ERNESTO PUXEDDU (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 124—129. Compare Abstr., 1909, i, 225).—The author considers it probable that the polymerisation of eugenol ethyl ether observed by Wassermann is preceded by an isomerisation, so that Wassermann's polymeride is a diisoeugenol diethyl ether, stereoisomeric with the diisoeugenol diethyl ether described by the author (*loc. cit.*). They differ not only in solubility and in m. p., but also give different bromine derivatives. Eugenol ethyl ether was prepared by the action of ethyl sulphate on eugenol dissolved in potassium hydroxide (10%), and also by Wassermann's method. When it was distilled, the residue which did not distil at 260° consisted of Wassermann's polymeride, but had m. p. 140° (Wassermann gave 125°). It is obtained in better yield by heating eugenol ethyl ether for fifteen hours in a bath at about 270°. In chloroform solution, it absorbs bromine, but no individual substance could be isolated from the product. The diisoeugenol diethyl ether previously described by the author, when treated with bromine in ethereal solution cooled with ice and salt, yields *monobromodiisoeugenol diethyl ether*,  $C_{24}H_{31}O_4Br$ , which forms yellowish-green, rhombohedral crystals, m. p. 118°.

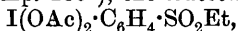
R. V. S.

**Iodothio-ethers, Iodosulphones, Iodosulphonic Esters, and their Derivatives with Multivalent Iodine.** CONRAD WILLGERODT and MAX KLINGER (*J. pr. Chem.*, 1912, [ii], 85, 189—198).—*p*-Iodothiophenetole (*p*-iodophenyl ethyl sulphide),  $C_6H_4I \cdot S\text{Et}$ , prepared by reducing *p*-nitrothiophenetole (*p*-nitrophenyl ethyl sulphide) with tin and hydrochloric acid and replacing the amino-group of the resulting *p*-aminothiophenetole (*p*-aminophenyl ethyl sulphide) by iodine by means of the diazo-reaction, is a yellow oil, b. p. 146—147°/11 mm. When treated with chlorine in chloroform solution, it yields an unstable *iododichloride*, which rapidly decomposes into *p*-iodothiophenetole and *p*-iodobenzenesulphonyl chloride. The formation of the latter compound is considered to be due to the decomposition of the iododichloride into ethyl chloride and the compound (I), which then reacts with the iodoso-compound (II), produced by the action of moisture on the iododichloride:



*Methyl p*-iodobenzenesulphonate, prepared from the sulphonyl chloride and methyl alcohol, crystallises in rhombohedra, m. p. 74°. It yields a yellow, crystalline *iododichloride*,  $ICl_2 \cdot C_6H_4 \cdot SO_3Me$ , which is converted by aqueous sodium carbonate into *methyl p*-iodobenzenesulphonate,  $IO \cdot C_6H_4 \cdot SO_3Me$  (decomp. 176—178°); the *iodosoacetate*,  $I(OAc)_2 \cdot C_6H_4 \cdot SO_3Me$ , forms rhombic prisms, m. p. 174°. *Methyl p*-iodoxybenzenesulphonate is prepared by the action of sodium hypochlorite and acetic acid on the iododichloride.

*p*-Iodophenylethylsulphone,  $C_6H_4I \cdot SO_2Et$ , obtained as a white powder, m. p.  $83^\circ$ , by oxidising *p*-iodothiophenetole with chromium trioxide in glacial acetic acid solution, yields an *iododichloride*,  $ICl_2 \cdot C_6H_4 \cdot SO_2Et$  (decomp.  $118^\circ$ ), which is converted by the usual methods into *p*-iodosophenylethylsulphone (decomp.  $235^\circ$ ), the *iodosoacetate*,

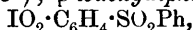


monoclinic needles, m. p.  $167-170^\circ$ , and *p*-iodoxyphenylethylsulphone,  $IO_2 \cdot C_6H_4 \cdot SO_2Et$ , which crystallises in small octahedra, exploding at  $220^\circ$ .

*p*-Iododiphenyl sulphide,  $C_6H_4I \cdot SPh$ , prepared from *p*-aminodiphenyl sulphide (Kehrmann and Bauer, Abstr., 1897, i, 27) by means of the diazo-reaction, crystallises in lustrous, white leaflets, m. p.  $35^\circ$ , b. p.  $230^\circ/11$  mm. Attempts to prepare the iododichloride by the action of chlorine in chloroform solution yielded a yellow oil, which on exposure to air is transformed into *p*-iododiphenyl sulphoxide,



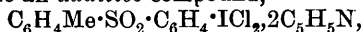
and *p*-iododiphenylsulphone,  $C_6H_4I \cdot SO_2Ph$ . The last-mentioned compound has also been prepared (1) by oxidation of *p*-iododiphenyl sulphide with chromium trioxide in glacial acetic acid solution, and (2) by the interaction of *p*-iodobenzenesulphonyl chloride and benzene in the presence of aluminium chloride. It crystallises in white needles, m. p.  $141^\circ$ , and forms an *iododichloride*,  $ICl_2 \cdot C_6H_4 \cdot SO_2Ph$ , rhombic crystals (decomp.  $130^\circ$ ). *p*-Iodosodiphenylsulphone is a pale yellow powder (decomp.  $210^\circ$ ); the *iodosoacetate*,  $I(OAc)_2 \cdot C_6H_4 \cdot SO_2Ph$ , forms white needles (decomp.  $195^\circ$ ); *p*-iodoxydiphenylsulphone,



crystallises in white leaflets, which explode at  $220-223^\circ$ .

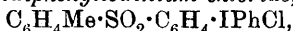
*p*-Iododiphenylsulphoxide, prepared by oxidising a cold glacial acetic acid solution of *p*-iododiphenyl sulphide with aqueous chromic acid, forms large, white, rhombic crystals, m. p.  $106^\circ$ . F. B.

**Iodosulphones and Their Derivatives with Multivalent Iodine.** CONRAD WILLGERODT and MAX PLOCKSTIES (*J. pr. Chem.*, 1912, [ii], 85, 198—207).—*p*-Iodophenyl-*p*-tolylsulphone (4-iodo-4'-methyl-diphenylsulphone),  $C_6H_4Me \cdot SO_2 \cdot C_6H_4I$ , is prepared by the interaction of *p*-iodobenzenesulphonyl chloride and toluene in carbon disulphide solution in presence of aluminium chloride; it crystallises in rhombs, m. p.  $162^\circ$ , and yields an *iododichloride*, which crystallises in slender, sulphur-yellow needles (decomp.  $120^\circ$ ), and forms with pyridine an *additive* compound,



decomposing at  $118-120^\circ$ .

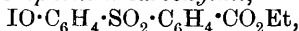
4-Iodosophenyl-*p*-tolylsulphone is a pale yellow powder (decomp.  $197^\circ$ ); the *iodosoacetate*,  $C_6H_4Me \cdot SO_2 \cdot C_6H_4 \cdot I(OAc)_2$ , crystallises in lustrous needles, decomposing at  $180^\circ$ . 4-Iodoxyphenyl-*p*-tolylsulphone,  $C_6H_4Me \cdot SO_2 \cdot C_6H_4 \cdot IO_2$ , forms a white powder (decomp.  $320^\circ$ ), and reacts with 4-iodosophenyl-*p*-tolylsulphone and silver oxide in the presence of water, yielding *di-p*-4-toluenesulphonylphenyliodinium hydroxide,  $OH \cdot I(C_6H_4 \cdot SO_2 \cdot C_6H_4Me)_2$ , which was obtained only in aqueous solution, and forms a yellow iodide.

*p*-4-Toluenesulphonyldiphenyliodinium chloride,

is obtained in aqueous solution by heating phenyl-*p*-tolylsulphone-4'-iododichloride with mercury diphenyl and water at 50°; the *iodide* (decomp. 132°) and *platinichloride*, slender, yellow needles (decomp. 178°), are described.

4-Iododiphenylsulphone-4'-carboxylic acid,  $\text{C}_6\text{H}_4\text{I}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , prepared by the oxidation of 4-iodophenyl-*p*-tolylsulphone with chromium trioxide in glacial acetic acid solution, crystallises in colourless, slender needles, m. p. 293°, and yields crystalline *sodium* and *silver* salts; the *iododichloride* could not be obtained in a pure condition.

*Ethyl* 4-iododiphenylsulphone-4'-carboxylate, prepared by esterifying the preceding acid, crystallises in slender needles, m. p. 140°; it yields a yellow, crystalline *iododichloride*,  $\text{ICl}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$  (decomp. 110°), which is converted by aqueous sodium carbonate into *ethyl* 4-iodosodiphenylsulphone-4'-carboxylate,



a pale yellow powder, decomposing at 235°.

4-Iodophenyl-2-*p*-xylylsulphone,  $\text{C}_6\text{H}_4\text{I}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_3\text{Me}_2$ , is obtained in quadrilateral prisms, m. p. 115°, by the interaction of *p*-iodobenzene-sulphonyl chloride and *p*-xylene in the presence of aluminium chloride. The *iododichloride*,  $\text{ICl}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{C}_6\text{H}_3\text{Me}_2$ , forms short, yellow needles (decomp. 138°); 4-iodosophenyl-2-*p*-xylylsulphone is a pale yellow powder (decomp. 134°).

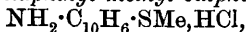
2-*p*-Xylenesulphonyldiphenyliodinium (2:5-dimethyldiphenylsulphone-4'-phenyliodinium) chloride,  $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\cdot\text{IPh}\cdot\text{Cl}$ , is obtained by the action of mercury diphenyl on the preceding iododichloride in chloroform solution; the *platinichloride* (decomp. 182°) and *iodide* (decomp. 135°) are also described. F. B.

4-Amino-1-naphthyl Mercaptan. THEODOR ZINCKE and FRANZ SCHÜTZ (*Ber.*, 1912, 45, 471—483).—4-Amino-1-naphthyl mercaptan,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SH}$ , m. p. 91—93°, yellow needles, is obtained by reducing 4-acetylamino-1-naphthalenesulphonyl chloride by alcohol, concentrated hydrochloric acid and zinc, and hydrolysing the resulting acetylamino-naphthyl mercaptan by alcohol and hydrochloric acid. The *hydrochloride*, *sulphate*, *acetyl* derivative, m. p. 173°, and *diacetyl* derivative, m. p. 152°, are described. With alcoholic benzaldehyde, it forms the *benzylidene* derivative,  $\text{CHPh}(\text{S}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}\cdot\text{CHPh})_2$ , m. p. 68°, yellow powder, in which the benzylidene group attached to the sulphur atoms is hydrolysed by alkalis, and those attached to nitrogen by acids. The *disulphide*,  $\text{S}_2[\text{C}_{10}\text{H}_6\cdot\text{NH}_2]_2$ , m. p. 168°, is obtained by oxidising the amino-mercaptan with 30% hydrogen peroxide in alcoholic or alkaline solution. It forms a *diacetyl* derivative, m. p. 265°, yellow needles, which is also obtained by the oxidation of the acetylaminonaphthyl mercaptan.

When a suspension of 4-acetylamino-1-naphthyl mercaptan in chloroform or carbon disulphide is treated in a freezing mixture with chlorine (1 mol.), the preceding disulphide is first formed, and then changes to 4-acetylamino-1-chlorothiolo-naphthalene,  $\text{NHAc}\cdot\text{C}_{10}\text{H}_6\cdot\text{SCl}$ , a yellow

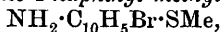
powder, which forms intensely yellow solutions, and is very reactive (compare Abstr., 1911, i, 368), yielding the disulphide with alcohol or formic or acetic acid, and 4-acetyl-amino-1-acetonylthiol-naphthalene,  $\text{NHAc}\cdot\text{C}_{10}\text{H}_6\cdot\text{S}\cdot\text{CH}_2\cdot\text{COMe}$ , m. p. 155—160°, white crystals, with acetone; the last compound is also obtained from chloroacetone and acetylaminonaphthyl mercaptan in dilute sodium hydroxide. 4-Acetyl-amino-1-bromothiolenaphthalene,  $\text{NHAc}\cdot\text{C}_{10}\text{H}_6\cdot\text{SBr}$ , is obtained in a similar manner; it can only be isolated in the form of the *hydrobromide*, a yellow powder. An excess of bromine converts 4-acetylaminonaphthyl mercaptan in chloroform into 1-bromo-4-acetylaminonaphthalene *hydrobromide*,  $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{NHAc}\cdot\text{HBr}$ , m. p. 205° (decomp.), straw-yellow needles.

4-Acetyl-amino-1-naphthyl methyl sulphide,  $\text{NHAc}\cdot\text{C}_{10}\text{H}_6\cdot\text{SMe}$ , m. p. 193°, yellow needles, is obtained by shaking methyl sulphate and 4-acetylaminonaphthyl mercaptan in a slight excess of 10% sodium hydroxide. By hydrolysis with alcohol and concentrated hydrochloric acid, it yields 4-amino-1-naphthyl methyl sulphide *hydrochloride*,

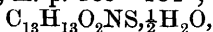


white needles, from which the free *base*,  $\text{C}_{11}\text{H}_{11}\text{NS}$ , m. p. 54°, is obtained. The base is sensitive to oxidising agents, forms solutions with blue fluorescence, reacts with benzaldehyde in alcohol to give 4-benzylideneamino- $\alpha$ -naphthyl methyl sulphide,  $\text{SMe}\cdot\text{C}_{10}\text{H}_6\cdot\text{N}\cdot\text{CHPh}$ , m. p. 56°, yellow needles (which forms an intensely red salt with hydrogen chloride in ether), and yields by methylation 4-dimethyl-amino-1-naphthyl methyl sulphide,  $\text{NMe}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SMe}$ , b. p. 199°/16—17 mm. (*hydriodide*, decomp. 171—173°).

4-Acetylaminonaphthyl methyl sulphide reacts with bromine in acetic acid to form a *dibromide* (impure),  $\text{C}_{13}\text{H}_{13}\text{ONSBr}_2$ , m. p. 157° (decomp.), a dark red, crystalline powder, which is converted by boiling glacial acetic acid into the *acetyl* derivative, m. p. 232°, white needles, of 3-bromo-4-amino-1-naphthyl methyl sulphide,



m. p. 138°, colourless needles. By oxidation in glacial acetic acid with 30% hydrogen peroxide and hydrolysis of the product by alcoholic potassium hydroxide at 100°, 4-acetylaminonaphthyl methyl sulphide yields the *sulphoxide*,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}\cdot\text{CH}_3$ , m. p. 171—172°, colourless crystals (*acetyl* derivative, m. p. 183—184°; a *hydrate*,



m. p. 109—111°, has also been obtained), the salts of which, unlike those of the parent sulphide, are only slightly hydrolytically dissociated. The sulphoxide reacts with hydrogen bromide in chloroform to form the preceding red dibromide, and its *acetyl* derivative is oxidised by an excess of hydrogen peroxide to the corresponding *sulphone*,  $\text{NHAc}\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_2\text{Me}$ , m. p. 236°, the hydrolysis of which yields 4-amino-1-naphthylmethylsulphone,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_6\cdot\text{SO}_2\text{Me}$ , m. p. 175° (*hydrochloride*, decomp. about 247°). By warming its solution in acetic acid with a little concentrated hydrochloric acid, 4-amino-1-naphthylmethylsulphoxide is converted into the *hydrochloride* of 3-chloro-4-amino-1-naphthyl methyl sulphide,  $\text{NH}_2\cdot\text{C}_{10}\text{H}_5\text{Cl}\cdot\text{SMe}$ , m. p. 71°.

C. S.

**Trimethylene** [*cyclo*Propane] Derivatives of the Type  $\begin{smallmatrix} \text{H}_2\text{C} \\ | \\ \text{H}_2\text{C} \end{smallmatrix} > \text{CHX}$ . LOUIS MICHIELS (*Bull. Acad. roy. Belg.*, 1912, 10—34. Compare Abstr., 1901, i, 581; 1902, i, 525; 1911, i, 62, 459).—A number of ketones, containing the *cyclo*propyl group, have been prepared, and from these the corresponding secondary alcohols have been obtained. Methylisopropylcarbinol has, in particular, been studied with regard to its behaviour towards hydrogen bromide. In the second half of the paper the author considers the physical properties of the *cyclo*propane derivatives as compared with those of the corresponding aliphatic compounds.

*cyclo*Propylmethylcarbinol,  $\begin{smallmatrix} \text{H}_2\text{C} \\ | \\ \text{H}_2\text{C} \end{smallmatrix} > \text{CH} \cdot \text{CHMe} \cdot \text{OH}$ , is obtained by the reduction of *cyclo*propyl methyl ketone with sodium and dry alcohol as a viscous, colourless liquid, b. p. 119—120°,  $D_4^{20}$  0·88045,  $n_D^{20}$  1·42461. With hydrogen chloride it readily yields the corresponding *chloride*, b. p. 105—106°/750 mm., and with hydrogen bromide, in the cold, the *bromide*, a colourless, mobile liquid, b. p. 118—120°/751 mm.,  $D_4^{20}$  1·1552. From the bromide by the further action of hydrogen bromide, or from the original carbinol by the action of concentrated hydrobromic acid, a dibromide is obtained, the trimethylene ring being opened, which is probably  $\gamma$ -pentylene dibromide (compare Lipp, Abstr., 1890, 20).

*cyclo*Propyl isoamyl ketone,  $\text{CHMe}_2 \cdot [\text{CH}_2]_2 \cdot \text{CO} \cdot \text{CH} < \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$ , a colourless liquid with an odour of mint, is obtained by the action of magnesium isoamyl bromide on *cyclo*propanecarboxylonitrile, the additive product being decomposed by water and acid. It has b. p. 183—185°/755 mm.,  $D_4^{20}$  0·87408,  $n_D^{20}$  1·44064; and yields a *semicarbazone*, m. p. 140—141°. On reduction with sodium and alcohol, *cyclo*propylisoamylcarbinol is formed as a colourless, viscous liquid with a citron-like odour, b. p. 188—189°/766 mm.,  $D_4^{20}$  0·8631,  $n_D^{20}$  1·44405.

*cyclo*Propyl isohexyl ketone,  $\text{CHMe}_2 \cdot [\text{CH}_2]_3 \cdot \text{CO} \cdot \text{CH} < \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$ , results from the interaction of magnesium isohexyl bromide and ethyleneacetonitrile. It is a colourless, mobile liquid, with an odour of mint, b. p. 200—202°/739 mm.,  $D_4^{20}$  0·8631,  $n_D^{20}$  1·44325; on reduction it yields the *carbinol*, a colourless, viscous liquid, with a citron-like odour, b. p. 206—207°/747 mm.,  $D_4^{20}$  0·8603,  $n_D^{20}$  1·44345.

*cyclo*Propylacetylcyclopropane,  $\begin{smallmatrix} \text{H}_2\text{C} \\ | \\ \text{H}_2\text{C} \end{smallmatrix} > \text{CH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH} < \begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$ , is prepared by the interaction of magnesium *cyclo*propylcarbinyl bromide and *cyclo*propanecarboxylonitrile as a colourless, mobile liquid, b. p. 175—177°/759 mm.,  $D_4^{20}$  0·9149,  $n_D^{20}$  1·45787, which yields a *semicarbazone*, m. p. 82—83°. On reduction it gives the corresponding *dicyclo*propylethanol,  $\text{C}_3\text{H}_5 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{C}_3\text{H}_5$ , b. p. 179—180°/770 mm.,  $D_4^{20}$  0·9054,  $n_D^{20}$  1·46036. This with hydrogen bromide gives a *bromide*,  $D_4^{20}$  1·535, in which only one of the *cyclo*propane groups has been opened.

The following secondary alcohols were prepared for comparison as regard their physical properties.

*isoPropylisobutylcarbinol*,  $\text{CHMe}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CHMe}_2$ , is formed by the interaction of magnesium *isobutyl* bromide and *isobutaldehyde*, and subsequent treatment with water and acid. It is a colourless, viscous liquid, smelling of thyme, b. p. 157—158°,  $D_4^{20}$  0.8212,  $n_D^{20}$  1.42461.

*isoPropylisoamylcarbinol*,  $\text{CHMe}_2 \cdot \text{CH}(\text{OH}) \cdot [\text{CH}_2]_2 \cdot \text{CHMe}_2$ , is similarly prepared, and is a colourless, viscous liquid with an odour of balm, b. p. 175°,  $D_4^{20}$  0.8212,  $n_D^{20}$  1.42461.

*isoPropylisohexylcarbinol* is a similar substance, b. p. 193—194/756 mm.,  $D_4^{20}$  0.8152,  $n_D^{20}$  1.43021.

A comparison of the boiling points of the ketones indicates that the loss of two hydrogen atoms accompanying the conversion of

$\text{CH}_3 > \text{C}$  into  $\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{C}$  produces in the case of the methyl-, ethyl-, and *n*-propyl- an increase of 19—20°, and for the *isopropyl*-, *isobutyl*-, and *isoamyl*- an increase of 13—15°. The replacement of a

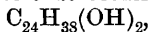
second  $\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_3 \end{smallmatrix} > \text{CH}-$  by  $\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{CH}-$  brings about a further rise of 14°.

Similar differences are shown by the alcohols.

A study of the densities of the alcohols of the two series shows that, on an average, the density of an alcohol of the *cyclopropyl* series is higher than that of the corresponding aliphatic alcohol by 0.043, and that this value is doubled by the introduction of another *cyclopropyl* group. The molecular refractions of the numerous *cyclopropane* derivatives containing one *cyclopropyl* group show on an average that the value found is higher than that calculated by 0.74 (compare Demjanoff, Abstr., 1907, i, 1032, who gave 0.66). W. G.

**Method for Preparing Aromatic Alcohols.** GUSTAVE VAVON *Compt. rend.*, 1912, 154, 359—361).—The reduction of aldehydes to alcohols by the ordinary method, employing sodium amalgam, gives yields not exceeding 50%. A theoretical yield is secured, however, by dissolving the aldehyde in a suitable solvent, adding a few grams of platinum black (prepared by the action of formaldehyde in alkaline solution on platonic chloride), and submitting it to the action of hydrogen under a pressure of about one atmosphere. Successful application to a number of aromatic aldehydes of varied types shows that the reaction is a general one. W. O. W.

**Betulin.** I. K. TRAUBENBERG (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 132—138).—The author's investigations on betulin (compare Hausmann, Abstr., 1877, i, 94; Franchimont and Wigman, Abstr., 1879, 468), which include the determination of the molecular weight in boiling chloroform by Landsberger's method and in freezing benzene and also the preparation and analysis of the diacetyl and dibenzoyl derivatives, indicate that betulin has the formula



and that it belongs, together with onocol, arnidiol, and faradiol to a group of dextrorotatory dihydric phytosterols.

Betulin, m. p.  $251^{\circ}$ ,  $[\alpha]_D + 15.68^{\circ}$ , gives a number of colour reactions similar to those for cholesterol. Its diacetyl compound has  $[\alpha]_D + 14.26^{\circ}$ , and its *dibenzoyl* derivative,  $C_{24}H_{38}O_2Bz_2$ , has m. p.  $145-147^{\circ}$ . When oxidised by means of alkaline permanganate, betulin yields acetic acid and a solid acid which was not investigated, whilst with chromic acid it gives a *ketone*,  $C_{24}H_{38}O_2$ , crystallising in prisms, m. p.  $177^{\circ}$ , and yielding a *phenylhydrazone*,  $C_{24}H_{38}O \cdot N_2HPh$ , m. p.  $130^{\circ}$ .  
T. H. P.

**Preparation and Estimation of Tyrosine and Glutamic Acid.** EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1912, 77, 75-76).—Tyrosine can be prepared from silk by the simple method of hydrolysing with hydrochloric acid; the acid is removed by evaporation, and then by the addition of sodium hydroxide; tyrosine then crystallises out from the hot aqueous solution. The yield, however, is not quantitative, and the mother liquor is not available for the separation of other amino-acids. These two disadvantages can be overcome in the following way. After hydrolysing with hydrochloric acid, the product is evaporated under reduced pressure to dryness; the residue is dissolved in water, and a stream of ammonia passed through the solution. It is then again evaporated to dryness, and the residue treated with cold water; tyrosine is left undissolved, or the whole residue may be boiled with water and animal charcoal; from the filtrate pure tyrosine crystallises out quantitatively. The mother liquor is again evaporated to dryness, and the residue treated by the ester method for the other mono-amino-acids. The method serves for the estimation of tyrosine, etc., in like products of hydrolysis.

Glutamic acid may be prepared from its hydrochloride by passing ammonia through the solution and then evaporating to dryness. The deposit is dissolved in hot water and recrystallised; the main amount of glutamic acid can be separated by fractional crystallisation, and the remainder can be obtained by precipitation with alcohol.

W. D. H.

[Di-iodotyrosine.] **A Correction.** ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1912, 76, 499-500).—Polemical (compare Abderhalden and Hirsch, Abstr., 1911, ii, 1119).  
E. F. A.

**Melting Point of 3:5-Di-iodotyrosine.** EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1912, 77, 183-184).—Polemical. A reply to Oswald (preceding abstract).  
W. D. H.

**Action of Hydrogen Sulphide on Imino-ethers. II. Formation of Thion Esters and Acids.** MOTOOKI MATSUI (*Mem. Koll. Sci. Eng. Kyōtō*, 1912, 3, 247-255. Compare Abstr., 1909, i, 463).—When hydrogen sulphide is passed into an ethereal solution of an imino-ether, a thion ester is produced, which ultimately reacts with the liberated ammonia with the formation of a thioamide. In alcoholic solution, however, ammonia decomposes thion esters with the formation of imino-ethers, hydroxylamine having a similar action.

By saponifying thion esters with cold alkali, it has been found possible to prepare the corresponding acids. Thion-fatty acids are volatile, pale yellow liquids, having a strong penetrating odour resembling that of acetic acid and a very acidic reaction; thion-aromatic acids are yellow, solid substances of characteristic odour. All are unstable, decomposing even in ethereal solution in the course of a few days. They show a marked difference from ordinary monocarboxylic acids, in that their silver and lead salts remain in the ethereal layer when an ethereal solution of the acid is shaken with an aqueous solution of silver nitrate or lead acetate. Silver salts of thion-fatty acids are very unstable, readily changing into silver sulphide, whilst those of the aromatic acids are comparatively stable at the ordinary temperature.

Ethyl thionbenzoate (*loc. cit.*) is a yellow liquid of b. p. 181°/360 mm. When its alcoholic solution is treated with ammonia, it yields ethyl iminobenzoate, whilst in ethereal solution, thiobenzamide is formed. Hydroxylamine reacts with an alcoholic solution of the ester, yielding a mixture of  $\alpha$ - and  $\beta$ -ethylbenzhydroxamic acids.

*Methyl thionbenzoate* resembles the ethyl ester. It has b. p. 195—197°/320 mm.

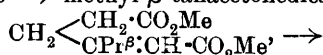
*Methyl thionacetate* has b. p. 85—90°; *methyl thionpropionate* has b. p. 110—115°.

*Ethyl thion-p-toluate* is a yellow oil, b. p. 205—207°/260 mm., m. p. about 1°.

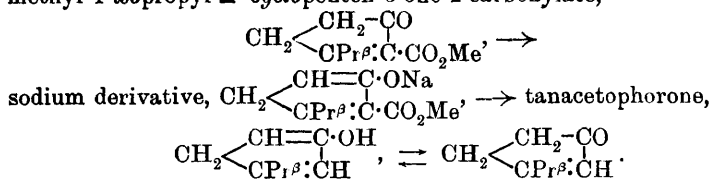
*Thionbenzoic acid* was prepared by hydrolysing ethyl thionbenzoate with cold sodium hydroxide. Its *silver*, *lead*, and *barium* salts were examined. *Thion-p-toluic acid* was similarly prepared, but in quantity insufficient for complete characterisation. *Thionacetic acid* could not be obtained free from ether, but has b. p. about 37°. The similar *thionpropionic acid* was also prepared, and its *lead* salt was investigated.

H. W.

**Terpenes and Ethereal Oils.** CVIII. OTTO WALLACH (*Annalen*, 1912, 388, 49—62).—Semmler's method of preparing tanacetophorone by the distillation of salts of tanacetonedicarboxylic acid is unsatisfactory with regard to yield and purity of product. A very convenient process is the following: *Methyl  $\alpha$ -tanacetonedicarboxylate*,  $\text{CH}_2 < \begin{matrix} \text{CH} \cdot \text{CO}_2\text{Me} \\ \text{CPr}^\beta \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}' \end{matrix}$  b. p. 244—247° or 126—127°/13 mm.,  $D^{20}_D$  1.0535,  $n^{20}_D$  1.4506,  $[\alpha]_D$  142.5°, obtained from the acid, methyl alcohol, and hydrogen chloride, forms with sodium in methyl alcohol a yellow, crystalline compound,  $\text{C}_{10}\text{H}_{13}\text{O}_3\text{Na} \cdot \text{H}_2\text{O}$ , which develops a violet coloration with ferric chloride, yields impure tanacetophoronesemicarbazone with aqueous semicarbazide hydrochloride, and is converted into tanacetophorone by the successive operations of boiling its aqueous solution, acidifying with sulphuric acid, and distillation with steam. The transformations in the preparation of the ketone are probably as follows. Methyl  $\alpha$ -tanacetonedicarboxylate  $\rightarrow$  methyl  $\beta$ -tanacetonedicarboxylate,



methyl 1-isopropyl- $\Delta'$ -cyclopenten-3-one-2-carboxylate,



The preceding constitution of the sodium compound is supported by the fact that the substance, dissolved in water saturated with carbon dioxide, is converted into dihydrotanacetophorone (1-*iso*-propylcyclopentan-3-one) by treatment with hydrogen and colloidal palladium, and subsequent acidification and distillation with steam.

[With FREDERIK CHALLENGER].—1-*iso*Propylcyclopentan-3-one, b. p. 188—189°,  $D_4^{21}$  0.9000,  $n_D^{21}$  1.4428 (compare Abstr., 1911, i, 472), forms a *dibenzylidene* derivative, m. p. 134—135°, yellow needles, and reacts with magnesium methyl iodide to yield ultimately *i*-1-methyl-3-isopropylcyclopentan-1-ol,  $\text{C}_9\text{H}_{18}\text{O}$ , b. p. 185—186°, m. p. 43—44°, which apparently is the inactive modification of the tertiary alcohol obtained by the action of nitrous acid on fenchylamine (Abstr., 1911, i, 311); by dehydration with oxalic acid, it yields a hydrocarbon,  $\text{C}_9\text{H}_{16}$ , b. p. 142—144°,  $D_4^{20}$  0.7970,  $n_D^{20}$  1.4418, which is almost identical in chemical and physical properties with that described previously (*loc. cit.*). C. S.

The Ethyl Ester of Naphthalic Acid. WILHELM WISLICENUS and OTTO PENNDORF (*Ber.*, 1912, 45, 410—411).—Naphthalic acid cannot be esterified directly. The diethyl ester described recently by Errera (Abstr., 1911, i, 465) had already been prepared by the authors by the action of ethyl iodide on silver naphthalate; it has m. p. 59—60° and b. p. 238—239°/19 mm.; the solution in strong sulphuric acid shows a blue fluorescence. D. F. T.

Methylamino- and Other Derivatives of Terephthalic Acid. RUDOLF WEGSCHEIDER, FRANZ FALTIS, SIEGMUND BLACK, and OSKAR HUPPERT (*Monatsh.*, 1912, 93, 141—168).—The object of the investigation was a convenient method for the preparation of methyl- and dimethyl-aminoterephthalic acids.

Aminoterephthalic acid was obtained by successive nitration and reduction of terephthalic acid; the corresponding methyl ester was obtained by esterification of the acid, and also by the reduction of the methyl ester of nitroterephthalic acid; the last-named substance can be prepared by careful nitration of the methyl terephthalate, as well as by esterification of nitroterephthalic acid.

The methyl ester of acetylaminoterephthalic acid (compare Cahn-Speyer, Abstr., 1907, i, 849) is obtained by simple acetylation with acetic anhydride; the alcoholic mother liquors from the recrystallisation of this substance contain *methyl diacetylaminoterephthalate*, which is also obtainable by the further acetylation of the monoacetyl compound; the crystals of the substance, m. p. 74—76°, belong to the triclinic system [ $a:b:c=0.5240:1:0.7912$ ;  $\alpha=91^\circ 12'$ ,  $\beta=85^\circ 22'$ ,  $\gamma=96^\circ 19'$ ]; water hydrolyses the substance into the monoacetyl compound.

Methylaminoterephthalic acid is best prepared by the action of methyl sulphate on aminoterephthalic acid in the presence of barium carbonate; it has m. p.  $273\cdot5$ — $274\cdot5^\circ$  (corr.) (compare Cahn-Speyer, *loc. cit.*); the solutions show a blue fluorescence. When the methyl-alcoholic solution is treated with hydrogen chloride at room temperature, 4-methyl 1-hydrogen 2-methylaminoterephthalate separates, m. p.  $186\cdot5$ — $187^\circ$  (corr.). The corresponding dimethyl ester was also obtained by esterification as an impure, dark yellow solid, m. p.  $86\cdot5$ — $90^\circ$ .

Acetylmethylaminoterephthalic acid was not obtainable by methylating the acetylaminino-acid with methyl sulphate, but was successfully prepared by acetylating the methylamino-acid; it crystallises in crusts, the m. p. of which,  $216$ — $216\cdot5^\circ$ , is much below that given by Cahn-Speyer; it is colourless and does not give fluorescent solutions. The acetyl group is removed by the action of dilute potassium hydroxide solution.

Methyl acetylmethylaminoterephthalate, obtained by the action of potassium and methyl iodide on a benzene solution of the methyl acetylaminoterephthalate, has m. p.  $78$ — $80^\circ$ ; the acetyl group is hydrolysed off by heating with water.

Dimethylaminoterephthalic acid is best prepared by energetic methylation of aminoterephthalic acid with methyl sulphate in the presence of barium carbonate; it is a white, crystalline solid, m. p.  $281^\circ$  (corr.; decomp.). The dimethyl ester, obtained from the acid by esterification in the usual way, crystallises in needles belonging to the triclinic system [ $a:b:c = 0\cdot7920:1:0\cdot8327$ ;  $\alpha = 82^\circ21'$ ,  $\beta = 94^\circ14'$ ,  $\gamma = 104^\circ50'$ ], m. p.  $68$ — $69^\circ$ .  
D. F. T.

**Reduction of Acids with Several Double Bonds by Paal's Method.** WALTHER BORSCHKE (*Ber.*, 1912, 45, 620—625).—Unsaturated acids when shaken with hydrogen and colloidal platinum are readily converted into the saturated substances.

Cinnamylideneacetic acid,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , yields phenylvaleric acid. Cinnamylidenemalononic acid,  $\text{CHPh}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{H})_2$ , gives  $\omega$ -phenyl- $n$ -propylmalonic acid, crystallising in colourless platelets, m. p.  $98^\circ$ . When heated, carbon dioxide is eliminated and  $\delta$ -phenylvaleric acid obtained; this is the most convenient method for its preparation.

Methyl  $\omega$ -phenylpropylmalonate, formed by reduction of methyl cinnamylidenemalonate, is a colourless oil, b. p.  $183$ — $184^\circ/10$  mm.

$\alpha$ -Cyano- $\delta$ -phenylvaleric acid, prepared by reduction of  $\alpha$ -cinnamylideneacetic acid, is obtained as an oil, which on distillation is converted into  $\delta$ -phenylvaleronitrile.

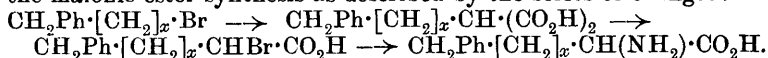
The ethyl ester of  $\alpha$ -cyano- $\delta$ -phenylvaleric acid is a colourless oil, b. p.  $192$ — $193^\circ/11$  mm.

$\alpha\delta$ -Diphenylvaleric acid,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ , from  $\alpha$ -phenylcinnamylideneacetic acid, crystallises in bunches of colourless needles, m. p.  $80$ — $81^\circ$  (compare Rupe and Liechtenhan, *Abstr.*, 1909, i, 927).

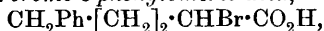
$\alpha\delta$ -Diphenylvaleronitrile from cinnamylidenephénylacetonitrile forms large, transparent crystals with lustrous faces, m. p.  $79^\circ$ ; it distils without decomposition.  
E. F. A.

**Syntheses in the Fatty Aromatic Series. III. [Amino-acids, Nitro-compounds, Aldehydes.]** JULIUS VON BRAUN and O. KRUBER (*Ber.*, 1912, 45, 384—402. Compare *Abstr.*, 1911, i, 968; 1910, i, 843).—The authors have attempted in several ways to prepare the series of aldehydes corresponding with the series of alcohols already described in the earlier papers; the most satisfactory source for the aldehydes proves to be the primary nitro-compounds.

Various phenyl substituted amino-acids were obtained by applying the malonic ester synthesis as described by the series of changes:



*δ-Phenylpropylmalonic acid*,  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{CH}(\text{CO}_2\text{H})_2$ , m. p. 94°, is obtained by hydrolysis of the *ethyl* ester, a colourless oil, b. p. 189—194°/13 mm. On distillation under reduced pressure, it loses carbon dioxide with the formation of *δ-phenylvaleric acid*. Bromination in ethereal solution yields *α-bromo-δ-phenylpropylmalonic acid*, m. p. 135—136°; this when heated above its m. p. loses carbon dioxide and forms *α-bromo-δ-phenylvaleric acid*,



m. p. 85°, b. p. 195—210°/15 mm.; the same substance is obtained in a less pure condition by brominating *δ-phenylvaleric acid*. If the bromo-acid is heated with a concentrated aqueous solution of ammonia, there is obtained *α-amino-δ-phenylvaleric acid*, m. p. 203—206°; the copper salt was prepared, also the *β-naphthalenesulphonyl* derivative, m. p. 83°.

*ε-Phenylbutylmalonic acid*,  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{CH}(\text{CO}_2\text{H})_2$ , needles, m. p. 111°, is obtained by hydrolysis of the *ethyl* ester, b. p. 215—218°/11 mm.; bromination gives *α-bromo-ε-phenylbutylmalonic acid*, m. p. 123—124° (decomp.), which on heating yields *α-bromo-ε-phenylhexoic acid*, a yellow oil, b. p. 210—230°/12 mm., which would not crystallise; the preparation of this last substance by bromination of *ε-phenylhexoic acid* is again unsatisfactory. When heated with aqueous solution of ammonia, the bromo-acid is converted into *α-amino-ε-phenylhexoic acid*, white, leafy crystals, m. p. 237—242° (decomp.); the copper salt and the *β-naphthalenesulphonyl* derivative, m. p. 112—113°, were prepared.

The above amino-acids failed to supply the desired easy passage to the required aldehydes.

Phenylbutyronitrile,  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{CN}$ , when treated in alcoholic solution with dry hydrogen chloride yields the *hydrochloride* of *phenylbutyrimido-ether*,  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{C}(\text{NH})\cdot\text{OEt}$ , HCl, which by the action of aniline in alcoholic solution is converted into the corresponding *diphenylamidine* compound,  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{C}(\text{NPh})\cdot\text{NHPh}$ , a white, crystalline solid, m. p. 81—82°. Reduction of this compound by sodium and alcohol yields a non-volatile, viscous oil, probably *di-δ-anilino-α-phenylbutane*,  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{CH}(\text{NHPh})_2$ , which on hydrolysis yields only a few drops of *δ-phenylbutaldehyde* (compare Merling, *Abstr.*, 1908, i, 653).

If phenylpropyl bromide is allowed to react with magnesium and then with ethyl orthoformate, the expected *phenylbutaldehyde diethyl acetal*,  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{CH}(\text{OEt})_2$ , is obtained; it is, however,

much decomposed during distillation (b. p. about 200°/20 mm.); hydrolysis gives a very poor yield of the aldehyde. Phenylbutyl bromide, magnesium and ethyl orthoformate yield no better result (compare Tschitschibabin, Abstr., 1904, i, 221; Bodroux, Abstr., 1904, i, 421).

The reaction of magnesium phenylpropyl bromide and formomethyl-anilide gives no trace of phenylbutaldehyde (compare Houben and Dörscher, Abstr., 1908, i, 27), whilst the action of sodium hypochlorite on a hot aqueous solution of  $\alpha$ -amino- $\delta$ -phenylvaleric acid or  $\alpha$ -amino- $\epsilon$ -phenylhexoic acid yields small quantities of  $\delta$ -phenylbutaldehyde and  $\epsilon$ -phenylvaleraldehyde respectively (compare Langheld, Abstr., 1909, i, 138).

The desired aldehydes were satisfactorily obtained by starting with the primary nitro-compounds, which by reduction are convertible into the aldoximes (Konowaloff, Abstr., 1899, i, 733).

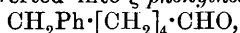
The interaction of  $\gamma$ -phenylpropyl iodide and silver nitrite produced  $\gamma$ -phenylpropyl nitrite, b. p. 115—125°/14 mm., and  $\gamma$ -nitro- $\alpha$ -phenylpropane, a colourless, inodorous oil, b. p. 147—148°/11 mm.; the latter on treatment with bromine in aqueous solution gives oily *di*- $\gamma$ -bromo- $\gamma$ -nitro- $\alpha$ -phenylpropane,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CBr}_2\cdot\text{NO}_2$ , whilst with a diazonium salt it yields  $\alpha$ -nitro- $\gamma$ -phenylpropaldimethylphenylhydrazone, small, red needle crystals, m. p. 133—134°; the  $\alpha$ -phenylpropanenitrolic acid has m. p. 75°. If the sodium compound of nitrophenylpropane is reduced in aqueous solution by stannous chloride, there is obtained  $\gamma$ -phenylpropaldoxime, m. p. 93—94°; this on hydrolysis yields  $\gamma$ -phenylpropaldehyde,  $\text{Ph}\cdot[\text{CH}_2]_2\cdot\text{CHO}$ , b. p. 110—113°/16 mm. (compare Fischer and Hoffa, Abstr., 1898, i, 659); the diphenylmethanedimethyldihydrazone,  $\text{CH}_2[\text{C}_6\text{H}_4\cdot\text{NMe}\cdot\text{N}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Ph}]_2$ , has m. p. 99—100°.

$\delta$ -Nitro- $\alpha$ -phenylbutane (together with  $\delta$ -phenylbutyl nitrite, b. p. 125—130°/15 mm.) is obtained similarly to the corresponding propane derivative as a colourless oil of feeble odour, b. p. 160—165°/15 mm.; reduction of the sodium salt in aqueous solution and subsequent hydrolysis yields  $\delta$ -phenylbutaldehyde,  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{CHO}$ , b. p. 129—131°/17 mm.; the semicarbazone has m. p. 104—105°; the phenylhydrazone is an oil; the diphenylmethanedimethyldihydrazone crystallises very slowly; the methyl acetal has b. p. 121—124°/9 mm.

$\epsilon$ -Nitro- $\alpha$ -phenylpentane is a colourless, inodorous liquid, b. p. 161—166°/9 mm., whilst the isomeric  $\epsilon$ -phenylamyl nitrite has b. p. 130—135°/10 mm. The dibromo-derivative of the phenylnitropentane is a yellow oil; the nitrolic acid derivative and the product of coupling with a diazonium salt also show little tendency to crystallise. Reduction and subsequent hydrolysis of the nitro-compound yield  $\epsilon$ -phenyl-*n*-valeraldehyde,  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{CHO}$ , as an oil, b. p. 129—131°/10 mm., strongly resembling citral in odour; the methyl acetal, b. p. 136—139°/11 mm., has only a faint ethereal odour. The oxime, semicarbazone, phenylhydrazone, and diphenylmethanedimethyldihydrazone are oily; the *p*-nitrophenylhydrazone slowly gives a solid, m. p. 82—84°.

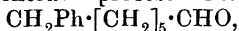
$\zeta$ -Nitro- $\alpha$ -phenylhexane has b. p. 174—178°/11 mm., whilst the isomeric  $\zeta$ -phenylhexyl nitrite has b. p. 143—148°/11 mm. The nitro-

compound is easily converted into  $\zeta$ -phenylhexaldehyde,



b. p. 141—144°/9 mm., of feeble and not unpleasant odour; the substance offers considerable resistance to satisfactory analysis by combustion.

$\eta$ -Nitro- $\alpha$ -phenylheptane has b. p. 182—186°/10 mm., and the isomeric  $\eta$ -phenylheptyl nitrite, b. p. 164—166°/13 mm. The nitro-compound is convertible by the general process into  $\eta$ -phenylheptaldehyde,



b. p. 155—159°/9 mm., which like the lower aldehyde offers resistance to satisfactory combustion; it has a feeble odour. The *p*-nitrophenylhydrazone is a brown powder, m. p. 68—70°.

The above series of aldehydes, with the striking exception of  $\delta$ -phenylvaleraldehyde, show a gradual weakening of the odour with increase in the length of the carbon chain; this is in marked contrast to the oscillatory effect observed with the corresponding series of alcohols.

D. F. T.

**Combination of Phenolcarboxylic Acids.** FERDINAND MAUTHNER (*J. pr. Chem.*, 1912, [ii], 85, 308—314).—An isomeride of the previously-described 3:4:5:2':6'-pentamethyl ether of methyl digallate (Abstr., 1911, i, 725) has been synthesised by condensing 3:4:5-trimethoxybenzoyl chloride with methyl 5-hydroxy-3:4-dimethoxybenzoate. The condensation was effected by shaking the ester in aqueous sodium hydroxide solution with an ethereal solution of the acid chloride.

*Methyl 5-(3':4':5')-trimethoxybenzoyloxy-3:4-dimethoxybenzoate*,  $\text{C}_6\text{H}_2(\text{OMe})_3 \cdot \text{CO}_2 \cdot \text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{CO}_2\text{Me}$ , thus obtained crystallises in colourless needles, m. p. 127—128°, and is the completely methylated derivative of the digallic acid isolated by Nierenstein (Abstr., 1910, i, 265) from tannin.

The following compounds were prepared in a similar manner:

*Methyl p-3:4:5-trimethoxybenzoyloxybenzoate*,  $\text{C}_{18}\text{H}_{18}\text{O}_7$ , obtained from 3:4:5-trimethoxybenzoyl chloride and methyl *p*-hydroxybenzoate, has m. p. 109—110°.

*Methyl 4-(3':4':5')-trimethoxybenzoyloxy-3-methoxybenzoate*,  $\text{C}_{19}\text{H}_{20}\text{O}_8$ , prepared from 3:4:5-trimethoxybenzoyl chloride and methyl vanillate, forms colourless needles, m. p. 131—132°.

*Methyl p-4-methoxybenzoyloxybenzoate*,  $\text{C}_{16}\text{H}_{14}\text{O}_5$ , obtained from anisoyl chloride and methyl *p*-hydroxybenzoate, crystallises in colourless needles, m. p. 146—147°.

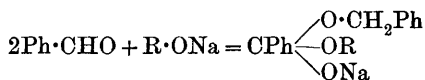
*Methyl 4-veratroyloxy-3-methoxybenzoate*,  $\text{C}_{17}\text{H}_{16}\text{O}_6$ , from veratroyl chloride and methyl vanillate, has m. p. 128—129°.

*Methyl p-veratroyloxybenzoate*,  $\text{C}_{18}\text{H}_{18}\text{O}_7$ , forms colourless needles, m. p. 148—149°.

F. B.

**Mechanism of Cannizzaro's Reaction.** VETCHESLAV E. TISTSHENKO, I. F. VELTSA, and I. L. RABTSEVITSCH-ZUBKOVSKY (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 138—151).—According to Claisen (Abstr., 1887, 574), when a sodium alklyoxide is heated in alcoholic solution

with benzaldehyde, a voluminous, white precipitate is formed, which is decomposed by water into benzyl alcohol and sodium benzoate, or by acetic acid into benzyl benzoate and alkyl benzoate; he regarded this precipitate as an intermediate compound formed according to the equation:



The authors have investigated this reaction under various conditions, and in all cases find the precipitate formed to consist simply of sodium benzoate. As has been previously asserted (Abstr., 1907, i, 282), Claisen's explanation must be abandoned. T. H. P.

**The Action of Solutions of Ethoxides on *m*-Nitrobenzylidene Chloride.** ALFRED KLIEGL (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 226—228. Compare Kliegl and Haas, Abstr., 1911, i, 433).—*m*-Nitrobenzylidene chloride yields with solutions of ethoxides the acetal of *m*-nitrobenzaldehyde, but this is accompanied into two compounds of the same composition and molecular weight, but higher boiling point. They are unchanged by boiling with dilute sulphuric acid. Heating with hydrogen bromide in acetic acid forms bromo-derivatives, from which the alcohols may be obtained. Oxidation with permanganate then yields compounds which are identified as ethers of 5-nitrosalicylic acid and 3-nitro-4-hydroxybenzoic acid respectively. The original compounds are therefore derived from *m*-nitrobenzylidene chloride by the wandering of a chlorine atom into the nucleus, followed by the replacement of chlorine by alkyloxy-groups. C. H. D.

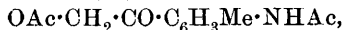
**Action of Benzaldehyde on Polyhydric Alcohols Derived from Sugars.** JEAN MEUNIER (*Ann. Chim. Phys.*, 1912, [viii], 25, 286—288).—The author points out that the condensation of polyhydric alcohols with benzaldehyde to form acetals was first noticed by him in 1888 (Abstr., 1888, 950, 1265; 1889, 233, 479; 1890, 730), and is wrongly attributed to E. Fischer in a recent paper (*Ann. Chim. Phys.*, 1911, [viii], 24, 398).

The sorbitol derivative described already (Abstr., 1889, 479) may be prepared by mixing the components at 0°, concentrating to a syrup of 33°Bé., and adding 60% sulphuric acid. The crystalline product which deposits is separated and washed, and can be used for the production of pure sorbitol by hydrolysing with 0.002% sulphuric acid at 100° and distilling under reduced pressure, when the benzaldehyde passes over in the steam, leaving pure sorbitol. T. A. H.

**Aromatic Amino-ketones.** FRANZ KUNCKELL (*Ber. deut. pharm. Ges.*, 1912, 22, 103—114. Compare Abstr., 1900, i, 663; 1911, i, 990).—The methods described in the preceding paper of this series (*loc. cit.*) have been applied to *p*-acetotoluidide and the products obtained are described.

[With CARL BLUMENREUTER.]—*ω*-Chloro-2-acetyl-amino-5-methylaceto

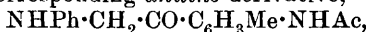
phenone,  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NHAc}$ , already described (Abstr., 1900, i, 663) reacts with potassium acetate to form an *acetate*,



m. p.  $94^\circ$ , and with bromine to give *ω-chloro-ω-bromo-2-acetylamino-5-methylacetophenone*, m. p.  $138^\circ$ , and this on hydrolysis with 20% hydrochloric acid loses 1 mol. of acetic acid and forms the corresponding *amine*, m. p.  $123^\circ$ , bright yellow needles. On treatment with warm dilute sodium hydroxide solution, the chlorobromo-ketone yields dimethylindigotin.

On nitration of *ω-chloro-2-acetylamino-5-methylacetophenone*, one nitro-group enters, probably in the unoccupied *o*-position to the acetyl-amino-group; the *nitro-derivative*, m. p.  $167^\circ$ , forms glancing, yellow needles, and on treatment with alkalis does not yield a substituted indigotin. With aniline the chlorine atom in the parent substance is replaced, and the *substance*,  $\text{NHPh}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NHAc}$ , m. p.  $146^\circ$ , formed, crystallising in yellow needles.

*ω-Chloro-3-acetylamino-6-methylacetophenone*, formed along with its isomeride (see above), yields (1) on bromination *ω-chloro-ω-bromo-3-acetylamino-6-methylacetophenone*, m. p.  $112^\circ$ , colourless leaflets, from which the corresponding *amine*, m. p.  $88^\circ$ , yellow needles, is produced on hydrolysis; (2) by nitration, indefinite products; (3) by treatment with aniline, the corresponding *aniline derivative*,

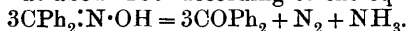


m. p.  $184^\circ$ , colourless needles; (4) with potassium acetate in dilute alcohol, the corresponding *acetate*,  $\text{OAc}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NHAc}$ , m. p.  $94^\circ$ , hard, colourless needles.

*m-Bromo-p-acetotoluidide* reacts with chloroacetyl chloride to form *ω-chloro-2(or 4)-bromo-3-acetylamino-6-methylacetophenone*, m. p.  $134^\circ$ , glancing, colourless leaflets, which on hydrolysis yields the corresponding *amine*, m. p.  $116^\circ$ , glancing, yellow needles, giving a *hydrochloride*, m. p.  $206^\circ$  (decomp.), colourless needles.

T. A. H.

**Interesting Decomposition of Some Oximes.** ANGELO ANGELI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 83—84).—Benzophenone-oxime decomposes at about  $180^\circ$  according to the equation:



If it is supposed that the nitrogen and ammonia are produced according to the equation:  $3\text{NH} = \text{N}_2 + \text{NH}_3$ , the Beckmann rearrangement becomes explicable on the hypothesis that a similar decomposition of the oxime first occurs, but the  $\text{NH}$  group takes up another position in the molecule instead of giving rise to nitrogen and ammonia. Analogous decompositions are those of some nitronic acids (Nef), and of phthalylphenylhydrazide (compare Croftaway, Cumming, and Wilsdon, *Trans.*, 1911, 99, 1950).

R. V. S.

**Preparation of  $\alpha$ -Diphenyl- $\beta\beta\delta\delta$ -tetramethylpentan- $\gamma$ -one and of  $\alpha$ -Phenyl- $\beta\beta\delta\delta$ -tetramethylpentan- $\gamma$ -one, Derivatives of Dibenzylacetone ( $\alpha$ -Diphenylpentan- $\gamma$ -one) and of  $\alpha$ -Phenylpentan- $\gamma$ -one.** ALBIN HALLER (*Compt. rend.*, 1912, 154, 555—559).— $\alpha$ -Diphenylpentanone was repeatedly methylated by means of sodamide and methyl iodide. The final product was  $\alpha$ -diphenyl-

*ββδδ-tetramethylpentan-γ-one*,  $\text{CH}_2\text{Ph}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{CH}_2\text{Ph}$ , an oily liquid, b. p. 203—208°/10 mm.; when heated with sodamide it undergoes scission in the normal way. The same method of methylation applied to *α*-phenylpentan-γ-one leads to the formation of *α*-phenyl-*ββδδ-tetramethylpentan-γ-one*,  $\text{CH}_2\text{Ph}\cdot\text{CMe}_2\cdot\text{CO}\cdot\text{CMe}_3$ , b. p. 139—144°/16 mm. The new tetra-alkyl ketones do not react with hydroxylamine, semicarbazide, or phenylhydrazine. W. O. W.

**Dihalogenoindones.** HUGO SIMONIS and CURT KIRSCHTEN (*Ber.*, 1912, 45, 567—579).—From his investigations on the condensation of 2:3-dibromo-1-indone and dibromo-derivatives of quinones with ethyl malonate and other substances containing a reactive methylene group, Liebermann (*Abstr.*, 1899, i, 219, 373, 522; 1900, i, 310, 666) has drawn the conclusion that the mobility of the halogen atoms in these compounds is due to the group  $\text{CBr}\cdot\text{CBr}\cdot\text{CO}$  being contained in a closed ring.

It is now shown that the mobility is connected with the presence of the carbonyl group, for compounds in which this group is lacking have their halogen atoms firmly attached; thus, 2:3-dibromo-1-methyl-1-indenol,  $\text{C}_6\text{H}_4\langle\text{CMe}(\text{OH})\text{CBr}\rangle\text{CBr}$ , does not condense with substances containing a reactive methylene group, and undergoes no change on treatment with potassium iodide or benzylamine.

The reaction between magnesium methyl bromide and 2:3-dibromo-1-indone yields 3-bromo-2-iodo-1-indone, which crystallises in brown prisms, subliming above 80° with partial decomposition, m. p. 158° (compare Roser and Haselhoff, *Abstr.*, 1888, 1317), and 2:3-dibromo-1-methyl-1-indenol. The latter compound crystallises in white platelets, m. p. 126·5—127°, combines with bromine to form 2:2:3:3-dibromo-1-methyl-1-hydrindenol,  $\text{C}_6\text{H}_4\langle\text{CMe}(\text{OH})\text{CBr}_2\rangle\text{CBr}_2$ , and is converted by hydrogen bromide in glacial acetic acid solution into 1:2:3-tribromo-1-methylindene,  $\text{C}_6\text{H}_4\langle\text{CMeBr}\text{CBr}\rangle\text{CBr}$ , pale yellow prisms, m. p. 78°; the acetyl derivative crystallises in lustrous, white needles, m. p. 82°.

2-Iodo-3-benzylamino-1-indone,  $\text{CO}\langle\text{C}_6\text{H}_4\text{Cl}\rangle\text{C}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$ , prepared either by heating 3-bromo-2-iodo-1-indone with benzylamine in alcoholic solution or from potassium iodide and 2-bromo-3-benzylamino-1-indone (Schlossberg, *Abstr.*, 1900, i, 665), crystallises in long, red needles, m. p. 138° (decomp.). The action of ethylamine and aniline on 3-bromo-2-iodo-1-indone yields orange-red compounds of a similar constitution.

Attempts to prepare 2-bromo-3-benzylamino-1-indone by brominating 3-benzylamino-1-indone (Schlossberg, *loc. cit.*) resulted in the removal of the benzylamino-group and the formation of a dibromo-1-indone,  $\text{C}_6\text{H}_3\text{Br}\langle\text{CO}\rangle\text{CH}$ , which crystallises in reddish-brown needles, m. p. 177°, and contains one of the bromine atoms in the benzene nucleus.

3-Bromo-2-iodo-1-indoneoxime,  $\text{C}_9\text{H}_5\text{ONBrI}$ , exists in two stereoisomeric forms, one crystallising in yellow needles, m. p. 206°, the

other in yellow, quadratic plates, m. p. 195—197°; the *p*-nitrophenyl-hydrazone forms brownish-red, microscopic needles, m. p. 212—214°.

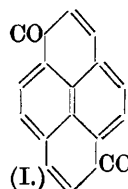
On treatment with bromine, 3-bromo-2-iodo-1-indone is converted into 2:2:3:3-tetrabromohydrindene (Roser and Haselhoff, *loc. cit.*); with magnesium methyl iodide it forms 3-bromo-2-iodo-1-methyl-1-indenol,  $C_6H_4 \begin{array}{c} \text{CBr} \\ \diagup \quad \diagdown \\ \text{CMe}(\text{OH}) \end{array} \text{Cl}$ , which crystallises in almost white leaflets, m. p. 137°.

2:3-Dibromo-1-ethyl-1-indenol,  $C_{11}H_{10}OBr_2$ , prepared from magnesium ethyl bromide and 2:3-dibromo-1-indone, crystallises in colourless prisms, belonging to the rhombic system, m. p. 77—78°, and yields an *acetyl* derivative, m. p. 91°.

2:3-Dibromo-1-phenyl-1-indenol could not be obtained in a pure condition, and was therefore characterised by means of its *acetyl* derivative,  $C_{17}H_{12}O_2Br_2$ , which forms pale grey, prismatic needles, m. p. 138—140°.

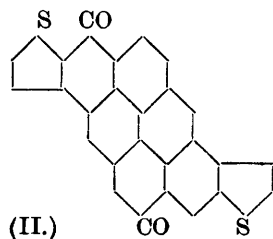
F. B.

**Catalytic Elimination of Hydrogen from Aromatic Nuclei and the Synthesis of Condensed Systems by means of Aluminium Chloride.** ROLAND SCHOLL and CHRISTIAN SEER (*Monatsh.*, 1912, 33, 1—8).—When aromatic compounds are heated with anhydrous aluminium chloride at from 80° to 140°, hydrogen is eliminated and a new ring formed. Previous examples of this are the conversion of naphthalene and  $\alpha$ -dinaphthyl into perylene (Scholl, Seer, and Weitzenböck, *Abstr.*, 1910, i, 616), and the conversion of *meso*-benzodianthrone into *meso*-naphthadianthrone (Scholl and Mansfeld, *Abstr.*, 1910, i, 494). The method has been extended to the following cases.



Phenyl  $\alpha$ -naphthyl ketone is converted at 140° into benzanthrone. Similarly, 6:7-phthaloylbenzanthrone is obtained from 2-anthraquinonyl  $\alpha$ -naphthyl ketone.

Dibenzoylpyrene is converted into pyranthrone, a synthesis which proves the benzoyl groups to occupy positions 3 and 8 in pyrene. Presumably oxidising agents act at these positions, so that pyrenequinone is 3:8-diketopyrene (formula I) and not 3:10-diketopyrene, as supposed by Bamberger and Philip (*Abstr.*, 1887, 496) and by Goldschmiedt (*Abstr.*, 1907, i, 310).



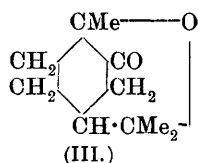
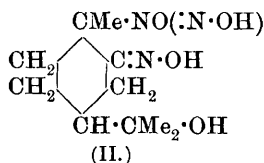
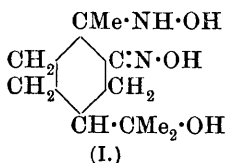
Dibenzpyranthrones are obtained on heating di- $\alpha$ - or di- $\beta$ -naphthoylpyrenes. These dyes give in blue vats much redder shades than pyranthrone.

4:4'-Dibenzoyl-1:1'-dinaphthyl when heated at 95—100° with aluminium chloride yields violanthrone.

Heterocyclic rings are condensed in similar manner; thus from 3:8-di- $\alpha$ -thenoylpyrene, a thiophen analogue of pyranthrone (formula II) is obtained; this is a brownish-red product, which behaves like the vat dyes of the anthraquinone series. Benzil is converted into phenanthraquinone below 100°.

E. F. A.

**Synthesis of a Ketone Derived from Cineole.** GUIDO CUSMANO and ARRIGO LINARI (*Gazzetta*, 1912, 42, i, 1—10).—The action of hydroxylamine on  $\alpha$ -terpineol nitrosochloride yields the hydroxylamine-oxime (I). From this by means of nitrous acid, the *o*-isonitroamine-oxime (II) is obtained. The *o*-isonitroamineoxime when heated with water yields an oxime,  $C_{10}H_{17}O_2N$ , which when oxidised or treated with ethyl nitrite and subsequently with ammonia gives a ketone,  $C_{10}H_{16}O_2$ , of the constitution indicated in formula (III).



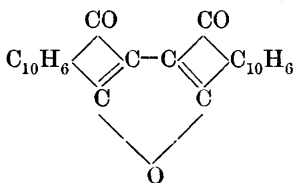
$\alpha$ -Terpineol-*o*-hydroxylamineoxime,  $C_{10}H_{20}O_3N_2$ , is prepared in the same way as the other hydroxylamineoximes previously described (compare Cusmano, Abstr., 1910, i, 685, 863). It forms tufts of colourless, acicular crystals, m. p.  $183^\circ$  (decomp.). It condenses with *p*-nitrobenzaldehyde, yielding a yellow, crystalline compound, m. p.  $183^\circ$ . When treated with dilute hydrochloric acid and sodium nitrite in the cold, it yields the *o*-isonitroamineoxime,  $C_{10}H_{19}O_4N_3$ , which forms colourless, prismatic crystals, which decompose at  $156\text{--}157^\circ$ . The substance yields a blood-red coloration with ferric chloride, and gives Liebermann's reaction. It dissolves in alkali carbonates, and forms crystalline *brucine* salts. When it is treated with an aqueous solution of an alkali hydroxide, nitrous oxide is evolved, and hydroxydihydrocarvoneoxime is formed quantitatively. When the isonitroamineoxime is heated with water alone, however, two other oximes are produced. One has the composition  $C_{10}H_{19}O_3N, H_2O$ , and m. p.  $95^\circ$ , the other has the composition  $C_{10}H_{17}O_2N$ , and m. p.  $139\text{--}140^\circ$ . In the presence of small quantities of mineral acids the isonitroamineoxime decomposes, yielding the oxime of m. p.  $139\text{--}140^\circ$ , hydroxydihydrocarvone, and the methyl ketone of homoterpenylic acid.

The oxime,  $C_{10}H_{17}O_2N$ , when treated with hydrobromic acid at the ordinary temperature yields the methyl ketone of homoterpenylic acid. Hydrochloric acid gives the *hydrochloride*,  $C_{10}H_{17}O_2N, HCl$ , and a product, which is decomposed by water with the formation of ammonium chloride and the methyl ketone of homoterpenylic acid. When the oxime,  $C_{10}H_{17}O_2N$ , is dissolved in ethyl nitrite, a *pernitrosyl* derivative,  $C_{10}H_{16}O_3N_2$ , is obtained; it forms large crystals, m. p.  $68\text{--}70^\circ$ . The ketone,  $C_{10}H_{16}O_2$ , is produced in small quantity by oxidising the oxime,  $C_{10}H_{17}O_2N$ , with acid permanganate, but is best prepared by decomposing the pernitrosyl derivative with concentrated ammonia. It crystallises in shining, colourless leaflets, and has a slight odour reminiscent of cineol. Its *semicarbazone*,  $C_{10}H_{19}O_2N_3$ , has m. p. about  $220^\circ$ . When oxidised with acid permanganate (1%), the ketone yields the methyl ketone of homoterpenylic acid almost quantitatively. Alkaline permanganate attacks it much less readily, the products being the above methyl ketone and cineolic acid.

R. V. S.

**Hydroxyketoperinaphthindene** (*peri* - Naphthindandione).

GIORGIO ERRERA and A. CUFFARO (*Gazzetta*, 1911, 41, ii, 807—814. Compare Errera, Abstr., 1911, i, 465).—Since the substance previously described under the name of *peri*-naphthindandione always behaves as a keto-enol containing the grouping  $\text{—CO}\cdot\text{CH}\cdot\text{C(OH)—}$ , and since no derivative of the corresponding diketonic form is known, and, moreover, the free substance contains an hydroxyl group, the authors propose to substitute for their original name that of hydroxyketoperinaphthindene. When the substance is oxidised with potassium dichromate and acetic acid (allowing one atom of oxygen per molecule), *anhydrobishydroxyketoperinaphthindene* (annexed formula) is obtained; it crystallises in

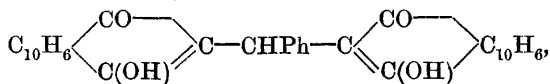


yellowish-brown needles, which, on heating, blacken at  $360^\circ$  and melt with decomposition at a higher temperature. The oxidation of hydroxyketoperinaphthindene by means of alkaline permanganate proceeds quite differently. Even when less than the theoretical quantity of permanganate is taken, a vigorous reaction occurs, and the following substances are

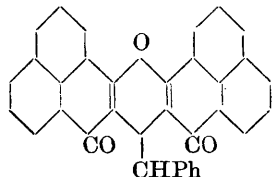
obtained: (1) unaltered hydroxyketoperinaphthindene; (2) naphthalic acid, and (3) a substance,  $\text{C}_{13}\text{H}_8\text{O}_5$ , which crystallises in tufts of very small, colourless needles, m. p. about  $225^\circ$  (decomp.). To this substance is assigned the constitution  $\text{CO}_2\text{H}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}\cdot\text{CO}_2\text{H}$ , and it is termed *naphthalonic acid*.

It is decomposed by heat in the same manner as is phthalonic acid (compare Graebe and Trümpy, Abstr., 1898, i, 318), naphthalic anhydride being formed, and also a substance,  $\text{C}_{24}\text{H}_{14}\text{O}_5$ , which is to be regarded as the *anhydride* of *naphthalaldehyde acid*; it has m. p.  $310\text{—}313^\circ$  (rapid heating), and is identical with a product obtained by Graebe and Gfeller (Abstr., 1893, i, 656).

When hydroxyketoperinaphthindene is boiled with benzaldehyde in alcoholic solution in presence of a trace of pyridine, *dihydroxyketoperinaphthindenilphenylmethane*,



is obtained; it is a golden-yellow, crystalline powder (from alcohol), or forms red crystals (from xylene), m. p.  $295\text{—}297^\circ$  (decomp.). The substance can give metallic derivatives, but both the sodium and potassium salts are very sparingly soluble in water. The *mono-sodium* salt,  $\text{C}_{23}\text{H}_{19}\text{O}_4\text{Na}$ , is a yellow, crystalline substance.



When dihydroxyketoperinaphthindenilphenylmethane is boiled with an alcoholic solution of sulphuric acid, a substance is precipitated to which the constitution of *phenyldiketoperinaphthindenexanthene* (annexed formula) is ascribed; it crystallises in yellow needles, melts with decomposition at

some temperature above  $365^{\circ}$ , and does not contain ethoxy-groups or form salts.

R. V. S.

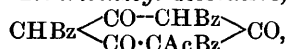
**Transformation of a Phloroglucinol Derivative into One of cycloHexantrione.** II. GUSTAV HELLER (*Ber.*, 1912, 45, 418—427. Compare Abstr., 1909, i, 656).—The author gives a summary of reactions in which the ester of a phenol has been observed to suffer rearrangement into a hydroxy-ketone, and indicates that in the preparation of hydroxy-ketones by the condensation of acyl chlorides with phenols, the phenolic esters must be intermediate products.

In extension of the previous investigation (*loc. cit.*), it is observed that tribromophloroglucinyl triacetate, trichlorophloroglucinyl triacetate, and 1:3:5-triacetyltri-aminobenzene when heated with zinc chloride show no sign of molecular rearrangement.

[With GEORG KRETZSCHMAR.]—*Phloroglucinol diacetate*, m. p.  $104^{\circ}$ , is obtainable by the action of phloroglucinol with sodium acetate and the theoretical quantity of acetic anhydride.

Triacetyl*cyclohexantrione* is so resistant to complete hydrolysis that this does not occur without rearrangement. If it is dissolved in dilute sodium hydroxide solution, slow hydrolysis occurs; the precipitate obtained on acidifying is treated with boiling water, when the undissolved residue consists of *diacetylcyclohexantrione*; this crystallises from benzene in needles, m. p.  $168^{\circ}$ . This substance is also obtained as a by-product in the transformation of phloroglucinyl triacetate into the triacetyl*cyclohexantrione*. *Tribenzoyldiacetylcyclohexantrione*,  $\text{CAcBz} \begin{smallmatrix} \text{CO-CHBz} \\ \text{CO-CAcBz} \end{smallmatrix} \text{CO}$ , obtained by benzylation, crystallises in needles, m. p.  $137-138^{\circ}$ ; it dissolves slowly in sodium hydroxide solution, but gives no coloration with ferric chloride. The action of a diazonium solution yields *benzeneazodiacetylcyclohexantrione*,  $\text{CHAc} \begin{smallmatrix} \text{CO-CHAc} \\ \text{CO-CH} \cdot (\text{N}_2\text{Ph}) \end{smallmatrix} \text{CO}$ , orange-coloured needle crystals, m. p.  $209^{\circ}$ . The action of nitrous acid gives *oximinodiacetylcyclohexantrione*,  $\text{CHAc} \begin{smallmatrix} \text{CO-CHAc} \\ \text{CO-C} \cdot (\text{NOH}) \end{smallmatrix} \text{CO}$ , golden leaflets, m. p.  $149^{\circ}$ , which by reduction gives a colourless substance, decomposing at  $200^{\circ}$ .

The hot aqueous filtrate from the diacetyl*cyclohexantrione* (above) on cooling deposits *monoacetylcyclohexantrione*; this gives pale rose-coloured crystals of a *monohydrate*, but when anhydrous it is colourless, m. p.  $209-210^{\circ}$ . Its *tribenzoyl* derivative,



forms colourless needles, m. p.  $116-117^{\circ}$ ; it reacts with a diazonium solution, forming a *bis-azo*-compound,  $\text{N}_2\text{Ph} \cdot \text{CH} \begin{smallmatrix} \text{CO-CHAc} \\ \text{CO-CH}(\text{N}_2\text{Ph}) \end{smallmatrix} \text{CO}$ , purple needles, m. p.  $241-242^{\circ}$  (decomp.). With nitrous acid a *bis-oximino*-compound is obtained, which decomposes at  $115-120^{\circ}$ .

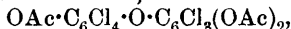
Di- and mono-acetyl*cyclohexantrione* resemble the triacetyl compound in dissolving in sodium hydroxide solution, giving a coloration

with ferric chloride, and in forming copper salts; the acid character is more marked the fewer the acetyl groups present. All three substances react with benzaldehyde in alkaline alcoholic solution, producing yellow, amorphous substances. Towards phenylhydrazine and hydroxylamine they are inert, whilst bromine attacks them all, the monoacetyl compound most readily.

D. F. T.

**Certain Derivatives of Tetrachloro-*o*-benzoquinone.** C. LORING JACKSON and GEORGE LESLIE KELLEY (*Amer. Chem. J.*, 1912, 47, 197—221).—A continuation has been made of the study of three substances prepared from tetrachloro-*o*-benzoquinone (Jackson and MacLaurin, *Abstr.*, 1907, i, 856).

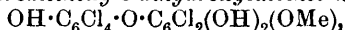
The compound, m. p. 215°, obtained by the action of benzyl alcohol on tetrachloro-*o*-benzoquinone, has proved to be the heptachloro-*o*-quinocatechol hemiether described by Jackson and Carleton (*Abstr.*, 1908, i, 428). This was confirmed by analyses of its acetyl derivative, m. p. 195°, its reduction product (heptachlorodihydroxycatechol hemiether), m. p. about 188—190°, and the *triacetyl* derivative,



m. p. 144°, which forms white, hexagonal prisms.

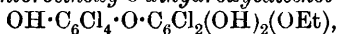
The other two compounds investigated were those, m. p. 198° and 210°, which were respectively obtained by the action of methyl and ethyl alcohol on tetrachloro-*o*-benzoquinone. They can also be prepared by the action of the alcohols on heptachloro- or hexachloro-*o*-quinocatechol hemiether.

The methyl compound was originally regarded as hexachloro-*o*-benzoquinomethylhemiacetalcatechol ether,  $\text{C}_6\text{Cl}_4\text{O}_2 \cdot \text{C}_6\text{Cl}_2\text{O}(\text{OH})(\text{OMe})$ , on account of its being produced by the action of methyl alcohol on the ether,  $\text{C}_6\text{Cl}_4\text{O}_2 \cdot \text{C}_6\text{Cl}_2\text{O}_2$ , but has now been found to be *hexachloromethoxy-*o*-quinocatechol hemiether*,  $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{O} \cdot \text{C}_6\text{Cl}_2\text{O}_2(\text{OMe})$ . On reducing the compound with zinc dust and sulphurous acid, it was converted into *hexachloromethoxy-*o*-dihydroxycatechol hemiether*,



m. p. 191°, which crystallises in long, colourless needles, and yields a *triacetyl* derivative, m. p. 128—129°, and a *monoacetyl* derivative, m. p. 186—188°. In the course of preparing these acetyl compounds another compound was obtained, m. p. 122°.

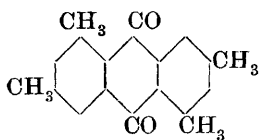
The compound, m. p. 210°, obtained by the action of ethyl alcohol on tetrachloro-*o*-benzoquinone, has been found to be *hexachloroethoxy-*o*-quinocatechol hemiether*,  $\text{OH} \cdot \text{C}_6\text{Cl}_4 \cdot \text{O} \cdot \text{C}_6\text{Cl}_2\text{O}_2(\text{OEt})$ ; its *acetyl* derivative has m. p. 195°. On reducing the compound with sulphurous acid, it is converted into *hexachloroethoxy-*o*-dihydroxycatechol hemiether*,



m. p. 173°, which forms white needles, and yields a *triacetyl* derivative, m. p. 165°. If, however, the reduction is effected by zinc and acetic acid, a *compound*, m. p. 249°, is produced, and readily undergoes decomposition with formation of hexachloro-*o*-dihydroxycatechol ether, which furnishes an *acetyl* derivative,  $\text{C}_6\text{Cl}_4\text{O}_2 \cdot \text{C}_6\text{Cl}_2(\text{OAc})(\text{OH})$ , m. p. 251°, as well as the diacetyl derivative described previously.

E. G.

**Method of Formation of Alkylated Anthraquinones from Alkylated Benzoyl Chlorides and Aluminium Chloride. II.** CHRISTIAN SEER [with EGON EHRENZWEIG] (*Monatsh.*, 1912, 33, 33—34. Compare Abstr., 1911, i, 386).—Mesitylenyl chloride,  $C_6H_3Me_3 \cdot COCl$ , reacts when heated with aluminium chloride at  $115-120^\circ$  to give 1:3:5:7-tetramethylantraquinone. The compound so obtained differs from all other anthraquinone derivatives in that it is not reduced by alkaline sodium hyposulphite or by zinc dust and sodium hydroxide. It is not attacked by acetyl or benzoyl chloride or by phosphorus pentachloride, and when distilled with zinc dust, tetramethylantracene is obtained.



The structure is confirmed by the synthesis from *m*-xylyl mesityl ketone, which was heated for some days, the tetramethylantracene formed separated by distillation, and oxidised with acetic and chromic acids to the quinone.

1:3:5:7-Tetramethylantraquinone is not identical with the substance obtained by Dewar and Jones (*Trans.*, 1904, 85, 212) by the action of nickel carbonyl on *m*-xylene, to which they ascribe the same constitution. It is, however, the same as the oxidation product of the tetramethylantracene obtained by Friedel and Crafts (*Abstr.*, 1887, 1102) from the reaction of methylene chloride and *m*-xylene in presence of aluminium chloride. It is now found that a little of the isomeride described by Dewar and Jones is produced at the same time; the constitution of 1:3:6:8-tetramethylantraquinone is ascribed to this.

1:3:5:7-Tetramethylantraquinone forms yellow needles, m. p.  $235^\circ$ ; it dissolves in concentrated sulphuric acid with a dark red coloration. The corresponding 1:3:5:7-tetramethylantracene forms yellowish-white platelets, m. p.  $155-157^\circ$ , or when purified by regeneration from the picrate, m. p.  $163-164^\circ$ . The *picrate* has m. p.  $189-190^\circ$ .

Anthraquinone-1:3:5:7-tetracarboxylic acid and its salts were obtained amorphous, m. p. above  $300^\circ$ .

4:8-Dinitro-1:3:5:7-tetramethylantraquinone, prepared by the action of potassium nitrate and concentrated sulphuric acid on the quinone, separates in greyish-brown needles, m. p.  $296^\circ$ . 2:4:6:8-Tetranitro-1:3:5:7-tetramethylantraquinone crystallises in yellow, microscopic plates. E. F. A.

**Action of Ammonia on Chrysophanic Acid Methyl Ether.** OTTO A. OESTERLE (*J. pr. Chem.*, 1912, [ii], 85, 230—232. Compare Abstr., 1910, i, 860).—It is pointed out that Fischer and Gross (*Abstr.*, 1911, i, 886) have erroneously attributed to the author the view that the action of ammonia on chrysophanic acid monomethyl ether leads to the replacement of the hydroxyl by an amino-group. The product of the action crystallises in long, glistening, brownish-red needles, m. p.  $237-239^\circ$ , and has the constitution of a 1-hydroxy-8-methoxymethylantraquinoneimide. F. B.

**Commercial Chrysarobin.** OSWALD HESSE (*Annalen*, 1912, 388, 65—96. Compare Tutin and Clewer, *Trans.*, 1912, 101, 290).—Commercial chrysarobin is demethylated by hydriodic acid, D 1·7, at 120—125°, or by equal volumes of hydrochloric acid, D 1·19, and glacial acetic acid at 130—140°, and the dried product is boiled with petroleum (which extracts a portion of the chrysophanol) and then with chloroform, in which chrysophanol is much more soluble than emodinol.

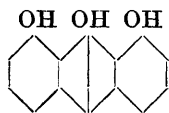
*Chrysophanol*,  $C_{15}H_{12}O_3$  (previously called chrysarobin by the author and by Jowett and Potter, *Trans.*, 1902, 81, 1575), has m. p. 204° (not 205—210°, as stated previously). The presence of a small amount of the methyl ether lowers the m. p. by 6—8°, and of emodinol raises it by about the same amount (compare Fischer, Falco, and Gross, *Abstr.*, 1911, i, 886). It is insoluble in alkali hydroxides or carbonates in the absence of air. By the admission of air, chrysophanol dissolves with the formation of chrysophanic acid; the latter is also formed by oxidising the anthranol with chromic and acetic acids at 60—70°. When heated with acetic anhydride at 90—100° for four hours, with occasional boiling for periods of ten minutes, chrysophanol yields a *triacetate*, m. p. 238—240° (Jowett and Potter's diacetate, *loc. cit.*), which is converted into diacetylchrysophanic acid, m. p. 208° (Liebermann and Seidler's "acetylchrysarobin") by acetic and chromic acids at 60—70°. Triacetylchrysophanol, like diacetylchrysophanic acid, yields diacetylrhein by oxidation with chromic acid in a hot solution of equal volumes of acetic acid and acetic anhydride (compare Fischer, Falco, and Gross, *loc. cit.*). *Hexa-acetyldichrysophanol*, m. p. 125°, is a by-product of the acetylation of chrysophanol.

Emodinol,  $C_{15}H_{12}O_4$ , isolated as described above, has m. p. 230—240° (decomp.), and yields *acetylemodinol*,  $C_{15}H_{11}O_4Ac$ , m. p. 199°, yellow leaflets, by heating with acetic anhydride at 90—100° for two hours. Emodinol and acetylemodinol yield emodin and acetylemodin respectively by oxidation with chromic and acetic acids. The acetylation of emodinol by acetic anhydride and sodium acetate at 90—100° for two hours yields *tetra-acetylemodinol*,  $C_{15}H_8O_4Ac_4$ , m. p. 197°, yellow prisms, *octa-acetyldiemodinol*,  $C_{30}H_{16}O_8Ac_8$ , m. p. 125°, yellow powder, being formed as a by-product. The tetra-acetate is oxidised by chromic (calculated quantity) and acetic acids at 50—60° to triacetylemodin, which is converted into triacetylemodic acid by chromic acid, acetic acid, and acetic anhydride at 60—70°. Octa-acetyldiemodinol is converted into triacetylemodin by chromic and acetic acids at 60—70°.

*Chrysarobol*,  $C_{15}H_{12}O_4$ , m. p. 250—252°, almost colourless needles, is obtained from the portion of commercial chrysarobin which is insoluble in ethyl acetate at 55°. It is unattacked by boiling, concentrated nitric acid, does not yield methyl iodide with hydriodic acid, dissolves in aqueous potassium hydroxide with a yellow colour, and in concentrated sulphuric acid with a purple-red colour changing to reddish-brown. It is insoluble in alcohol, and therefore does not develop a coloration with alcoholic ferric chloride. It yields  $\beta$ -methylantracene by reduction with zinc dust. It is converted into *acetylchrysarobol*,  $C_{15}H_{11}O_4Ac$ , m. p. about 245°, yellow needles, by hot acetic anhydride, and into *tetra-acetylchrysarobol*,  $C_{15}H_8O_4Ac_4$ , m. p. about 190°, greenish-yellow flocks, by acetic anhydride and

sodium acetate at 90—100°. The tetra-acetate is oxidised by chromic and acetic acids at 50° to a red, amorphous substance, which does not yield emodin by hydrolysis. The substance, which crystallises from the ethyl acetate extracts of commercial chrysarobin (obtained in the isolation of chrysarobol), consists essentially of emodinol methyl ether.

It is seen from the preceding that commercial chrysarobin contains chrysophanol and its methyl ether, emodinol and its methyl ether, and chrysarobol. Of these, only the first and the last can be isolated directly and pure. These results are confirmed by the direct oxidation of chrysarobin, with and without previous acetylation or demethylation. By direct oxidation, by oxygen in alkaline solution, or by chromic and acetic acids, chrysarobin yields chrysophanic acid and emodin and their methyl ethers. When acetylated and subsequently oxidised by chromic acid, chrysarobin yields diacetylchrysophanic acid, diacetylemodin methyl ether, acetylchrysophanic acid methyl ether, and a small quantity of a substance, m. p. 202°, orange-yellow needles, which Me is probably *chrysarobic acid*.



The paper closes with a discussion of the constitutions of some of the preceding anthranols. Chrysophanol has probably the annexed formula, not that previously given (compare Oesterle, Abstr., 1911, i, 887). C. S.

**Derivatives of Menthone.** EYVIND BÖDTKER (*Compt. rend* 1912, 154, 437—439. Compare Abstr., 1907, i, 857).—The constitution previously ascribed to the compounds obtained by acting on benzylidenementhone with magnesium alkyl bromides is confirmed by an examination of their oxidation products.

When benzylidenementhone is treated with magnesium methyl iodide and benzoyl chloride added before the addition of water, *phenylmenthylmethylmethane benzoate*,  $C_8H_{16} \begin{smallmatrix} \diagup C \cdot CHMePh \\ | \\ C \cdot OBz \end{smallmatrix}$ , is formed, having m. p. 152—153°,  $[\alpha]_D^{20.5} 145^\circ 40'$ ; on hydrolysis it yields *phenylmenthylmethylmethane*,  $C_8H_{16} \begin{smallmatrix} \diagup CH \cdot CHPhMe \\ | \\ CO \end{smallmatrix}$ , m. p. 111—112°,  $[\alpha]_D^{19} + 95^\circ 16'$ . *Phenylmenthylisoamylmethane*,  $C_{21}H_{32}O$ , is a viscous liquid, b. p. 215°/15 mm.,  $[\alpha]_D^{20.5} + 13^\circ 45'$ ,  $n_D^{20.2} 1.50568$ ; the *benzoate* has m. p. 93—94°,  $[\alpha]_D^{19.5} + 186^\circ 29'$ . *Benzoylmenthone*,  $C_{17}H_{22}O_2$ , was obtained as a yellow liquid by treating a toluene solution of menthone successively with sodamide and benzoyl chloride; it has b. p. 185°/12 mm.,  $[\alpha]_D^{20.5} + 32^\circ 11'$ ,  $n_D 1.51745$ .

The rotations given are for benzene solutions.

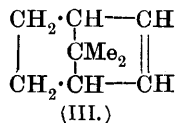
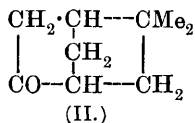
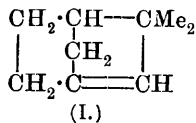
W. O. W.

**The Camphenilone Group. II. *iso*Camphenilone and Constitution of Camphenilene and of *apo*Bornylene.** S. V. HINTIKKA and GUSTAV KOMPPA (*Annalen*, 1912, 387, 293—316. Compare Abstr., 1909, i, 500).—The generally accepted view that camphenilone and fenchone are homologous is further strengthened by the conversion of the former into *isocamphenilone* through the following

series of compounds, the change being quite analogous to that whereby fenchone has been converted into *isofenchone*.

Camphenilone, the preparation of which from camphene by a very simple process is described, is reduced to camphenilol, a camphenilone pinacone, m. p. 146°, being obtained as a by-product. Camphenilol, which forms a *benzoate*,  $C_9H_{15}\cdot OBz$ , b. p. 172°/15 mm., is converted into camphenilene by phosphoric oxide at 140—150°. Camphenilene has also been prepared by converting camphenilol into camphenilyl chloride and heating this with aniline at 175—180°, with diethylaniline at 180—185°, with alcoholic potassium hydroxide, or, most frequently, by direct distillation with aniline after the mixture has been boiled under reflux for five hours. The hydrocarbon obtained by these processes has b. p. 140—141°,  $D_4^{20}$  0.8693,  $n_D^{20}$  1.46848,  $n_D^{20}$  1.47850,  $n_D^{20}$  1.47425, and  $n_a^{20}$  1.46507. Camphenilene forms a *hydrochloride*,  $C_9H_{15}Cl$ , m. p. 60—61°, needles or plates (which is probably identical with camphenilyl chloride, since mixtures of the two substances show no depression of the m. p.), and a *nitrosite*,  $C_9H_{14}O_3N_2$ , m. p. 122° (decomp.), bluish-green prisms, and is converted by the Bertram-Walbaum mixture of acetic and sulphuric acids at 50—55° into an *acetate*,  $C_9H_{15}\cdot OAc$ , b. p. 195°, the hydrolysis of which by alcoholic potassium hydroxide yields *isocamphenilol*,  $C_9H_{15}\cdot OH$ , b. p. 196°, m. p. 78°. This alcohol forms a *benzoate*, m. p. 79°, *phenyl-carbamate*, m. p. 65°, and *hydrogen phthalate*, m. p. 118—119°, and is oxidised by potassium dichromate and dilute sulphuric acid to *isocamphenilone*,  $C_9H_{14}O$ , m. p. 55—57°, large, white plates (*semicarbazone*, m. p. 225—226°, clusters of short, monoclinic prisms).

Camphenilene in glacial acetic acid yields with 17% ozone an *ozonide*, by the distillation of which in a vacuum is obtained a *keto-aldehyde*,  $C_9H_{14}O_2$ , b. p. 123—125°/15 mm.,  $D_4^{22}$  1.0325,  $n_D^{22}$  1.46571,  $n_D^{23}$  1.46867,  $n_D^{23}$  1.47969, which reduces Fehling's and ammoniacal silver solutions, forms a *disemicarbazone*, m. p. 205—206°, and by further oxidation with ozone yields a *keto-acid*,  $C_7H_{12}(CO)\cdot CO_2H$ . These results prove that camphenilene must have the constitution (I), assuming that Wagner's camphenilone formula is correct. Moreover, it follows that *isocamphenilone* probably has the constitution (II).

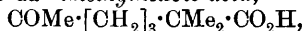


Finally, since *apobornylene*, which is also derived from camphenilone, yields by ozonisation an *ozonide* by the decomposition of which is obtained a di-aldehyde which oxidises to *apocamphoric acid* in the air, it follows that *apobornylene* has the constitution (III); the formation of a substance of this constitution from camphenilone (Wagner's formula) is readily explicable. C. S.

**Rotatory Power of Camphor in Carbon Tetrachloride Solution.** A. FAUCON (*Compt. rend.*, 1912, 154, 652—655).—The specific rotatory power of camphor in solutions of carbon tetrachloride of different concentrations is given, together with empirical formulæ

expressing the connexion between rotation and concentration. For solutions containing 25—55 grams per 100 c.c. of solvent,  $[\alpha]_D^{15} = 43.56^\circ + 0.1148c$ . The variation in rotatory power with temperature depends on concentration, especially when this is high. The increase for a rise of  $1^\circ$  is greater at  $12^\circ$  than at  $40^\circ$ . W. O. W.

**The Principal Constituents of Labdanum Oil. Ketonic Compounds.** HENRI MASSON (*Compt. rend.*, 1912, 154, 517—519).—Gum labdanum from *Cistus creticus* or *C. ladaniferus* gave 0.7—0.9% of a yellow oil when distilled in steam. The oil had b. p.  $50\text{--}185^\circ/15\text{ mm.}$ , and contained alcohols, phenols, esters, terpenes, and ketones. The latter were removed, and on fractionation yielded acetophenone and a fraction, b. p.  $70\text{--}78^\circ/15\text{ mm.}$ , containing 1:1:5-*trimethylcyclohexanone*,  $C_9H_{16}O$ . When regenerated from the *oxime* (m. p.  $106^\circ$ , b. p.  $126\text{--}127^\circ/17\text{ mm.}$ ) this was obtained as a liquid, b. p.  $66\text{--}67^\circ/10\text{ mm.}$ ,  $178\text{--}179^\circ/760\text{ mm.}$ ,  $D_{20} 0.922$ ,  $n_D^{20} 1.4494$ . It does not form a bisulphite compound, but yields a *semicarbazone*, m. p.  $220\text{--}221^\circ$ , and a *monobromo-derivative*, m. p.  $41^\circ$ . Reduction with sodium and alcohol gives 1:1:5-*trimethylcyclohexanol*, m. p.  $51^\circ$ , b. p.  $87^\circ/28\text{ mm.}$  Oxidation with potassium permanganate leads to the formation of  *$\epsilon$ -keto- $\alpha\alpha$ -dimethylhexoic acid*,



b. p.  $190\text{--}191^\circ/31\text{ mm.}$  (*semicarbazone*, m. p.  $164^\circ$ ). The constitution of the acid was established by converting it into  *$\alpha\alpha$ -dimethyladipic acid* by means of sodium hypobromite. W. O. W.

**Bee Resin (Propolis).** KARL DEITERICH (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 315—318. Compare Küstenmacher, *Abstr.*, 1911, ii, 127).—Extraction of propolis with light petroleum removes wax and balsam, and these are separated by means of 70% alcohol. Resin, m. p.  $90\text{--}106^\circ$ , is extracted from the residue by absolute alcohol, and tannin is then extracted from the resin by water. The resin is then extracted with cold absolute alcohol, when an insoluble residue, proporesen, remains. Ether precipitates  $\alpha$ -proporesen from the solution, and the filtrate after evaporation is separated by chloroform into a soluble part, the "pure resin," and an insoluble part,  $\beta$ -proporesen.

Propolis balsam is free from cinnamic acid, but contains vanillin. Proporesen is chemically indifferent, fluoresces in concentrated sulphuric acid, sinters at  $76^\circ$  and has m. p.  $83^\circ$ , and is insoluble in chloral hydrate solution.  $\alpha$ -Proporesin has m. p.  $187^\circ$ , and is not fluorescent in sulphuric acid.  $\beta$ -Proporesin is completely soluble in chloral hydrate solution, fluoresces in sulphuric acid, and yields an alcohol on hydrolysis. The acid sublimes in needles, sinters at  $88\text{--}90^\circ$ , and melts at  $124\text{--}125^\circ$ . The "pure resin" fraction is also fluorescent, and yields an acid and a resinotannol on hydrolysis.

C. H. D.

**Structure of Polymerised Vinyl Bromide and Caoutchouc.** IWAN I. OSTROMISSENSKY (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 204—240).—The author shows that polymerised vinyl bromide (compare Hofmann, *Annalen*, 1860, 115, 271; Baumann, *Annalen*, 1872,

163, 315), to which he gives the name *caouprene bromide*, exists in three modifications possessing identical chemical but different physical properties, and readily convertible one into the others. Caouprene bromide is a simpler homologue of the bromide of natural Para caoutchouc, which contains methyl groups; further, it is either identical with butadiene-caoutchouc bromide (compare Harries, Abstr., 1911, i, 798) or isomeric with it, the isomerism being due to a difference in the distribution of the halogen atoms in the molecule. The compounds obtained by the action of aniline or phenols on these bromides and the hydrocarbon resulting from the removal of hydrogen bromide from them are also discussed.

$\alpha$ -Caouprene bromide is alone formed by the action of sunlight on vinyl bromide, the velocity of the polymerisation being dependent in high degree on the presence of traces of contact substances, which may either retard or accelerate the change; hydrocarbons of low boiling point, such as light petroleum, retard or even arrest completely the reaction. The  $\alpha$ -bromide dissolves readily in carbon disulphide and a number of other solvents, from some of which it may be precipitated in the form of asbestos-like threads, from others in an amorphous state, and from others as a milky emulsion. It resists the action of energetic oxidising agents, concentrated alcoholic potassium hydroxide, and concentrated mineral acids.

$\beta$ - and  $\gamma$ -Caouprene bromides are obtained by the action of the ultraviolet light of a quartz-mercury lamp on vinyl bromide, best in the gaseous state. The  $\beta$ -compound is soluble in carbon disulphide, but the  $\gamma$ -bromide is quite insoluble, and merely swells up in this solvent and forms two layers, the upper one of pure carbon disulphide and the lower, which shows intense violet fluorescence, of the gelatinous bromide retaining a considerable proportion of the solvent.

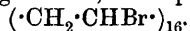
On prolonged heating at  $50^{\circ}$  of the  $\alpha$ -bromide or boiling of its carbon disulphide solution, isomeric change into the  $\beta$ -form takes place. The change  $\alpha \rightarrow \beta \rightarrow \gamma$ -modification is readily brought about by ultraviolet light or by protracted boiling with anhydrous acetic acid. The  $\gamma$ - may be changed completely into the  $\beta$ -bromide by dissolving in boiling chlorobenzene and precipitating with light petroleum.

The compound described by Harries (*loc. cit.*) as butadiene-caoutchouc tetrabromide is also found to exist in three modifications, one of which does not dissolve, but swells, in carbon disulphide, forming a fluorescent jelly. The other two forms are soluble in carbon disulphide, in which one gives a fluorescent and the other a non-fluorescent solution.

The tetrabromide of neutral Para caoutchouc, which is homologous with caouprene bromide, also exists in certain analogous modifications (compare Weber, Abstr., 1900, i, 353). Free Para caoutchouc is likewise obtainable in three forms (Harries, *loc. cit.*), which are probably due to the same cause as the three caouprene bromides and the three butadiene-caoutchouc bromides, since in all three cases the inter-conversions take place under similar conditions. The differences between the three modifications of any one of these compounds are probably due to differences in the physical structures of their mole-

cules, for example, such differences as exist between sodium chloride in the ordinary and colloidal states. In some instances, however, the variation in properties seems to depend on the absence or presence, in the surface layers, of oxidation products.

$\beta$ - and  $\gamma$ -Caouprene bromides give exclusively colloidal solutions, as is shown by the boiling and freezing points of their solutions. Cryoscopic measurements in ethylene dibromide indicate for  $\alpha$ -caouprene bromide the molecular weight 1809, corresponding with



Each of the three caouprene bromides, and also butadiene caoutchouc bromide, react with phenol at  $150^\circ$  (compare Weber, *loc. cit.*), giving a reddish-violet, elastic, amorphous compound,  $(\text{CH}_2\cdot\text{CH}\cdot\text{OPh})_n$ .

When an aniline solution of caouprene bromide is heated, it assumes a cherry-red colour, the quaternary ammonium salt,



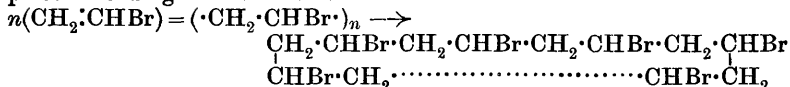
being formed. Rapid cooling of the solution results in the deposition of a spongy mass, to which the name *meta-caouprene bromide* is given:  $(\text{CH}_2\cdot\text{CH})_n(\text{NH}_2\text{Ph})_{n/2}\text{Br}_{n/2} = \text{meta-}(\text{CH}_2\cdot\text{CH})_n\text{Br}_{n/2} + n/2\text{NH}_2\text{Ph}$ . The meta-bromide dissolves readily in carbon disulphide at the ordinary temperature giving an intensely fluorescent, violet solution, and, unlike the normal bromide, dissolves readily in fused phenol with formation of a pale brown solution, from which benzene precipitates a brown powder; normal caouprene bromide gives an intense violet solution with phenol, the compound  $(\text{CH}_2\cdot\text{CH})_n(\text{OPh})_{n/2}$  being formed. The rearrangement of halogen atoms, to which the formation of the meta-bromide is due, is not effected by quinoline, caouprene bromide precipitated from this solvent retaining its original chemical and physical characters.

When a 10% solution of caouprene bromide in aniline is heated for thirty minutes at  $120$ – $130^\circ$  out of contact with air, subsequent precipitation with alcohol or ether yields a new bromo-compound which does not give Weber's reaction with phenol. This compound, which has not yet been obtained pure and is apparently non-homogeneous, dissolves in fused phenol to a pale, reddish-yellow solution not precipitated by benzene; when heated in nitrobenzene it gives up hydrogen bromide.

The removal of hydrogen bromide from caouprene bromide, its *meta*-modification, butadiene-caoutchouc bromide, and the bromide of natural caoutchouc leads to the formation of a hydrocarbon,  $(\text{CH})_n$ , and may be effected in various ways: (1) by prolonged heating with water in sealed tubes at  $150^\circ$ ; (2) by heating solutions of the bromides in various solvents, such as aniline, quinoline, dichloroacetic acid, aromatic nitro-derivatives, etc., best in absence of air; the influence of these organic compounds on the removal of hydrogen bromide from the molecule of the complex bromide depends, not entirely on their power of dissolving the latter or the hydrocarbon formed, but also on their ability to absorb the hydrogen bromide.

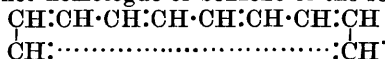
From a consideration of the above results, of the possible compounds obtainable by the polymerisation of vinyl bromide and of the fact that Weber's colour reaction with phenol is given by bromides of the terpene series in which the number of halogen atoms is a multiple of four, the

conclusion is drawn that the formation of caouprene bromide takes place according to the scheme :

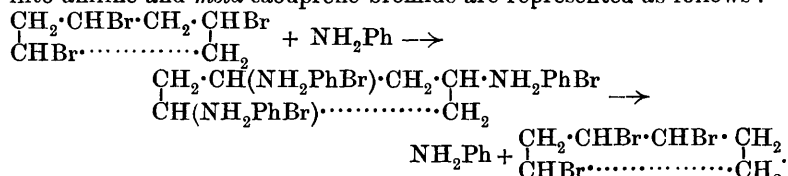


(the dotted line representing an unknown number of  $\text{CH}_2\text{:CHBr}$  groups), the value of  $n$  being not less than 12. The alternate distribution of the bromine atoms is rendered probable by the fact that the autopolymerisation of halogen derivatives of ethylene or acetylene yields exclusively symmetrical trihalogen compounds of benzene ; bromoacetylene, for example, gives 1 : 3 : 5-tribromobenzene.

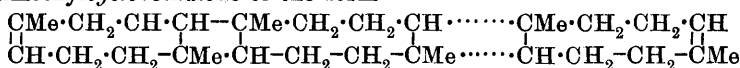
The hydrocarbon, *dehydrocaouprene*, obtained by the removal of hydrogen bromide from caouprene bromide and its isomerides, is regarded as a higher homologue of benzene of the formula :



The action of aniline on caouprene bromide and the subsequent decomposition of the quaternary ammonium compound thus obtained into aniline and *meta*-caouprene bromide are represented as follows :

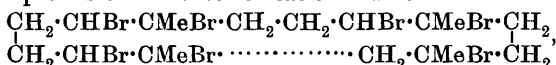


In view of the results of Hinrichsen and Kindscher (Abstr., 1911, ii, 445) and of Pickles (Trans., 1910, 97, 1085), the statement made by Harries that caoutchouc must be regarded as an associated dimethylcyclooctadiene of the form :



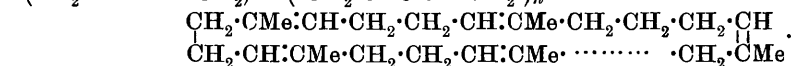
is admissible only on the assumption that, when caoutchouc is brominated, it undergoes preliminary splitting with formation of dimethylcyclooctadiene. The author hence regards this formula as discordant with the facts.

The most probable structure for caoutchouc bromide is :



which is similar to the formula given by Pickles.

The polymerisation of isoprene to caoutchouc is best represented thus :



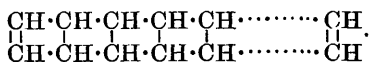
The positions of the double linkings are here fixed, and isomerism is possible only in so far as the positions of the methyl groups are concerned.

The name caoutchouc tetrabromide is irrational, this compound

being at the least a hexabromide of the formula  $C_{15}H_{24}Br_6$ ; for the present it is best termed simply caoutchouc bromide.

The various properties of caouprene bromide, synthetic butadiene-caoutchouc bromide, and natural Para caoutchouc bromide are collected in tabular form.

Willstätter and Waser's results (this vol., i, 17), published after the author's paper was in the press, compel the assumption that dehydro-caouprene is not a higher homologue of benzene, but that it has the following structure, or one similar to it:



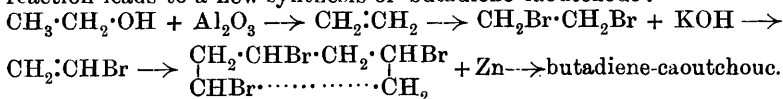
T. H. P.

**Regeneration of Caoutchouc from its Bromide. Synthesis of Butadiene-caoutchouc.** IWAN I. OSTROMISLENSKY (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 240—244. Compare preceding abstract).

—The action of zinc dust on caouprene bromide or butadiene-caoutchouc bromide dissolved in either naphthalene or chlorobenzene yields free caoutchouc, possessing identical chemical and physical properties in the two cases. The action of sodium on these bromides, especially in presence of ether, proceeds to some extent in the same direction, but is complicated by secondary processes, such as the formation of dehydro-caouprene,  $(CH)_n$ . The action of sodium on a 2·3% solution of caouprene bromide in chlorobenzene containing a little ether is accompanied by sudden heating, the solvent boiling vigorously, and the chlorobenzene (which alone is quite inactive towards sodium) as well as the caouprene bromide being acted on by the sodium.

The solution of caouprene bromide or butadiene caoutchouc bromide in naphthalene or chlorobenzene shows a violet-red fluorescence.

As caouprene bromide is readily obtainable from alcohol, the above reaction leads to a new synthesis of butadiene caoutchouc:



T. H. P.

**Sphingosine.** PHÆBUS A. LEVENE and WALTER G. JACOBS (*Proc. Amer. Soc. Biol. Chem.*, 1911, xxix; *J. Biol. Chem.*, 11).—Sphingosine, obtained originally from phrenosin by Thudichum, appears to be an unsaturated amino-alcohol of the olefine series. The substance obtained later by Thierfelder in the filtrate from sphingosine sulphate and described by him as a nameless base is dimethylsphingosine. Full data will be published later.

W. D. H.

**Physcion.** OSWALD HESSE (*Annalen*, 1912, 388, 97—102).—Physcion (parietin) yields emodin by demethylation by concentrated sulphuric acid at 160°. It is demethylated and also reduced by hydriodic acid, D 1·7, yielding a substance (protophyscihydron), m. p. 230—240°, which is shown to be emodinol by its conversion by acetylation into tetra-acetylemodinol, m. p. 198°, which yields

triacetylemodin by oxidation by chromic and acetic acids. The further proof that physcion is emodin methyl ether (compare Oesterle and Johann, Abstr., 1910, i, 860) is given by its methylation, whereby emodin trimethyl ether, m. p. 226°, is obtained. Physcihydron, the product of the reduction of physcion by zinc and acetic acid, is proved to be emodinol methyl ether by its conversion into triacetylemodinol methyl ether.

C. S.

**Duality of Chlorophyll.** C. A. JACOBSON and LEON MARCHLEWSKI (*Bull. Acad. Sci. Cracow*, 1912, A, 28—40; *Amer. Chem. J.*, 1912, 47, 221—231).—Evidence is given to support the contention that the ratio of chlorophyll to allochlorophyll varies with different species of plants, and also with changing conditions of growth of the same species. The actual amount of allochlorophyllan, the nearest acid derivative of allochlorophyll, isolated from a given weight of chlorophyllan from *Acer platanoides* of different years is very different. The absorption bands in the visible spectrum of the chlorophyllans obtained by identical methods from different species differ considerably. The same applies to the chlorophyllan bands in the ultra-violet part of the spectrum. The extinction coefficients, in monochromatic light, of equally concentrated solutions of chlorophyllans from different species vary considerably. The variable ratio between the two constituents of chlorophyll ranges from almost pure allochlorophyll in *Acer negundo* to a product very rich in neochlorophyll in the nettle.

E. F. A.

**Chlorophyll. XIX. Chlorophyllides.** RICHARD WILLSTÄTTER and ARTHUR STOLL (*Annalen*, 1912, 387, 317—386).—The isolation of pure chlorophyll is difficult on account of its solubility, decomposibility, and chemical indifference. So far as the degradation of chlorophyll is concerned, the phytol group is without significance. Hence for working out the early steps of the degradation of chlorophyll, it is convenient to use the substance in the form of the sparingly soluble, crystalline alkylchlorophyllides. Hitherto, no description and analyses of an individual chlorophyll derivative have been given, the crystallised ethylchlorophyllide previously described (Abstr., 1911, i, 659) being a mixture of the *a* and *b* compounds. The authors have now succeeded in separating methylchlorophyllides *a* and *b* from one another, and also in the separation of the chlorophyllides *a* and *b*, the methylphæophorbides *a* and *b*, and the phæophorbides *a* and *b*. The mixture of methylchlorophyllides *a* and *b* has been obtained by the methanolysis of the fresh leaves of the acanthus (*Heracleum spondylium*) by Willstätter and Isler's process (Abstr., 1911, i, 392). The separation of the two components has been effected by the partition method, the *b* compound being much less soluble in ether than the *a* compound. For practical purposes, the two partition liquids consist of 66% aqueous methyl alcohol, and a mixture of ether and petroleum, b. p. 30—50°. The method of procedure varies somewhat, according as the methylchlorophyllide mixture is rich or not in the *b* compound, but in principle the process consists in shaking the ether-petroleum solution of the methylchlorophyllides with successive quantities of 66% methyl

alcohol until the *b* compound, together with some of the *a* compound, has passed into the aqueous alcoholic layer. The ether-petroleum layer is then frequently shaken with water to remove the bulk of the ether, whereby methylchlorophyllide-*a*, which is insoluble in petroleum, is precipitated. The methylchlorophyllide-*b* is isolated from the aqueous alcoholic extracts by a somewhat complicated process, and is finally purified by the fractional precipitation of its ethereal solution by petroleum and talc.

*Methylchlorophyllide - a*,  $C_{32}H_{80}ON_4Mg(CO_2Me)_2 \cdot \frac{1}{2}H_2O$ , crystallises from ether in bluish-green, rhombic leaflets, yields bluish-green solutions with red fluorescence, exhibits the "brown phase" reaction, and is converted, when quite pure, only into phytochlorin-*e* by treatment with methyl-alcoholic potassium hydroxide under definite conditions. *Methylchlorophyllide - b*,  $C_{32}H_{78}O_2N_4Mg(CO_2Me)_2 \cdot \frac{1}{2}H_2O$ , crystallises in olive-green or brown, rhombic plates, and forms in absolute alcohol a greenish-yellow solution with brownish-red fluorescence, is more stable than the *a* compound towards dilute hydrochloric acid, develops in the phase tests initially a red coloration which changes to brownish-red and finally to yellowish-green, and yields phytorhodin-g by proper treatment with methyl-alcoholic potassium hydroxide.

The enzymatic hydrolysis of chlorophyll by chlorophyllase yields a mixture of the free chlorophyllides *a* and *b*; the hydrolysis is effected best by extracting fresh leaves (of *Heracleum* or *Stachys*) with 60—80% aqueous acetone (also the enzymatic hydrolysis of the preceding methylchlorophyllides *a* and *b* in aqueous acetone yields the corresponding free chlorophyllides; the process, however, is more difficult than is the case with crude chlorophyll). The separation of the chlorophyllides *a* and *b* is effected, as in the case of the methyl esters, by the partition method with aqueous methyl alcohol and ether-petroleum. *Chlorophyllide-a*,  $CO_2H \cdot C_{32}H_{80}ON_4Mg \cdot CO_2Me \cdot \frac{1}{2}H_2O$ , crystallises from aqueous ether or acetone in six-sided plates, which are bluish-black by reflected and green to bluish-green by transmitted light. Its solutions are bluish-green with red fluorescence. By treatment with dry ammonia, the substance absorbs  $2NH_3$ , one of which is easily lost, the other only with difficulty. In consequence of its acid nature, chlorophyllide-*a* is extracted from its ethereal solution by *N*/1000-potassium hydroxide. The separation of chlorophyllide from alkyl-chlorophyllides is conveniently effected by leading ammonia into the ethereal solution, whereby the former is precipitated as the ammonium salt. By prolonged warming in a vacuum or by keeping in the solid state or in dilute solution, the chlorophyllide changes to magnesium phæophorbide, which is insoluble in ether. *Chlorophyllide-b*,  $CO_2H \cdot C_{32}H_{78}O_2N_4Mg \cdot CO_2Me$ , crystallises from acetone in yellow to olive-green, six-sided leaflets, forms yellowish-green solutions with brownish-red fluorescence, absorbs  $2NH_3$ , one of which is retained even in a vacuum, and is more strongly acidic than the *a* compound, being extracted from ethereal solution by *N*/2000-potassium hydroxide.

Methylchlorophyllide-*a* is easily and quantitatively converted into methylphæophorbide-*a* by treating its ethereal solution with 10% hydrochloric acid for two minutes; the pure, crystalline methylphæophorbide-*a* is then obtained by concentrating the ethereal

solution. In a similar manner, methylchlorophyllide-*b* is converted into methylphæophorbide *b* by 15% hydrochloric acid. On account of their difference in basicity, mixtures of methylphæophorbides *a* and *b* are separated much more conveniently by hydrochloric acid than by the partition method. The *a* compound is extracted completely from its ethereal solution by 18% hydrochloric acid, whilst the *b* compound requires the use of 23% acid. The ethylphæophorbides *a* and *b* (Abstr., 1911, i, 659) can be separated in a similar manner. Methylphæophorbide-*a*,  $C_{32}H_{32}ON_4(CO_2Me)_2$ , crystallises in rhombic leaflets or twinned prisms, which have a violet-black lustre, appear brownish-yellow or brownish-red under the microscope, and form a dark violet powder. The ester dissolves in formic or hydrochloric acid with a blue colour, and in ether or other indifferent solvents with an olive-green colour, similar to that of phytochlorin-*e*, but differing by exhibiting a red fluorescence. Methylphæophorbide-*a* has acid number 16. When heated slowly it softens at about 150° and has m. p. 210—220° (decomp.); at 220° it still yields mainly phytochlorin-*e* after hydrolysis. Methylphæophorbide-*b*,  $C_{32}H_{30}O_2N_4(CO_2Me)_2$ , forms large, olive-green or brown, rhombic crystals, and yields a reddish-brown, fluorescent solution in ether and a green solution in hydrochloric acid. The ester, which has acid number 21, softens at 200° and begins to decompose at about 250°; after being heated at this temperature it still yields nearly pure phytorhodin-*g* by hydrolysis with potassium hydroxide.

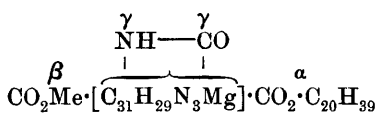
Excluding phytochlorin-*e* and phytorhodin-*g*, the free phæophorbides *a* and *b* are the most easily obtainable chlorophyll derivatives. They can be prepared by three methods: (1) By shaking an ethereal solution of the chlorophyllides *a* and *b* with 16% hydrochloric acid, the magnesium compounds are decomposed and the phæophorbide-*a* passes entirely into the acid solution, the *b* compound remaining in the ethereal layer; (2) an ethereal solution of the methylchlorophyllides *a* and *b* is treated for two hours with 25% hydrochloric acid, whereby the magnesium compounds are decomposed and the carbomethoxy-group *a* is hydrolysed. The mixture of phæophorbides *a* and *b* is then isolated, and is separated as in method (1). The best process is (3), in which phæophytin (phytylphæophorbide *a* and *b*) in ethereal solution is treated with 34—35% hydrochloric acid for three-quarters to one hour. The solution is diluted with water, the phytol removed by ether, and the solution is further diluted with water; the phæophorbides are extracted by an excess of ether, and the ethereal solution is concentrated and treated with 16% hydrochloric acid, whereby phæophorbide *a* is removed.

Phæophorbide-*a*,  $CO_2H \cdot C_{32}H_{32}ON_4 \cdot CO_2Me$ , crystallises in bluish-black, rhombic plates, which appear olive-green or olive-brown under the microscope. The colours of its solutions in different solvents are like those of methylphæophorbide-*a*. The substance absorbs  $2NH_3$ , one of which is lost only in a vacuum. The acid number is 15. Phæophorbide-*a* is extracted from its ethereal solution by *N*/100-ammonia or potassium hydroxide, by 0.1% sodium carbonate, and by 1% sodium hydrogen carbonate or phosphate. Phæophorbide-*b*,  $CO_2H \cdot C_{32}H_{30}O_2N_4 \cdot CO_2Me$ , crystallises from ether in small, rhombic

plates and needles, which appear olive-green or brown under the microscope. The substance absorbs approximately  $2\text{NH}_3$ , which is almost entirely lost at the ordinary pressure. It forms a reddish-brown, fluorescent solution in ether, and a green solution, in hydrochloric acid. Phæophorbide-*b* is more acidic than the *a* compound; its acid number is 19—20, and it is extracted from ethereal solution by 0.2% sodium hydrogen carbonate or by 0.25% disodium hydrogen phosphate. By treatment with methyl-alcoholic potassium hydroxide it gives a "red phase."

The term "allomerism" is employed to denote the changes which the chlorophyllides and the alkylchlorophyllides undergo in alcoholic solution (Abstr., 1911, i, 660). Allomerism in alcoholic solution is catalytically accelerated by the presence of glass, but not of platinum or silver; it is prevented by the presence of a trace of acid. Allomeric changes are to be explained probably by the rupture of the lactam group in the chlorophyll derivative, and the formation of a new lactam group.

The degradation of chlorophyll (for example, chlorophyll-*a*, annexed formula) can now be effected in three ways, in each of



which the reagent attacks the chlorophyll molecule at a different point. (1) By the enzymatic action of chlorophyllase, changes only occur at the  $\alpha$ -group; in methyl or ethyl alcohol the phytol group is replaced by methyl or ethyl, whilst in aqueous acetone it is replaced by hydrogen, this being the only method by which the free chlorophyllides can be obtained. (2) By gentle treatment with acids, the magnesium is replaced by hydrogen and phæophytin is obtained. By more energetic treatment, hydrolysis occurs at the  $\alpha$ -group, and the free phæophorbides are produced; since these still exhibit the "brown phase," the  $\gamma$ -lactam group is still intact. (3) Alkalis first attack the  $\gamma$ -lactam group in the "brown phase"; subsequently a new lactam group is formed. Then follows hydrolysis at the  $\alpha$ -group, and, finally, with difficulty at the  $\beta$ -group. At higher temperatures, alkalis cause an elimination of carbon dioxide, and degradation to di- and mono-basic phyllins and porphyrins ensues. A diagrammatic representation of these changes is given.

The formulæ of the compounds in this paper are to replace those previously recorded (Abstr., 1911, i, 659). C. S.

**Phylloporphyrins.** LEON MARCHLEWSKI (*Annalen*, 1912, 388, 63—65).—Willstätter and Fritzsche (Abstr., 1910, i, 136) state that Schunck and Marchlewski's phylloporphyrin is a mixture of two substances of different basicity. The author, therefore, has heated *allophylloaonin* (Abstr., 1907, i, 866) with 10% alcoholic potassium hydroxide at  $200^\circ$ , whereby only Schunck and Marchlewski's phylloporphyrin together with feebly basic by-products is obtained. Chlorophyllanic acid, however, by the same treatment, yields two markedly basic products, which are separated by 0.25% hydrochloric acid. One of these products, called phylloporphyrin-*a*, is identical

with Schunck and Marchlewski's phylloporphyrin; the other more basic product is called phylloporphyrin- $\beta$ . By treatment with alcoholic potassium hydroxide at 200°, phyllocyanin and *allochlorophyllanic acid* each yield mainly phylloporphyrin- $\beta$ , very little of the  $\alpha$ -compound being produced (compare following abstracts). C. S.

**The Chlorophyll Group. XII.  $\beta$ -Phylloporphyrin.** LEON MARCHLEWSKI and J. ROBEL (*Biochem. Zeitsch.*, 1912, 39, 6—11; *Bull. Acad. Sci. Cracow*, 1912, 4, 41—46).—The authors believe that the so-called pyrroporphyrin of Willstätter and Fritzsche is essentially the phylloporphyrin of Schunck and Marchlewski, which had not been sufficiently purified, in that the former investigators had underestimated the basicity of the less basic product in the mixture. When these porphyrins are prepared from crude chlorophyllanic acid (from maple chlorophyll) by the method described in detail by the authors, two products are formed simultaneously, namely, a strongly basic  $\beta$ -phylloporphyrin, which can be dissolved out from its solution in ether by  $\frac{1}{4}\%$  hydrochloric acid, and the phylloporphyrin of Schunck and Marchlewski. If  $\frac{1}{2}\%$  acid be used instead, appreciable quantities of the last-named porphyrin are also dissolved. A comparison of the spectra of the two substances is given. S. B. S.

**The Chlorophyll Group. XIII. Porphyrins from Phyllocyanin and Phylloxanthin.** LEON MARCHLEWSKI and B. ŻURKOWSKI (*Biochem. Zeitsch.*, 1912, 39, 59—63).—In view of the possibility of separating  $\alpha$ - and  $\beta$ -phylloporphyrins (see Marchlewski and Robel, preceding abstract), investigations were made with the object of finding the parent substance of these two derivatives. The  $\beta$ -derivative is not obtained at all from the phyllotaonin of Schunck and Marchlewski, or from the pure *allophyllotaonin* of Marchlewski and Robel. These yield the  $\alpha$ -substance. On the other hand, phyllocyanin and phylloxanthin, which stand in near relationship to *neochlorophyll* and *allochlorophyll*, yield chiefly the  $\beta$ -derivative. The previously-expressed views on the subject are not correct, owing at the time to the want of a satisfactory method for separating the two porphyrins. The experimental details of the method of preparing the  $\beta$ -substance from phyllocyanin and phylloxanthin are given in full. S. B. S.

**The Red and Blue Pigments of the Algæ.** HARALD KYLIN (*Zeitsch. physiol. Chem.*, 1912, 76, 396—425. Compare Abstr., 1910, i, 866).—The occurrence of phycoerythrin and phycocyanin in a number of varieties of *Florideæ* and *Cyanophyceæ* has been investigated.

In addition to the properties previously given (*loc. cit.*), phycoerythrin crystallises in hexagonal prisms usually without pyramidal faces; these are optically negative. The same modification has been isolated from twenty species of *Florideæ*; from three species, *Polysiphonia Brodiaei*, *P. nigrescens*, and *Rhodomela subfusca*, a modification was obtained which lacked the fluorescent properties. So far, phycoerythrin has only been obtained from the *Florideæ*.

Three modifications of phycocyanin have been identified.

*Bluish-green phycocyanin* shows a remarkable dark carmine-red fluorescence, and has an absorption band in the orange between C and D

with a maximum at  $\lambda = 624\text{--}618$ . It crystallises in hexagonal rhombohedra.

*Blue phycocyanin* also gives a splendid dark carmine-red fluorescence, and has two absorption bands, one in the orange between C and D with a maximum at  $\lambda = 615\text{--}610$ , and the other in the yellow-green between D and E, but nearer to D, with a maximum at  $\lambda = 577\text{--}573$ ; it was not obtained crystalline. This modification is widely distributed amongst the *Cyanophyceae*.

*Bluish-violet phycocyanin* has the same fluorescence, and shows absorption bands in the orange between C and D with a maximum at  $\lambda = 618\text{--}613$ , and in the green between D and E, but nearer E, with the maximum at  $\lambda = 553\text{--}549$ . It crystallises in rhombic plates, which are blue across the shorter diagonal, violet across the longer. This modification occurs in *Ceramium rubrum*.

Phycocyanin is characteristic of the *Cyanophyceae*, but occurs in a few *Florideae*.  
E. F. A.

**Melanin.** ROSS AIKEN GORTNER (*Biochem. Bulletin*, 1911, 1, 207—215. Compare Abstr., 1911, ii, 908).—Melanins are probably formed by the interaction of an oxydase and an oxydisable chromogen. They differ in solubility in dilute acids; those which are soluble contain a protein complex; those which are insoluble are the granules seen in hairs and tissues. Tyrosine, lysine, and arginine are obtained as hydrolytic products from the former class (melano-proteins).

W. D. H.

**Formation of Gallamide from Acetyltannin.** MAXIMILIAN NIERENSTEIN (*Ber.*, 1912, 45, 533—534. Compare Abstr., 1910, i, 487).—The formation of gallamide from acetyltannin by heating with alcoholic ammonia is regarded as doubtful; the former analytical values were calculated incorrectly.  
E. F. A.

**Hydroxyhydrofurans.** GEORGES DUPONT (*Compt. rend.*, 1912, 154, 599—601. Compare Abstr., 1911, i, 554, 804).—Ketohydrofurans are not reduced by zinc and alkalis, by sodium amalgam, or by hydrogen in presence of platinum. Sodium ethoxide at  $120^\circ$ , however, gives red compounds, which on treatment with water yield the corresponding hydroxyhydrofurans, together with viscous, high-boiling liquids.

3-Hydroxy-2:2:5:5-tetramethyltetrahydrofuran, 
$$\begin{array}{c} \text{OH} \cdot \text{CH} \cdot \text{CMe}_2 \\ | \\ \text{CH}_2 \cdot \text{CMe}_2 \end{array} > \text{O},$$

has b. p.  $84^\circ/15$  mm.,  $D^{17}_D$  0.9483,  $n_D$  1.4435; the acetate has b. p.  $181\text{--}182^\circ$ ,  $D^{15}_D$  0.9587,  $n_D$  1.4256, and the acid phthalate, m. p.  $139\text{--}141^\circ$ . 3-Hydroxy-2:5-dimethyl-2:5-diethyltetrahydrofuran has b. p.  $107^\circ/19$  mm.,  $D^{15}_D$  0.9539,  $n_D$  1.4547; the acetate has b. p.  $97\text{--}98^\circ/15$  mm.,  $D^{15}_D$  0.9589,  $n_D$  1.4382.

Ketodimethylhydrofuran reacts with organo-magnesium halides, giving derivatives of hydroxyhydrofurans, whereas the ketotetraalkylhydrofurans react in the enolic form, yielding hydrocarbons. The following compounds have been obtained:

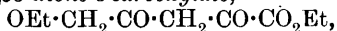
3-Hydroxy-2:3:5-trimethyltetrahydrofuran, b. p.  $71\text{--}73^\circ/16$  mm.,

171—173°/755 mm.,  $D^{21}_D$  0.9719,  $n_D$  1.4420; 3-hydroxy-2:5-dimethyl-3-ethyltetrahydrofuran, b. p. 79—81°/16 mm.,  $D^{21}_D$  0.9693,  $n_D$  1.4485; 3-hydroxy-3-phenyl-2:5-dimethyltetrahydrofuran, b. p. 138—140°/16 mm.,  $D^{20}_D$  1.0827,  $n_D$  1.5310; 3-hydroxy-3-benzyl-2:5-dimethyltetrahydrofuran, b. p. 146—147°/15 mm.,  $D^{15}_D$  1.0598,  $n_D$  1.5251; 3-hydroxy-3-p-tolyl-2:5-dimethyltetrahydrofuran, b. p. 149—150°/15 mm.,  $D^{15}_D$  1.0456,  $n_D$  1.5288; 3-hydroxy-3-benzyl-2:2:5:5-tetramethyltetrahydrofuran, m. p. 89°. W. O. W.

**Action of Sodium Hydroxide on 5-Methylfurfuraldehyde.** JAN J. BLANKSMA (*Chem. Weekblad*, 1912, 9, 186—187).—Sodium hydroxide converts 5-methylfurfuraldehyde into the corresponding alcohol, 5-methyl-2-hydroxymethylfuran, and acid, 5-methylpyromucic acid. The alcohol is a colourless, mobile liquid of fruit-like odour. It has b. p. 100°/11 mm. Exposure to light and air converts it into a yellow syrup, which gradually becomes brown and viscous, and ultimately changes to a dark-coloured resin. A. J. W.

**Synthesis of Pyromeconic Acid.** ALBERTO PERATONER (*Gazzetta*, 1911, 41, ii, 686—697).—The author has effected the synthesis of pyromeconic acid by direct oxidation of 4-pyrone, after unsuccessful attempts to obtain derivatives of meconic acid from the substance  $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{OEt})\cdot\text{CO}\cdot\text{CO}_2\text{Et}$  by dehydration.

When ethyl acetol ether is condensed with one molecule of ethyl oxalate in the presence of sodium ethoxide, the vessel being cooled externally with ice, and the solvent subsequently evaporated in a vacuum below 40°, a sodium salt is produced, which, on treatment with concentrated acetic acid and distillation in a vacuum, yields ethyl  $\alpha$ -ethoxybutane- $\beta\delta$ -dione- $\delta$ -carboxylate,



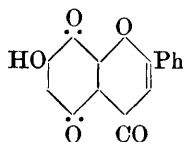
which is a slightly yellow oil, b. p. 135—140°/20 mm. Its aqueous solution gives a cherry-red coloration with ferric chloride, and with copper acetate it yields a green salt,  $\text{C}_{18}\text{H}_{26}\text{O}_{10}\text{Cu}$ . By the action of a second molecule of ethyl oxalate on the sodium salt above described, and proceeding as suggested by Willstätter and Pummerer in the case of xanthochelidonic acid (*Abstr.*, 1904, i, 1043), diethyl  $\beta$ -ethoxypentane- $\alpha\gamma\epsilon$ -trione- $\alpha\epsilon$ -dicarboxylate,  $\text{CO}_2\text{Et}\cdot\text{CO}\cdot\text{CH}(\text{OEt})\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ , is obtained. The triketone is purified by sublimation at 20 mm., treatment with water and resublimation, and then forms colourless, acicular crystals or scales, m. p. 124—125°. With alkalis it yields yellow, amorphous xantho-salts, but with ferric chloride it gives a dirty green coloration which becomes reddish-brown, whilst copper acetate yields a green copper salt. It was not found possible to eliminate the elements of water from the triketone in any way, but when it is boiled for half an hour with hydriodic acid ( $D$  1.7) *n*-pimelic acid is produced.

Pyromeconic acid is formed when one molecule of hydrogen peroxide (3% solution) is added slowly to a solution of one molecule of 4-pyrone, one molecule of ferrous sulphate, and sulphuric acid, the mixture being cooled in ice. The isolation of the acid may be effected either by treating the liquid at its boiling point with ammonia and air until the

pyrone is converted into pyridone and the iron is precipitated, or by prolonged extraction of the liquid with chloroform, the product in either case being purified by sublimation in a vacuum below 100° and by recrystallisation.

R. V. S.

**Anthocyanins. II. An Anthocyanin-like Oxidation Product of Chrysin.** MAXIMILIAN NIERENSTEIN (*Ber.*, 1912, 45, 499—501. Compare this vol., i, 42).—By oxidation with chromic and acetic acids in the cold, chrysin yields *chryson* (annexed formula), m. p. above 360°, dark red needles. It exhibits the blue and the red colour reactions of anthocyanin with alkalis and concentrated sulphuric acid respectively. It forms an *acetyl* derivative,  $C_{17}H_{10}O_6$ , m. p. 324—326° (decomp.), red needles, and when heated with acetic anhydride and zinc dust yields an acetylated hydroxychrysin, by the hydrolysis of which 1:3:4-*trihydroxyflavone*, m. p. 304—305°, is obtained (*triacetyl* derivative, m. p. 214—217°, colourless needles).



Fisetin is not oxidised by chromic and acetic acids.

C. S.

**Some Derivatives of Hydroxyquinol. VII.** GUIDO BARGELINI and ERMANNO MARTEGIANI (*Gazzetta*, 1911, 41, ii, 612—618).—The paper deals with two coumarins obtained by condensation of hydroxyquinol with ethyl acetoacetate and ethyl benzoylacetate respectively. When hydroxyquinol triacetate and ethyl acetoacetate are heated together for half an hour on the water-bath with 73% sulphuric acid,  $\beta$ -methylæsculetin is obtained, identical with that prepared by von Pechmann and von Krafft (*Abstr.*, 1901, i, 285). Its *diacetyl* derivative,  $C_{14}H_{12}O_6$ , has m. p. 149—151°; it dissolves in concentrated sulphuric acid, giving a yellowish-green coloration. The *dibenzoyl* derivative,  $C_{24}H_{16}O_6$ , crystallises in colourless needles, m. p. 152°; it dissolves in concentrated sulphuric acid, giving a slight yellow coloration. The *dimethyl ether* crystallises in colourless needles, m. p. 130—134°. The *monomethyl ether*,  $C_{11}H_{10}O_4$ , formed in its preparation, crystallises in slightly yellow needles, m. p. 173—175°.

$\beta$ -*Phenylæsculetin*,  $C_{15}H_{10}O_4$ , is a yellow, crystalline powder, obtained by condensation of hydroxyquinol triacetate with ethyl benzoylacetate in the presence of 73% sulphuric acid. It dissolves in concentrated sulphuric acid, giving a yellow coloration, and with ferric chloride in alcoholic solution it gives a green coloration. The *diacetyl* derivative,  $C_{19}H_{14}O_6$ , crystallises in colourless needles, m. p. 156°. The *benzoyl* derivative crystallises in colourless needles, m. p. 162—164°. The dimethyl ether was not obtained in crystalline form, but crystals of a substance, m. p. 122—124°, were obtained, which was probably the *monomethyl ether*.

R. V. S.

**New Method for the Preparation of Thiophen.** WILHELM STEINKOPF (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 220—221).—Acetylene is passed through an iron tube containing pyrites at a temperature of 300°. The tube is provided with a transporting screw for the removal of spent pyrites. The liquid

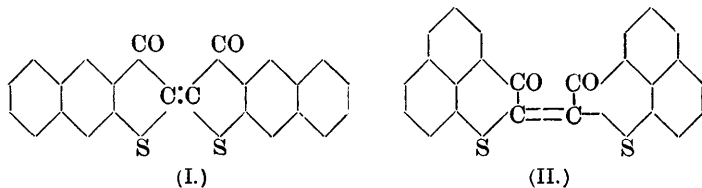
product obtained in the condensing vessel contains 40% of thiophen. In seven or eight hours, 800 grams of distillate may be obtained, using 8 kilograms of pyrites. The thiophen is easily obtained with a purity of 95—96%, the impurities being sulphur compounds with traces of benzene. Larger quantities of benzene are not obtained in the process. The remainder of the distillate is a complex mixture, from which only a single compound,  $C_4H_8S_3$ , b. p. 36—38°, with a very penetrating odour of garlic, has been isolated. C. H. D.

**s-Dioxythionaphthen.** MAURICE LANFRY (*Compt. rend.*, 1912, 154, 519—521. Compare Abstr., 1911, i, 555, 740, 1009).—*s-Dioxythionaphthen*,  $C_8H_6O_2S$ , is prepared by the action of hydrogen peroxide on thionaphthen (Gattermann, Abstr., 1894, i, 92), employing 0.5—0.8 gram of active oxygen per gram of thionaphthen. The compound crystallises in colourless needles, m. p. 142—143°; it does not give the Laubenheimer reaction, and does not show the properties of a phenol, a ketone, or a quinone. It follows, therefore, that the oxygen is attached directly to sulphur, as indicated by the name the author suggests for the compound.

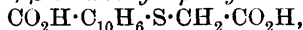
Dioxythionaphthen unites with bromine to form a *dibromide*,  $C_8H_6O_2SBr_2$ , occurring in slender needles, m. p. 168—170°. When treated with fuming nitric acid, it yields a *mononitro-derivative*,  $C_8H_5O_2S \cdot NO_2$ , crystallising in yellow rhombohedra, m. p. 187—188°.

W. O. W.

**“Thio-indigo” Dyes of the Naphthalene Series.** PAUL FRIEDLÄNDER and N. WOROSHZOW (*Annalen*, 1912, 388, 1—23).—The series of reactions whereby anthranilic acid has been converted into “thio-indigo” (Abstr., 1906, i, 378; 1907, i, 334), is applicable in the naphthalene series to the preparation of “*bis-2:3-naphthathiophen-indigo*” [*bis-2:3-naphthathiophen*] and *bis-1:8-naphthapenthathiophen-indigo*” [*bis-1:8-naphthathiophen*] (formulæ I and II respectively).



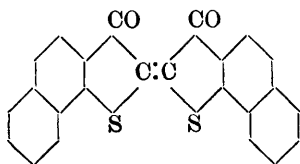
[With E. ECKSTEIN.]—The sodium salt which is precipitated by the addition of sodium chloride to the not too dilute, diazotised solution of 2-amino-3-naphthoic acid is added to a hot solution of potassium xanthate. When the oil which separates has become solid, it is dissolved in sodium hydroxide and warmed with chloroacetic acid. By acidification, *β-3-carboxynaphthylthiolacetic acid*,



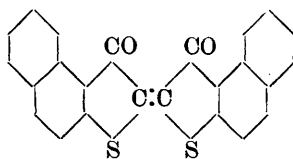
m. p. 224° (decomp.), white needles, is obtained. Its sodium salt is boiled with acetic anhydride and sodium acetate, the resulting acetoxynaphthathiophen is hydrolysed by dilute sodium hydroxide,

and the hydroxynaphthathiophen is oxidised by alkaline potassium ferricyanide, whereby *bis*-2:3-naphthathiophen is obtained. The dye crystallises in almost black needles, sublimes without decomposition, yields an orange-red vat with alkaline hyposulphite, and develops an olive-green coloration with fuming sulphuric or chlorosulphonic acid. Naphthastyril (Abstr., 1910, i, 201) is converted by boiling 10% sodium hydroxide into sodium 8-amino-1-naphthoate, the diazotised solution of which is converted by reactions similar to the preceding into *bis*-1:8-naphthapenthiophen, which crystallises in long needles with a copper lustre and sublimes with decomposition. The intermediate products isolated in its preparation are the anhydride of 8-thiol-1-naphthoic acid,  $C_{10}H_6 \begin{smallmatrix} S \\ \diagup \diagdown \\ CO \end{smallmatrix}$ , m. p. 144·5—145·5°, yellow needles,  $\alpha$ -8-carboxynaphthylthiolacetic acid,  $CO_2H \cdot C_{10}H_6 \cdot S \cdot CH_2 \cdot CO_2H$ , m. p. 177°, and hydroxy-1:8-naphthapenthiophen,  $C_{10}H_6 \begin{smallmatrix} C(OH) \\ \diagup \diagdown \\ S \end{smallmatrix} CH$ , m. p. 84·5—85·5°, yellow prisms (acetyl derivative, m. p. 130·5°, yellow leaflets), which is oxidised to the dye best by atmospheric oxygen.

"*Bis*-1:2-naphthathiophenindigo" [*bis*-1:2-naphthathiophen] and *bis*-2:1-naphthathiophen [*bis*-2:1-naphthathiophen] (formulae I and II respectively) cannot be prepared by the preceding method,

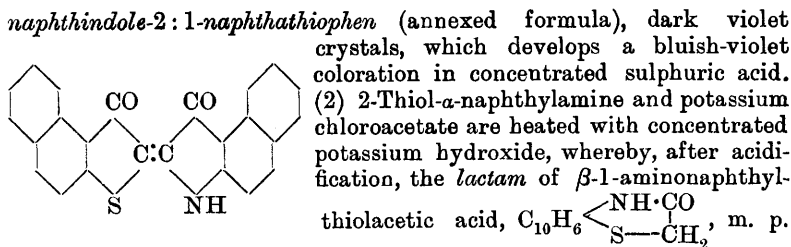


(I.)

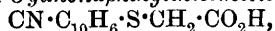


(II.)

because the necessary aminonaphthoic acids are unknown. The latter dye has been prepared in three ways: (1)  $\alpha$ -Naphthylamine-2-sulphonic acid is converted in the usual way into 1-cyanonaphthalene-2-sulphonic acid, the potassium salt of which yields the chloride,  $CN \cdot C_{10}H_6 \cdot SO_2Cl$ , m. p. 141—142°, by heating with phosphorus pentachloride. The chloride is reduced by zinc and hydrochloric acid to the mercaptan, which reacts with sodium chloroacetate in alkaline solution to form, after acidification,  $\beta$ -1-carboxynaphthylthiolacetic acid,  $CO_2H \cdot C_{10}H_6 \cdot S \cdot CH_2 \cdot CO_2H$ , m. p. 69° (134·5° when anhydrous), colourless needles. By prolonged boiling with concentrated sodium hydroxide and acidification of the hot solution, this acid yields hydroxy-2:1-naphthathiophen,  $C_{10}H_6 \begin{smallmatrix} C(OH) \\ \diagup \diagdown \\ S \end{smallmatrix} CH$ , m. p. 121°, colourless needles, which reacts with benzaldehyde and *p*-nitrobenzaldehyde to form the thioindogenides,  $C_{10}H_6 \begin{smallmatrix} CO \\ \diagup \diagdown \\ S \end{smallmatrix} C:CHPh$ , m. p. 159°, yellow needles, and  $C_{10}H_6 \begin{smallmatrix} CO \\ \diagup \diagdown \\ S \end{smallmatrix} C:CH \cdot C_6H_4 \cdot NO_2$ , m. p. 287°, yellow needles, respectively, and with  $\beta$ -naphthisatin chloride in hot xylene to form



203°, is obtained.  $\beta$ -1-Cyanonaphthylthiolacetic acid,



m. p. 173°, which is prepared from the preceding compound, is converted by hot potassium hydroxide into *potassium 3-aminonaphthathiophen-2-carboxylate*, an acidified solution of which yields hydroxy-2:1-naphthathiophen by boiling. (3)  $\beta$ -Naphthylthiolacetic acid,  $C_{10}H_7 \cdot S \cdot CH_2 \cdot CO_2H$ , m. p. 91°, obtained by heating  $\beta$ -naphthyl mercaptan and chloroacetic acid in alkaline solution, is converted directly into hydroxy-2:1-naphthathiophen by 10% chlorosulphuric acid in chloroform at the ordinary temperature.

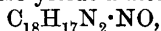
*Bis-2:1-naphthathiophen*, which is obtained by the oxidation of hydroxy-2:1-naphthathiophen, best by alkaline potassium ferricyanide, crystallises in reddish-brown needles with a bronze lustre, develops a dark blue coloration with concentrated sulphuric acid, and yields a yellow vat with alkaline hyposulphite.

*Bis-1:2-naphthathiophen*, which can be obtained by methods analogous to the preceding, forms dark red needles, develops a brownish-red coloration with concentrated and an intense blue with fuming sulphuric acid, and yields a yellow vat. The *lactam* of  $\alpha$ -2-aminonaphthylthiolacetic acid,  $C_{10}H_6 \begin{smallmatrix} \text{S} - \text{CH}_2 \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$ , m. p. 210°,  $\alpha$ -2-cyanonaphthylthiolacetic acid,  $CN \cdot C_{10}H_6 \cdot S \cdot CH_2 \cdot CO_2H$ , m. p. 137—138°, and *hydroxy-1:2-naphthathiophen*,  $C_{10}H_6 \begin{smallmatrix} \text{C}(\text{OH}) \\ \text{S} \end{smallmatrix} \text{CH}_2$ , m. p. 142° (*benzylidene* derivative, m. p. 181°, yellow leaflets), are also described.

C. S.

**Organic Syntheses by means of Sunlight.** VII. Photosynthesis of a New Alkaloid from Acetophenone and Ammonia. EMANUELE PATERNÒ and CONCETTOMASELLI (*Gazzetta*, 1912, 42, i, 65—75; *Atti R. Accad. Lincei*, 1912, [v], 21, i, 235—243).—When acetophenone dissolved in saturated alcoholic ammonia is exposed to sunlight for several months, a substance is produced which, from its properties, is to be regarded as an alkaloid. The yield does not exceed 20%. The new *alkaloid*,  $C_{15}H_{18}N_2$ , forms large, transparent crystals [ZAMBONINI: the crystals belong to the triclinic system:  $a:b:c = 1.5017:1:1.5993$ ;  $\alpha$  91° 21.5',  $\beta$  106° 14',  $\gamma$  79° 50'], which have m. p. 227° and dissolve in alcohol, giving a strongly alkaline solution. The substance has about the normal molecular weight in freezing acetic acid. The *nitrate* is a white, crystalline powder, m. p. 258°. The *hydrochloride*,  $C_{15}H_{18}N_2 \cdot HCl$ ,

crystallises in tufts of long, colourless needles, and does not change when heated in a current of dry hydrogen chloride in a bath at  $350^{\circ}$ . The *platinichloride*,  $(C_{18}H_{18}N_2)_2 \cdot H_2PtCl_6$ , forms silky, flesh-coloured laminæ, which begin to blacken at  $260^{\circ}$ . The *silver* salt is a white, amorphous powder. The base yields a *mononitroso*-derivative,



when warmed with potassium nitrite in solution in glacial acetic acid and alcohol; the substance crystallises in lustrous laminæ, m. p.  $218^{\circ}$  (decomp.).

Negative results were obtained in attempts to oxidise the alkaloid with permanganate and to determine its alkyloxy-groups. When the substance is heated in a sealed tube for three hours at  $370^{\circ}$ , a portion of it is converted into a reddish-brown oil, but the greater part remains unchanged. When the alkaloid was heated with hydriodic acid and phosphorus for six days, the product consisted of the *hydriodide* of the base, together with a small quantity of a yellow oil. R. V. S.

**Rearrangement of Cinchonine and Quinine into Their Poisonous Isomerides Cinchotoxine and Quinotoxine.** HENRY C. BIDDLE (*Ber.*, 1912, 45, 526—528. Compare Rabe, 1911, ii, 33).—Salts of cinchonine and quinine when heated at  $95$ — $98^{\circ}$  in aqueous solution with or without excess of acid undergo rearrangement into their poisonous isomerides cinchotoxine and quinotoxine. The velocity of the reaction is increased when the dissociation constant of the acid used is lessened; this applies to the action of acids both on salts and on free alkaloid. With acetic or propionic acid the change is practically complete after forty-eight hours' heating; under the same conditions, using an excess of hydrochloric acid, practically no rearrangement takes place. The same change also takes place slowly when the salts are heated at  $36^{\circ}$ , or when the salt solutions are exposed to direct sunlight at the ordinary temperature; in this case much resinous matter is also formed, which colours the solution brown.

It is possible that cinchotoxine and quinotoxine are formed similarly in the human organism. E. F. A.

**The Symmetry of Sparteine.** CHARLES MOUREU and AMAND VALEUR (*Compt. rend.*, 1912, 154, 309—312. Compare this vol., i, 210).—The action of methyl iodide on *isosparteine* hydriodide at  $135^{\circ}$  leads to the formation of *isosparteine*  $\alpha$ -methiodide. The action of methyl iodide on sparteine has already been described; since it leads to analogous results, it follows that both bases are symmetrical. As this is impossible owing to the mode of formation of *isosparteine*, it follows that the action of methyl iodide on the hydriodides is not purely one of simple addition, but involves displacement of the halogen hydride by the alkyl iodide and direct addition of the displaced hydrogen iodide. There is therefore no absolute proof of the symmetry of the sparteine molecule.

Reasons are adduced in support of the view that stereoisomerism of the groups about the nitrogen atom is sufficient to explain the existence of two isomeric methylsparteine methiodides. W. O. W.

**Methylation of Brucine.** GUSTAV MOSSLER (*Monatsh.*, 1912, 33, 19—32).—*Methylbrucine acetate*,  $C_{24}H_{30}O_5N_2 \cdot C_2H_4O_2 \cdot 5H_2O$ , prepared by the cautious addition in portions of silver acetate to a finely divided suspension of brucine methiodide in water, crystallises in rhombic plates, m. p. (anhydrous) 208—209° (decomp.),  $[\alpha]_D^{20} - 9.97^\circ$ . The same substance was obtained by the action of acetic acid on methylbrucine. When warmed with hydrochloric acid, brucine methochloride is obtained.

On treatment with methyl iodide in methyl-alcoholic solution, *dimethylbrucine iodide*,  $C_{25}H_{33}O_5N_2I \cdot 2\frac{1}{2}H_2O$ , is obtained in flat, right-angled plates, m. p. 268° (decomp.).

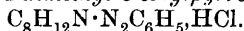
*Dimethylbrucine acetate*,  $C_{27}H_{36}O_7N_2 \cdot 5H_2O$ , is very similar to the monomethyl compound, m. p. 205—206°,  $[\alpha]_D^{20} - 7.14^\circ$ . With hydrochloric acid the salt,  $C_{25}H_{34}O_5N_2Cl_2$ , is obtained, m. p. 261°.

Crystalline products could not be obtained by the oxidation of methylbrucine.

Methyl- and dimethyl-brucine are considered to have the structure of betaines, whereas dimethylbrucine iodide is a quaternary iodide.

E. F. A.

**Hæmopyrrole.** J. GRABOWSKI and LEON MARCHLEWSKI (*Ber.*, 1912, 45, 453—456).—The authors have subjected 2:4-dimethyl-3-ethylpyrrole (Knorr and Hess, Abstr., 1911, i, 1019) to the action of benzenediazonium chloride, and find that its behaviour differs from that of hæmopyrrole obtained from hæmin, since it yields orange needles of *benzeneazo-2:4-dimethyl-3-ethylpyrrole hydrochloride*,

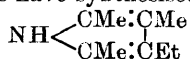


This substance has no definite m. p., but begins to decompose at 120°, and evolves gas at about 155°. Attempts to convert it into a disazo-derivative were unsuccessful. The authors draw the conclusion that trisubstituted derivatives of pyrrole are incapable of reacting with more than one molecule of a diazonium salt, and doubt the view that one  $-N_2C_6H_5$  group of the hæmopyrrole derivative,  $C_8H_{11}N(N_2C_6H_5)_2$ , is attached to the nitrogen atom. The stability of the hæmopyrrole dyes towards hydrochloric acid and the so-called *H*-acid is a further argument against an azo-diazoamino-constitution.

The reduction of methyl-*n*-propylmaleiminide (Marchlewski and Buraczewski, Abstr., 1905, i, 399; 1906, i, 779) has been repeated with larger quantities of material. From the product of the reduction, two crystalline dyes were isolated in the form of hydrochlorides, but in quantity insufficient for analysis. In hydrochloric acid and in neutral solution, however, their spectra are identical with those of the dyes prepared from hæmopyrrole.

H. W.

**Syntheses of Phyllopyrrole. Chemistry of Hæmopyrrole.** HANS FISCHER and E. BARTHOLOMÄUS (*Ber.*, 1912, 45, 466—471).—When substituted pyrroles are heated with alcoholic solutions of sodium methoxide or ethoxide, alkylation occurs at a carbon atom. In this manner the authors have synthesised phyllopyrrole,



(compare Willstätter and Asahina, Abstr., 1912, i, 42), from 2:4-dimethyl-3-ethylpyrrole and sodium methoxide, from 2:4:5-trimethylpyrrole and sodium ethoxide, and from hæmopyrrole and sodium methoxide. The highest m. p. observed for phylopyrrole was 69°. Phylopyrrole picrate has m. p. 104—105°.

Similarly, 2:4-dimethyl-3-ethylpyrrole was converted by means of sodium ethoxide into 2:4-dimethyl-3:5-diethylpyrrole.

When hæmopyrrole is heated with sodium ethoxide, it yields a dimethyldiethylpyrrole (isolated in the form of its *picrate*, m. p. 102—103°) differing from that described above. Since the relative positions of the methyl and ethyl groups in hæmopyrrole have been determined by its oxidation to methylethylmaleinimide, the authors are led to propose the formula  $\text{NH} \begin{array}{l} \text{CMe} \cdot \text{CMe} \\ \diagup \quad \diagdown \\ \text{CH} - \text{CEt} \end{array}$  for hæmopyrrole, and regard its product of its ethylation as 2:3-dimethyl-4:5-diethylpyrrole.

By coupling 2:4:5-trimethylpyrrole with diazobenzenesulphonic acid, a red *dye*,  $\text{C}_{13}\text{H}_{15}\text{O}_3\text{N}_3\text{S}$ , was obtained.

The preparation of phylopyrrole from hæmin is fully described.

H. W.

**Mirror Image Isomerism with Iron Compounds.** ALFRED WERNER (*Ber.*, 1912, 45, 433—436).—In order to show that ethylenediamine is not a necessary cause of optical activity in complex metal ammonias, the author has investigated the tri-*a*-dipyridylferrous compounds,  $[(\text{Dipyr})_3\text{Fe}]\text{X}_2$ , and has succeeded in obtaining the optically active lævo-isomerides by means of *d*-ammonium tartrate. The observed specific rotations are very great ( $>500^\circ$ ), but racemisation takes place very quickly in aqueous solution, the rotation falling to half its original value in half-an-hour.

The compounds obtained belong to the class of molecular asymmetry II (this vol., i, 166); they prove that optical activity does not depend on the presence of ethylenediamine, and also, that it can occur with co-ordination compounds of a divalent element.

Tri-*a*-dipyridylferrous bromide was prepared in a manner described previously (Blau, Abstr., 1889, 1212; 1899, i, 387), and resolved as follows: 2.5 grams were dissolved in 112 c.c. of water and 60 grams of *d*-ammonium tartrate added to the filtered solution, which was then cooled to  $-4^\circ$ . After some time, intense red crystals of l-tri-*a*-dipyridylferrous-*d*-tartrate separate, which cannot be recrystallised without loss of activity. A 0.125% solution gave  $\alpha - 0.35^\circ$  in a decimetre tube at  $15^\circ$ ; after three and a-half hours the rotation had fallen to zero.

l-Tri-*a*-dipyridylferrous bromide,  $[\text{Fe}(\text{Dipyr})_3]\text{Br}_2 \cdot 6\text{H}_2\text{O}$ , was obtained from the tartrate by double decomposition with potassium bromide; it could not be recrystallised, owing to rapid racemisation. It forms dark red, flat crystals, and has  $[\alpha] - 520^\circ$  and  $[\text{M}] - 4117.8^\circ$ , although these values are probably too low, because of racemisation. The *iodide*,  $[\text{Fe}(\text{Dipyr})_3]\text{I}_2 \cdot 5\text{H}_2\text{O}$ , was similarly prepared from the tartrate and sodium iodide, and forms glistening, dark red, flat leaflets; it has  $[\alpha] - 440^\circ$  and  $[\text{M}] - 3818.7^\circ$ .

T. S. P.

**The Preparation of Nitropyridine.** FRANZ FRIEDL (*Ber.*, 1912, 45, 428—430).—The direct nitration of pyridine has been accomplished by gradually adding potassium nitrate to a solution of pyridine in 18% fuming sulphuric acid heated at 330°. *β*-Nitropyridine crystallises in long, colourless needles, m. p. 41°, b. p. 216°. *β*-Nitropyridine nitrate has m. p. 150—151°.

The position of the nitro-group in the molecule was determined by reducing nitropyridine by means of stannous chloride to *β*-aminopyridine (Pollak, *Abstr.*, 1895, i, 391), and, further, by the transformation of this compound into *β*-hydroxypyridine (Fischer and Renouf, *Abstr.*, 1884, 1370).

Nitropyridine is also formed in small quantity by the action of concentrated nitric acid on a solution of pyridine in fuming sulphuric acid at 330° and atmospheric pressure. H. W.

**4-Oxypyrrone and Some of its Derivatives.** ALBERTO PERATONER (*Gazzetta*, 1911, 41, ii, 619—685. Compare Ost, *Abstr.*, 1879, 708; 1882, 601; 1883, 791; 1884, 1302; 1885, 48; Peratoner, *Abstr.*, 1902, i, 421, 493; Peratoner and others, *Abstr.*, 1905, i, 806, 807; Palazzo, *Abstr.*, 1905, i, 458; Palazzo and Onorato, *Abstr.*, 1905, i, 459).—The paper deals with Ost's nitrosopyrromeconic acid, and with some of its transformation products and their derivatives. The author discusses fully the constitution of the substances concerned, in the light of the previous work of himself and others and of the new experimental data now obtained.

Further details are given as to the preparation of Ost's nitrosodipyrrromeconic acid by the action of ethyl nitrite on pyrromeconic acid. The author also finds that phenol, catechol, resorcinol, pyrogallol, *α*-naphthol, and thymol yield traces of the corresponding nitroso-derivatives when they are treated with alkyl nitrites at a low temperature. Benzoylacetone and ethyl benzoylacetate yield nitroso-derivatives in this way at the ordinary temperature.

When nitrosodipyrrromeconic acid,  $C_5H_3O_4N, C_5H_4O_3$ , is treated with rather more than two molecules of phenylhydrazine in glacial acetic acid, two products are obtained: (1) a *substance* crystallising in yellow needles, m. p. 165°; (2) a greyish-white, crystalline *substance*, which by treatment with hot benzene is converted into a *substance* crystallising in yellow needles, m. p. 199—200°. Both compounds have the

composition required by the formula: 
$$\begin{array}{c} O \cdot C(N:OH) \cdot C:N \cdot NHPH \\ | \qquad \qquad \qquad | \\ CH:CH \qquad \qquad C:N \cdot NHPH \end{array}$$
 and

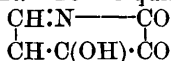
are to be regarded as stereoisomerides. Both yield the same *osotetrazone*,  $C_{17}H_{13}O_2N_5$ , when treated with warm alcoholic ferric chloride solution. The osotetrazone crystallises in red needles, m. p. 137—138°, which appear black with a metallic lustre when viewed by reflected light. Both hydrazo-oximes when kept at 210° lose one molecule of water, yielding a *substance*,  $C_{17}H_{13}ON_5$ , which forms white needles, m. p. 242°.

Ost's nitrosodipyrrromeconic acid also yields a *quinoxaline*,  $C_{11}H_7O_2N_3$ , when treated with *o*-phenylenediamine hydrochloride in glacial acetic acid in the presence of sodium acetate. The substance forms lemon-

yellow crystals, gives a green coloration with sulphuric acid, and dissolves in alkali hydroxides, forming yellow solutions, from which the original substance is precipitated by carbon dioxide.

[With A. TAMBURELLO.]—In proof of the constitution previously given for Ost's pyromecazonic acid (2 : 3-dihydroxy-4-pyridone), it is found that the product of the reaction of its diacetyl derivative with diazomethane yields about the same figures for -OMe and :NMe groups when analysed by the methods of Zeisel and of Herzig and Meyer respectively. The pyromecazonic acid does not react with ethyl nitrate, and therefore does not contain a ketomethylenic grouping.

Ost's pyromecazone (obtained by oxidation of pyromecazonic acid) behaves in the same way when treated with diazomethane, for the yellow oil which is obtained contains only half the calculated amount of -OMe group. The action of diazoethane is different: the product, both from the free quinone and from its additive product with ethyl alcohol, contains almost the amount of -OEt group corresponding with the formula  $C_5H_3O_2N \cdot OEt$ . To the quinone the constitution



is assigned. It gives the reddish-violet coloration with potassium hydroxide described by Bamberger as characteristic of *o*-quinones, and with *o*-phenylenediamine it forms a *quinoxaline*,  $C_{11}H_7ON_3$ , which crystallises in canary-yellow needles, and for which the formula  $\begin{array}{c} CH \cdot NH \cdot C:N \\ | \\ CH-CO-C:N \end{array} > C_6H_4$  is suggested. The *acetyl* derivative of the quinoxaline,  $C_{13}H_9O_2N_3$ , forms greenish-yellow needles.

In support of the conclusion that Ost's oxyppyromecazonic acid is 1 : 2 : 3-trihydroxy-4-pyridone, the author finds that when a saturated aqueous solution of the substance is treated with ferric chloride, a red *iron* salt is precipitated, having the composition  $Fe(C_5H_4O_4N)_3 \cdot 3H_2O$ . The acid also forms a *triacetyl* derivative,  $C_5H_2O_4NAc_3$ , which crystallises in aggregates of minute needles, m. p. 123—124°, and a *tribenzoyl* derivative,  $C_5H_2O_4NBz_3$ , crystallising in colourless needles, m. p. 162—163°. The position of the third hydroxyl group (attached to nitrogen) follows from the fact that it is readily reduced by tin and hydrochloric acid or by hydriodic acid, and from the production of the iron salt above mentioned.

[With A. TAMBURELLO.]—By the action of hydroxylamine on the ethers of comenic acid, derivatives of 1-hydroxypyridone can be obtained. When ethylcomenic acid is treated with hydroxylamine, an acid,  $C_5H_5O_5N$ , is obtained, m. p. 174—175° (with evolution of carbon dioxide). The substance gives a red coloration with ferric chloride. Its *ethyl* ester,  $OEt \cdot C_5H_2O(CO_2Et) : N \cdot OH$ , forms colourless needles, m. p. 156°. The *acetyl* derivative,  $OEt \cdot C_5H_2O(CO_2Et) : N \cdot OAc$ , forms rosettes of colourless needles, m. p. 81—82°. The action of hydroxylamine on ethyl ethylcomenate yields the above ethyl ester of m. p. 156°. To the acid of m. p. 174—175° the structure of 1-*hydroxy-2-ethoxy-4-pyridone-6-carboxylic acid* is ascribed. When it is reduced with tin and hydrochloric acid, it yields a substance,  $C_8H_9O_4N$ , which crystallises with  $1H_2O$  in rosettes of colourless needles, m. p. 224—225°.

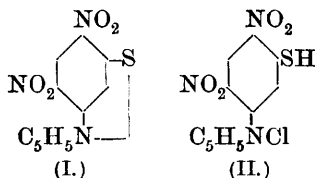
but when dehydrated (at  $150^{\circ}$ ) it melts at  $235^{\circ}$  (decomp.). It gives an orange-yellow coloration with ferric chloride, and to it is assigned the constitution of *3-ethoxy-4-pyridone-6-carboxylic acid*. It is identical with the product of the action of ammonia on ethylcomenic acid, and is also obtained by reduction of the ethyl ester above mentioned (m. p.  $156^{\circ}$ ), since the ester is saponified at the same time. *3-Ethoxy-4-pyridone-6-carboxylic acid* is hydrolysed when boiled for two hours with hydriodic acid (D 1.74), yielding *3-hydroxy-4-pyridone-6-carboxylic acid* (Ost's comenamic acid). When *1-hydroxy-3-ethoxy-4-pyridone-6-carboxylic acid* is kept at  $190^{\circ}$  for some time, *1-hydroxy-3-ethoxy-4-pyridone* is obtained; it crystallises in colourless needles, m. p.  $156^{\circ}$ , and gives a brownish-red coloration with ferric chloride.

[With E. CARAPELLE.]—The phenylhydrazones of pyromeconic acid and some of their derivatives have also been investigated. When a solution of phenyldiazonium acetate is treated with a solution of pyromeconic acid at  $0^{\circ}$ , the *monophenylhydrazone*,  $C_{11}H_8O_3N_2$ , is produced; it forms dark red or purple crystals, which decompose at  $176^{\circ}$ . When it is treated with two molecules of phenylhydrazine, it yields two *triphenylhydrazones*,  $C_5H_2O(N \cdot NHPh)_3$ , which are apparently stereoisomeric. One of these has m. p.  $161-162^{\circ}$ , the other has m. p.  $212-214^{\circ}$ . The former is converted into the latter if hydrogen chloride is passed through its alcoholic solution for half an hour. The monohydrazone reacts with *o*-phenylenediamine, yielding a *quinoxaline*,  $C_{17}H_{12}ON_4$ . The monohydrazone is also readily converted into an hydroxypyridone derivative, and this indicates the analogy between its structure and that of oximinopyromeconic acid. When it is mixed with a little water and treated with sulphur dioxide at  $0^{\circ}$ , a substance,  $C_{11}H_{10}O_3N_2$ , is obtained, which forms crystalline scales, m. p.  $220^{\circ}$ , and is assigned the constitution of *1-anilino-2:3-dihydroxy-4-pyridone*. Its *hydrochloride*,  $C_{11}H_{10}O_3N_2 \cdot HCl$ , crystallises in colourless needles. Its *diacetyl* derivative,  $C_{11}H_8O_3N_2 \cdot Ac_2$ , crystallises in lustrous scales, m. p.  $155-156^{\circ}$ . *1-Anilino-2:3-dihydroxy-4-pyridone* gives with ferric chloride a deep blue coloration, which disappears when excess of ferric chloride has been added. The *quinone* thus produced reacts with *o*-phenylenediamine, yielding a *quinoxaline*,  $C_{17}H_{12}ON_4$ , which forms golden-yellow scales, m. p.  $181-182^{\circ}$ . The quinone is best obtained by oxidising the pyridone with silver oxide, but it has been isolated only in the form of its *additive product* with methyl alcohol,  $C_{11}H_8O_3N_2 \cdot MeOH$ , which dissociates and melts (forming a red liquid) at  $87-88^{\circ}$ .

[With A. D'ANGELO.]—The authors have also prepared some derivatives of dibromocomenic acid. Dibromocomenic acid (compare Mennel, Abstr., 1883, 656) reacts with basic lead acetate, losing both atoms of bromine, and the corresponding *quinone* is formed, but could not be isolated. Both dibromocomenic acid and this quinone react with *o*-phenylenediamine, yielding a *quinoxaline*, to which the formula  $CO_2H \cdot \underset{\text{CH} \cdot CO \cdot C:N}{\overset{\text{C}}{\text{O}}} \cdot C:N > C_6H_4$  is ascribed. It dissolves in alkalis, giving a yellowish-red coloration, and in concentrated sulphuric acid, giving a red coloration. When heated it decomposes above  $200^{\circ}$ . It yields a *phenylhydrazone*, which decomposes about  $170^{\circ}$ , to which the formula

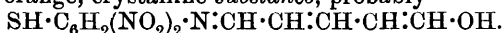


dinium chloride leads to the removal of one of the pyridine groups and the formation of a *thiobetaine anhydride* (I), similar in constitution to the anhydride previously described (Abstr., 1910, i, 585). The thiobetaine anhydride exists in two forms, an orange-red modification,



containing  $1\text{H}_2\text{O}$ , obtained by passing hydrogen sulphide into an aqueous solution of the pyridinium chloride, and a dark red form, which crystallises in leaflets and explodes on heating. The latter modification is produced by (1) the action of hydrogen sulphide on a 90% alcoholic solution of the pyridinium chloride, and (2) by dissolving

the orange-red variety in concentrated hydrochloric acid and diluting the solution with water. The anhydride forms salts, which are instantly decomposed by water; the *hydrochloride* (II), prepared from the anhydride and hydrogen chloride in alcoholic solution, crystallises in white needles; the *platinichloride* is also described. The anhydride is converted by successive treatment with aqueous alkalis and acetic acid into an orange, crystalline *substance*, probably



A similar removal of the pyridine group takes place by the action of hydrogen sulphide on 2:4-dinitrophenylpyridinium chloride in aqueous solution, the product in this case consisting of 2:4-dinitrophenylmercaptan, accompanied by a small amount of 2:2':4:4'(?)-tetra-nitrodiphenyl sulphide. The latter compound forms the main product when the hydrogen sulphide is replaced by sodium sulphide, or the action carried out in alcoholic solution.

F. B.

**Trinitrophenylpyridinium Chloride.** THEODOR ZINCKE (*J. pr. Chem.*, 1912, [ii], 85, 217—221. Compare Busch and Kögel, this vol., i, 50).—2:4:6-Trinitrophenylpyridinium chloride is best prepared by the interaction of picryl chloride and pyridine in ethereal solution. It has m. p.  $128-129^\circ$  (decomp.), and is resolved by alcoholic hydrogen chloride at  $100^\circ$  into its components; the yellow, crystalline *platinichloride*,  $(\text{C}_{11}\text{H}_7\text{O}_6\text{N}_4\text{Cl})_2\text{PtCl}_6$ , has m. p.  $255^\circ$  (decomp.).

On successive treatment with hydrogen sulphide and hydrochloric acid, it yields a *substance*, which crystallises in dark violet leaflets of a metallic lustre. It reacts with aniline, forming the dianilide,  $\text{C}_{17}\text{H}_{16}\text{N}_2$ , previously described (Abstr., 1904, i, 921).

The  $\psi$ -base,  $\text{C}_{11}\text{H}_8\text{O}_7\text{N}_4$ , obtained by the action of alkalis, forms brown crystals, m. p.  $190-193^\circ$  (decomp.), yields a *sodium salt*, and is converted by acetic and hydrochloric acids into picramide and the original pyridinium salt.

F. B.

**Conversion of Oxindole into Coumaran-1-one.** CHARLES MARSCHALK (*Ber.*, 1912, 85, 582—585).—Oxindole has been transformed into coumaran-1-one by heating it with barium hydroxide in aqueous solution at  $150^\circ$ , converting the resulting barium *o*-aminophenylacetate (Baeyer and Comstock, Abstr., 1883, 1130) by means of

the diazo-reaction into *o*-hydroxyphenylacetic acid, and removing water from the latter compound by distillation. The diazotisation is accomplished by the addition of an aqueous solution of the barium salt and sodium nitrite to cold dilute sulphuric acid.

Oxindole is readily prepared by the reduction of isatin with sodium hyposulphite to dioxindole and subsequently reducing this by means of sodium amalgam in aqueous alcoholic solution. Dioxindole has m. p. 167—168°, and not 180° as given by Baeyer and Knop (*Annalen*, 1866, 140, 11). When dissolved in aqueous sodium hydroxide and the solution treated with alcohol, it yields a crystalline *sodium* salt, which, however, is too unstable to be isolated, is converted by dilute sulphuric acid into dioxindole, but is apparently different from the sodium salt obtained by Baeyer and Knop by reducing isatin with sodium amalgam.

F. B.

**Some New Derivatives of Carbazole.** BRUNO LEVY (*Monatsh.*, 1912, 33, 177—184).—It has been discovered that the high temperature (170—190°) used by Graebe and von Adlerskron (*Abstr.*, 1880, 660) in the preparation of methyl- and ethyl-carbazole was unnecessary, and that potassium carbazole reacts with methyl iodide almost quantitatively at the ordinary temperature. In extending the reaction to other alkyl halides, it is found that the velocity of the reaction decreases as the series is ascended, and also that the normal alkyl halides give a greater reaction velocity than the branched ones. Although no exact measurements were made, allyl iodide and benzyl chloride were found to react much more readily than ethyl iodide.

*n*-Propylcarbazole was obtained by the reaction of the iodide with potassium carbazole on the water-bath; it forms needle crystals, m. p. 50°, and gives a *picrate*, m. p. 98°.

isoPropylcarbazole, obtained similarly, has m. p. 120°, and gives a *picrate*, m. p. 143°.

*n*-Butylcarbazole forms needles, m. p. 58°, and gives a *picrate*, m. p. 89°. sec.-Butylcarbazole is an oil, which gives a *picrate*, m. p. 64°. isoButylcarbazole is also an oil; the *picrate* has m. p. 177°.

isoAmylcarbazole is an oil; the *picrate* has m. p. 85°. sec.-Amylcarbazole is also an oil; m. p. of *picrate*, 93°.

Allylcarbazole, obtained by reaction at room temperature, crystallises in colourless rhombs, m. p. 56°; the *picrate* has m. p. 86°.

Benzylcarbazole, also prepared at the ordinary temperature, forms colourless needles, m. p. 114°; m. p. of *picrate*, 105°.

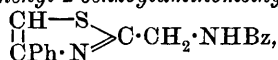
Triphenylmethylcarbazole, obtained by reaction of triphenylmethyl chloride and potassium carbazole in boiling benzene, forms rhombic crystals, m. p. 245°.

D. F. T.

**Thioamides. IV. Action of Hydrogen Sulphide on Nitrogen-substituted Aminoacetonitriles.** TREAT B. JOHNSON and GERALD BURNHAM (*Amer. Chem. J.*, 1912, 47, 232—242).—In an earlier paper (*Abstr.*, 1911, i, 712) it has been shown that aminoacetonitrile reacts with hydrogen sulphide to form the corresponding thioamide, which is unstable and undergoes condensation in alcoholic

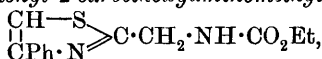
solution with production of thioglycylglycinethioamide. This thio-polypeptide is also unstable, and becomes converted into dithio-piperazine. The present investigation was undertaken in order to ascertain whether thioamides of *N*-substituted amino-acids of the type  $R \cdot NH \cdot CH_2 \cdot CS \cdot NH_2$  would undergo similar transformations. It has been found that phenylaminoacetonitrile, *p*-tolylaminoacetonitrile, anisoylaminoacetonitrile, hippuronitrile, carbethoxyaminoacetonitrile, and carbamidoacetonitrile all combine smoothly with hydrogen sulphide at the ordinary temperature to form the corresponding thioamides, which are stable compounds, and can be heated with alcohol without undergoing any change. When these thioamides are heated above their m. p.'s they suffer decomposition, but without producing a thiopolypeptide derivative or dithiopiperazine.

*Hippurothioamide*,  $C_6H_5 \cdot CO \cdot NH \cdot CH_2 \cdot CS \cdot NH_2$ , m. p.  $150^\circ$  (decomp.), crystallises in transparent blocks, and reacts with bromoacetophenone with production of 4-phenyl-2-benzoylaminoethylthiazole,

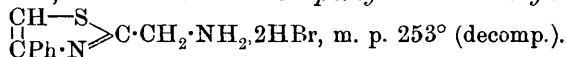


m. p.  $148^\circ$ , which forms rosettes of needles.

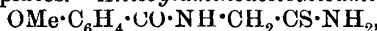
*Carbethoxyaminoacetothioamide*,  $CO_2Et \cdot NH \cdot CH_2 \cdot CS \cdot NH_2$ , m. p.  $118^\circ$ , crystallises in rectangular blocks, and condenses with bromoacetophenone to form 4-phenyl-2-carbethoxyaminomethylthiazole,



m. p.  $59-61^\circ$ , which crystallises in prisms, and yields an unstable *hydrobromide*. When this hydrobromide is heated with hydrobromic acid, it is converted into 4-phenyl-2-aminomethylthiazole *hydrobromide*,



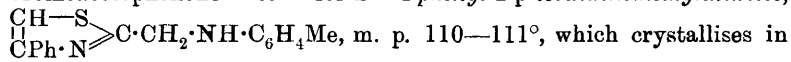
*Anisoylaminoacetonitrile*,  $OMe \cdot C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot CN$ , m. p.  $153-154^\circ$ , prepared by treating an aqueous solution of aminoacetonitrile sulphate with anisoyl chloride and potassium hydroxide, forms thin, transparent plates. *Anisoylaminoacetothioamide*,



m. p.  $189^\circ$  (decomp.), crystallises in slender prisms.

*Anilinoacetothioamide*,  $NHPh \cdot CH_2 \cdot CS \cdot NH_2$ , m. p.  $166^\circ$  (decomp.), forms stout blocks.

*p*-Toluidinoacetothioamide,  $C_6H_4Me \cdot NH \cdot CH_2 \cdot CS \cdot NH_2$ , m. p.  $152^\circ$ , crystallises in rhombic plates or tabular prisms, and reacts with bromoacetophenone to form 4-phenyl-2-*p*-toluidinomethylthiazole,



prisms. When *p*-toluidinoacetonitrile is heated with phenylthiocarbimide, 2-thio-5-phenylthiocarbamido-1-phenyl-3-*p*-tolylidihydro-

glyoxaline,  $NHPh \cdot CS \cdot NH \cdot C \begin{array}{l} \nwarrow NPh \cdot CS \\ \nearrow CH-N \cdot C_6H_4Me \end{array}$ , m. p.  $201^\circ$ , is produced, which crystallises in bright yellow needles.

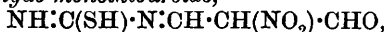
*Carbamidoacetothioamide*,  $NH_2 \cdot CO \cdot NH \cdot CH_2 \cdot CS \cdot NH_2$ , m. p.  $190-191^\circ$  (decomp.), forms colourless prisms, and condenses with bromoacetophenone with formation of 4-phenyl-2-carbamidomethyl-

thiazole,  $\begin{array}{c} \text{CH-S} \\ | \\ \text{C}_{\text{Ph}} \cdot \text{N} \end{array} \gg \text{C} \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , m. p. 190°, which crystallises in slender needles, and yields a *hydrobromide*, m. p. 214° (decomp.).  
E. G.

**Formation of 1:3-Thiazines from Thiocarbamide.** WILLIAM J. HALE and HARVEY C. BRILL (*J. Amer. Chem. Soc.*, 1912, 34, 295—300).—In an earlier paper (this vol., i, 216) it has been shown that carbamide condenses with nitromalonaldehyde with formation of 5-nitro-2-hydroxypyrimidine. It has now been found that the condensation of thiocarbamide with nitromalonaldehyde takes place in an entirely different manner.

When thiocarbamide and nitromalonaldehyde are allowed to react in aqueous solution in presence of a very small quantity of sodium hydroxide or diethylamine, the monothioureide of the aldehyde is produced. If piperidine is used as the condensing agent, however, 5-nitro-2-imino-1:3-thiazine separates, whilst a small amount of the thioureide remains in the mother liquor.

*Nitromalonaldehyde monothioureide*,

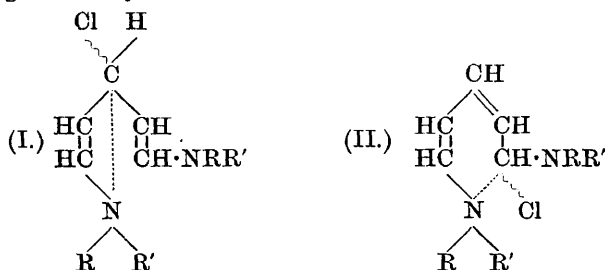


m. p. 206—207° (corr.), crystallises in lustrous, yellow leaflets, and is readily desulphurised by treatment with basic lead acetate solution or mercuric oxide; its *potassium* salt forms reddish-brown crystals; the *lead* salt was also prepared. The *methyl ether*, m. p. 78—79° (corr.), obtained by the action of methyl sulphate on an aqueous solution of the potassium salt, forms yellow plates. Phenylhydrazine acetate reacts with the thioureide with formation of the *phenylhydrazone*. When the thioureide is suspended in alcohol and piperidine added, it is transformed into 5-nitro-2-imino-1:3-thiazine.

5-Nitro-2-imino-1:3-thiazine,  $\text{NO}_2 \cdot \text{C} \begin{array}{c} \text{CH} \cdot \text{S} \\ \text{CH} \cdot \text{N} \end{array} \gg \text{C} \cdot \text{NH}$ , m. p. 151—152° (corr.), crystallises in long, yellow needles, and is not affected when boiled with an alkaline solution of lead acetate or with mercuric oxide. Phenylhydrazine and aniline do not have any effect on the compound, but benzenesulphonyl chloride reacts with it to form a yellow mass, thus establishing the presence of the imino-group. By the action of acetic anhydride, it is converted into the *acetyl* derivative,  $\text{NO}_2 \cdot \text{C} \begin{array}{c} \text{CH} \cdot \text{S} \\ \text{CH} \cdot \text{N} \end{array} \gg \text{C} \cdot \text{N} \cdot \text{Ac}$ , m. p. 141° (corr.). E. G.

**A Peculiar Auxochrome Action.** WALTER KÖNIG (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 221—223).—The colour of the pyridine dyes, obtained from pyridine and primary or secondary amines, is not satisfactorily accounted for by the usual formula:  $\text{NRR}' \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{NClRR}'$ . The yellow colour of the simplest representative, obtained from methylaniline, becomes more green when the side-chain is lengthened by saturated alkyl groups, or when an ortho-substituent is introduced into the benzene ring. On the other hand, cyclic secondary amines, such as tetrahydroquinoline or dihydroindole, change the colour to red. These changes are

accounted for if one or other of the following formulæ is used, involving subsidiary valencies :



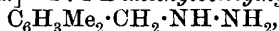
In accordance with Kaufmann's hypothesis, the subsidiary valency indicated by the dotted line should shift the colour more towards red the stronger it is. This is explained by a comparison with Kaufmann's views on benzene compounds. C. H. D.

**Optically Active Hydrazino-acids.** AUGUST DARAPSKY (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 215—216).—Hydrazino-acids of the formula  $\text{NH}_2\cdot\text{NH}\cdot\text{CHR}\cdot\text{CO}_2\text{H}$  have only been obtained in the racemic form by Traube (*Abstr.*, 1896, i, 340) and Thiele (*ibid.*, 341). The author's simpler method of preparation (*Chem. Zeit.*, 1910, 34, 1280) allows of the preparation of the active modifications.

*l*-Hydrazinophenylacetic acid,  $\text{NH}_2\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ , prepared from the *d*-chloro-acid and hydrazine hydrate, has  $[\alpha]_D^{20} - 157\cdot8^\circ$  in 2·7% solution in *N*/1-hydrochloric acid; the *d*-acid, prepared from the *l*-chloro-acid, has  $[\alpha]_D^{20} + 158\cdot0^\circ$ . The rotation is nearly the same as that of the analogous amino-acid ( $\pm 157\cdot9^\circ$ ) and of the hydroxy-acid (mandelic acid,  $\pm 157^\circ$ ). *d*- and *l*-Hydrazinophenylacetic acids crystallise from water in silvery leaflets, m. p. 183—184° (racemic compound, 188—189°). Condensation with benzaldehyde yields active *benzylidene* compounds, crystallising from dilute alcohol in slender needles, m. p. 136—138°, whilst the racemic compound has m. p. 150°. The rotatory power is  $[\alpha]_D^{20} \pm 166\cdot5^\circ$  in acetone, 2·5% solution. It has not been found possible to resolve the racemic compounds. C. H. D.

**Reduction of Aromatic Aldazines.** THEODOR CURTIUS (*J. pr. Chem.*, 1912, 85, [ii], 137—188).—A continuation of previous work (this vol., i, 137).

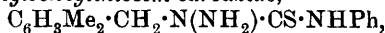
[With FRITZ MAYER.]—2 : 4-Dimethylbenzylhydrazine,



is obtained as a colourless, viscid liquid, b. p. 136—137°/13 mm., by distilling the monohydrochloride (*Abstr.*, 1900, i, 610) with calcium oxide under diminished pressure. It is very unstable, giving off nitrogen when kept, and is much less basic than the lower homologues previously described (*Abstr.*, 1901, i, 573); its *dihydrochloride*, m. p. 164°, loses hydrogen chloride very readily, and is almost completely resolved into the monohydrochloride by crystallisation from alcohol. The *sulphate*, microscopic crystals, m. p. 163°, *oxalate*, m. p. 192°, and *picrate*, lustrous, yellow needles, m. p. 148°, are described.

On exposure to air, it is oxidised to 2:4-dimethylbenzaldehyde-2:4-dimethylbenzylhydrazone, m. p. 78° (Abstr., 1900, i, 610); the oxidation may also be effected by heating the hydrochloride with mercuric oxide and alcoholic sodium hydroxide. When heated with dilute hydrochloric acid, it yields 2:4-dimethylbenzyl chloride,  $C_6H_3Me_2 \cdot CH_2Cl$ , a colourless, viscid liquid, b. p. 103—104°/19 mm., having a pleasant aromatic odour. The *dibenzoyl* derivative,  $C_6H_3Me_2 \cdot CH_2 \cdot N_2HBz_2$ , crystallises in short, colourless columns, m. p. 169—170°; the *diacetyl* derivative,  $C_{13}H_{18}O_2N_2$ , forms colourless leaflets, m. p. 129°.

2:4-Dimethylbenzylhydrazine hydrochloride reacts with potassium cyanate in aqueous solution, yields 2:4-dimethylbenzylsemicarbazide,  $C_6H_3Me_2 \cdot CH_2 \cdot N(NH_2) \cdot CO \cdot NH_2$ , columnar crystals, m. p. 162°, and with phenylthiocarbimide and alcoholic potassium hydroxide, yielding *phenyl-2:4-dimethylbenzylthiosemicarbazide*,

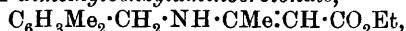


which crystallises in short, colourless columns, m. p. 138·5°.

*α-2:4-Dimethylbenzylhydrazonopropionic acid* is obtained as a yellow oil by the interaction of the hydrochloride, sodium acetate, and pyruvic acid in aqueous solution.

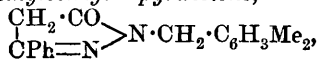
*α-Nitroso-α-2:4-dimethylbenzylhydrazine*,  $C_6H_3Me_2 \cdot CH_2 \cdot N(NO) \cdot NH_2$ , prepared from the hydrochloride and sodium nitrite, crystallises in colourless leaflets or needles, m. p. 60·5°; it reacts with 2:4-dimethylbenzaldehyde, yielding 2:4-dimethylbenzaldehyde-2:4-dimethylbenzyl-nitrosohydrazone (*loc. cit.*), and when heated at 80° with 10% sulphuric acid is converted into 2:4-dimethylbenzylazoimide,  $C_6H_3Me_2 \cdot CH_2 \cdot N_3$ . This forms a colourless liquid, b. p. 114°/15 mm., and is stable towards alkalis; it is hydrolysed by 20% sulphuric acid to hydrazoic acid and 2:4-dimethylbenzyl alcohol, small quantities of ammonia, 2:4-dimethylbenzaldehyde, 2:4-dimethylbenzylamine, and *m*-4-xyldine being produced simultaneously.

When heated with ethyl acetoacetate, 2:4-dimethylbenzylhydrazine yields *ethyl β-2:4-dimethylbenzylaminocrotonate*,



colourless leaflets, m. p. 85°, together with an oil, consisting probably of ethyl β-aminocrotonate. The formation of these two substances is considered to be due to the reduction of the hydrazine base by ethyl acetoacetate to ammonia and 2:4-dimethylbenzylamine, which then react with the ester to form ethyl β-aminocrotonate and ethyl β-2:4-dimethylbenzylaminocrotonate respectively.

3-Phenyl-1-op-dimethylbenzyl-5-pyrazolone,



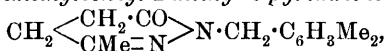
prepared by heating the hydrazine base with ethyl benzoylacetate, crystallises in colourless needles, m. p. 162°, dissolves in both acids and alkalis, and combines with *p*-toluenediazonium sulphate to form a scarlet-red *azo-dye*; its solution in aqueous ammonia gives sparingly soluble, crystalline precipitates with nickel, cobalt, copper, and silver salts.

4-Oximino-3-phenyl-1-op-dimethylbenzyl-5-pyrazolone,  $C_{18}H_{17}O_2N_3$ , obtained by the action of sodium nitrite on the preceding compound in

acetic acid solution, crystallises in slender, red needles, m. p. 128° (decomp.). On treatment with silver nitrate it forms a brownish-yellow *silver* salt, which becomes green when warmed with glacial acetic acid, and then has the composition  $C_{18}H_{16}O_3N_3Ag$ . The latter compound decomposes at 236°, and is probably the *silver* salt of 4-nitro-3-phenyl-1-op-dimethylbenzyl-5-pyrazolone.

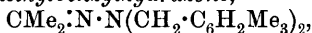
3-Phenyl-1-op-dimethylbenzyl-2-methyl-5-pyrazolone, prepared from methyl iodide and the above-mentioned phenyldimethylbenzylpyrazolone, is a brown oil.

3-Phenyl-1-op-dimethylbenzyl-2-methyl-6-pyridazinone,



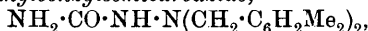
is obtained by the interaction of dimethylbenzylhydrazine hydrochloride, sodium acetate, and levulic acid in aqueous solution; it has m. p. 79·5°.

[With HARTWIG FRANZEN.]—*αα-Di-2 : 4 : 5-trimethylbenzylhydrazine*,  $NH_2 \cdot N(CH_2 \cdot C_6H_2Me_3)_2$ , prepared from the hydrochloride (Abstr., 1901, i, 293) and sodium hydroxide in aqueous alcoholic solution, crystallises in white needles, m. p. 75°, and forms a *sulphate*, needles, m. p. 151°; *nitrate*, leaflets or needles, m. p. 118° (decomp.), and *platinichloride*, m. p. 95° (decomp.). It reacts with acetone, yielding *acetonedi-2 : 4 : 5-trimethylbenzylhydrazone*,



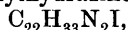
crystallising in small needles, m. p. 132°, and with isobutaldehyde to form *isobutaldehydedi-2 : 4 : 5-trimethylbenzylhydrazone*,  $C_{24}H_{34}N_2$ , m. p. 112°. When heated with acetic anhydride, it yields a *diacetyl* derivative,  $C_{24}H_{32}O_2N_2$ , m. p. 126°; the *monobenzoyl* derivative,  $C_{27}H_{32}ON_2$ , has m. p. 129°.

*Di-2 : 4 : 5-trimethylbenzylsemicarbazide*,

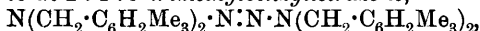


prepared from the hydrochloride and potassium cyanate in aqueous solution, crystallises in needles or leaflets, m. p. 173°.

*αα-Di-2 : 4 : 5-trimethylbenzylhydrazine* forms an *ethiodide*,

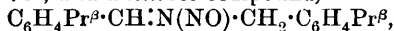


white needles, m. p. 160°, and is oxidised by mercuric oxide in chloroform solution to *di-2 : 4 : 5-trimethylbenzyltetrazone*,



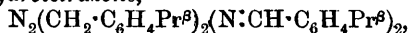
which forms white needles or leaflets.

[With REINHOLD KORTE.]—*p-Cuminaldazine*, prepared from cuminaldehyde and hydrazine sulphate, has m. p. 111° (compare Gattermann, Abstr., 1906, i, 592). On reduction with sodium amalgam in alcoholic solution it yields *p-cuminaldehyde-p-cuminyldiazine*,  $C_6H_4Pr^β \cdot CH : N \cdot NH \cdot CH_2 \cdot C_6H_4Pr^β$ , which crystallises in small, lustrous, strongly refractive, yellowish-green columns of a rhombic habit, m. p. 75° (decomp.). The diazine is unstable, becoming oily when kept. It forms a *benzoyl* derivative,  $C_{27}H_{30}ON_2$ , m. p. 78°, and a *nitroso*-compound,



crystallising in light yellow, felted needles, m. p. 59°. When heated in alcoholic solution, the nitroso-compound is converted into cuminaldazine.

*s-Di-p-cuminyldihydrazine*,  $N_2H_2(C_6H_4Pr^{\beta})_2$ , obtained by the prolonged reduction of cuminaldazine with sodium amalgam and alcohol, forms a white, wax-like mass, which rapidly decomposes; the *hydrochloride* crystallises in hexagonal plates, m. p.  $217^{\circ}$  (decomp.), the *diacetyl* derivative,  $C_{24}H_{32}O_2N_2$ , in large, rhombic columns, m. p.  $71^{\circ}$ . The *dinitroso*-derivative,  $N_2(NO)_2(C_6H_4Pr^{\beta})_2$ , forms small tufts of yellow needles, m. p.  $59^{\circ}$ , and when heated in alcoholic solution yields the above-mentioned *p*-cuminaldehydenitroso-*p*-isopropylbenzylhydrazone, together with cuminaldazine and *di-p-cuminyldiene-di-p-cuminyldihydrotetrazone*,

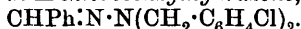


m. p.  $194^{\circ}$ . The formation of the latter compound is considered to be due to the intermediate formation of *p*-cuminaldehyde-*p*-cuminyldiazone, which is then oxidised by the nitrous acid, produced by the hydrolysis of the corresponding nitrosohydrazone, but all attempts to prepare the tetrazone by oxidising *p*-cuminyldiazone with mercuric oxide in alcoholic or benzene solution proved unsuccessful, the sole product of the oxidation consisting of cuminaldazine.

*p-Cuminyldihydrazine*,  $C_6H_4Pr^{\beta} \cdot CH_2 \cdot NH \cdot NH_2$ , obtained in the form of its *hydrochloride* (slender needles, m. p.  $199^{\circ}$ , with previous sintering at  $143^{\circ}$ ) by hydrolysing *p*-cuminaldehyde-*p*-cuminyldiazone with dilute hydrochloric acid, has m. p.  $46^{\circ}$ ; it is very unstable, and rapidly loses nitrogen at the ordinary temperature. The *nitroso*-compound,  $C_6H_4Pr^{\beta} \cdot CH_2 \cdot N(NO) \cdot NH_2$ , forms very slender, felted needles, m. p.  $63^{\circ}$ , and when heated with 10% sulphuric acid is converted into *p-cuminylazoidine*,  $C_6H_4Pr^{\beta} \cdot CH_2 \cdot N_3$ , a pale yellow oil, b. p.  $118^{\circ}/23$  mm., which is stable towards alkalis, but is decomposed by 40% sulphuric acid with the evolution of nitrogen; hydrazoic acid is not produced.

[With HERMANN WEWER].—*m*-Chlorobenzaldazine, m. p.  $141^{\circ}$  (compare Curtius and Melsbach, Abstr., 1910, i, 508), is reduced by zinc dust and glacial acetic acid in alcoholic solution to di-*m*-chlorobenzylamine. This crystallises from alcohol in small needles, m. p.  $112^{\circ}$ , and is identical with Berlin's " $\beta$ -gechlortes Bibenzylamin" (*Annalen*, 1869, 151, 141). The following salts of the amine are described: the *hydrochloride*, m. p.  $227^{\circ}$ ; *nitrate*, m. p.  $203^{\circ}$ ; *platinichloride*, brown needles, m. p.  $222^{\circ}$  (decomp.), and *nitrite*, lustrous, white needles, m. p.  $133^{\circ}$ .

*Di-m-chlorobenzylnitrosoamine*,  $NO \cdot N(CH_2 \cdot C_6H_4Cl)_2$ , prepared by boiling an alcoholic solution of the nitrite, forms clusters of yellowish-white needles, m. p.  $53^{\circ}$ , and is reduced by zinc and acetic acid in alcoholic solution to di-*m*-chlorobenzylamine and *aa-di-m-chlorobenzylhydrazine*,  $NH_2 \cdot N(CH_2 \cdot C_6H_4Cl)_2$ , which reacts with benzaldehyde, yielding *benzaldehyde-di-m-chlorobenzylhydrazone*,

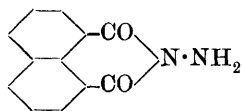


This crystallises in small, yellow needles, m. p.  $66^{\circ}$ , and is hydrolysed by hydrochloric acid to benzaldehyde and *aa-di-m-chlorobenzylhydrazine hydrochloride*, white leaflets, m. p.  $200^{\circ}$ . On treatment with sodium nitrite the preceding hydrochloride yields di-*m*-chlorobenzylamine nitrite.

*s-Di-m-chlorobenzylhydrazine*,  $N_2H_2(CH_2 \cdot C_6H_4Cl)_2$ , prepared by reducing *m*-chlorobenzaldazine with sodium amalgam and alcohol,

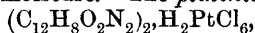
crystallises in small, white needles, m. p.  $43^{\circ}$ ; the *hydrochloride*, yellowish-white needles, m. p.  $191^{\circ}$ , the *dibenzoyl* derivative, m. p.  $88^{\circ}$ , and the *diacetyl* derivative, m. p.  $73^{\circ}$ , are described. The yellow *nitroso*-derivative,  $\text{N}_2(\text{NO})_2(\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Cl})_2$ , m. p.  $48^{\circ}$ , when heated in alcoholic solution is converted into *m-chlorobenzaldehydenitroso-m-chlorobenzylhydrazone*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}\cdot\text{N}\cdot\text{N}(\text{NO})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Cl}$ , which forms yellow needles, m. p.  $98^{\circ}$ , and is hydrolysed by hydrochloric acid to *m-chlorobenzylhydrazine hydrochloride*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{NH}_2\cdot\text{HCl}$ , colourless needles, m. p.  $134^{\circ}$ . F. B.

*N*-Aminonaphthalimide and its Derivatives. ADRIANO OSTROGOVICH and M. MIHAILESCU (*Gazzetta*, 1911, 41, ii, 757—807). —By the action of hydrazine sulphate on naphthalic anhydride the

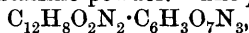


authors have obtained *N*-aminonaphthalimide, for which the annexed symmetrical formula is to be adopted in view of the reactions of the substance described below. The same substance is obtained when naphthalimide, or even naphthalic acid, is taken instead of naphthalic anhydride.

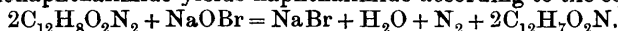
*N*-Aminonaphthalimide is obtained by treating a boiling solution of naphthalic anhydride in glacial acetic acid with a boiling aqueous solution of hydrazine sulphate and sodium acetate. Ebullition is continued for a few minutes, and, on cooling, the imide,  $\text{C}_{12}\text{H}_8\text{O}_2\text{N}_2$ , is deposited in long, lemon-yellow needles, m. p.  $262^{\circ}$  after recrystallisation. The same substance is obtained by heating hydrazine sulphate and sodium acetate with a solution of naphthalimide in aqueous glacial acetic acid for some hours in a sealed tube at  $200$ — $220^{\circ}$ . The imide can also be prepared by boiling hydrazine sulphate (or, better, hydrochloride) with a solution of naphthalic acid in aqueous potassium hydroxide. *N*-Aminonaphthalimide is a stable substance, which sublimes unchanged and is not attacked by boiling concentrated acids or alkalis. It dissolves in boiling concentrated alkalis, however, and is reprecipitated by carbon dioxide, but the solution is not to be ascribed to the production of a metallic derivative. The *sulphate* is obtained in tabular, colourless crystals by adding concentrated sulphuric acid to a solution of the base in glacial acetic acid; it is stable only in the presence of sulphuric acid of sufficient concentration. The *hydrochloride* forms small, colourless needles, and is immediately hydrolysed by traces of moisture. The *platinichloride*,



is an orange-yellow, crystalline powder. The *picrate*,

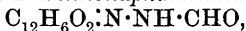


forms orange-yellow needles, m. p.  $192^{\circ}$ . When treated with sodium nitrite in the presence of glacial acetic acid, *N*-aminonaphthalimide yields naphthalimide, identical with that of Jaubert (*Abstr.*, 1895, i, 239), and nitrous oxide is evolved. With sodium hypobromite, *N*-aminonaphthalimide yields naphthalimide according to the equation:



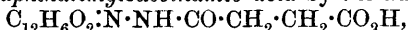
*N*-Aminonaphthalimide yields acyl derivatives, for the convenient naming of which the author proposes the term naphthalimyl to denote

the group  $C_{10}H_6 \begin{smallmatrix} <CO \\ CO > \end{smallmatrix} N-$ . For these derivatives the two tautomeric forms  $R \cdot NH \cdot CO \cdot R'$  and  $R \cdot N : C(OH) \cdot R'$  are possible, but the enolic formula is excluded, because the substances give no coloration with ferric chloride. *Formyl-N-aminonaphthalimide*,

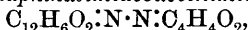


is obtained by heating *N*-aminonaphthalimide with formamide at 140° for about an hour; it forms almost colourless, prismatic crystals, m. p. 245—246°. It is a very stable substance, which dissolves unchanged in cold, strong acids or alkalis, and is hydrolysed only when these solutions are boiled. *Acetyl-N-aminonaphthalimide*,  $C_{12}H_6O_2N_2H \cdot Ac$ , obtained by boiling *N*-aminonaphthalimide with an excess of acetic anhydride, crystallises in colourless needles, m. p. 260—261°; in stability it resembles the formyl derivative. *Benzoyl-N-aminonaphthalimide*,  $C_{12}H_6O_2N_2HBz$  (from benzoic anhydride), forms colourless needles, which begin to soften at 280° and melt at 290—291°, and is also very stable towards acids and alkalis.

*N*-Aminonaphthalimide reacts with the anhydrides of dibasic acids, giving, in the case of phthalic and naphthalic anhydrides, the corresponding imide, one molecule of water being eliminated; succinic, maleic, and citraconic anhydrides yield amic acids, from which the imides may be obtained by dehydration. *N-Naphthalimidossuccinamic acid* (termed *N-naphthalimylsuccinamic acid* by the author),

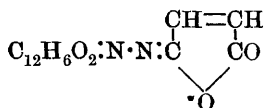


obtained by the interaction of *N*-aminonaphthalimide and succinic anhydride, either in the warm or at the ordinary temperature, forms acicular crystals, m. p. 213° (with evolution of gas, presumably steam). When it is boiled with glacial acetic acid or heated at 180° in a current of dry air, *N-naphthalimidossuccinimide*,



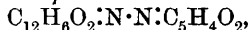
is produced; it is a white, crystalline powder, which begins to ball together towards 260°, and melts at 272—273°. This imide may be reconverted into the acid by dissolving it in dilute potassium hydroxide and adding a slight excess of dilute acetic acid or hydrochloric acid.

*N-Naphthalimidomaleinamic acid*,  $C_{12}H_6O_2 \cdot N \cdot NH \cdot CO \cdot CH : CH \cdot CO_2H$ , is a white, microcrystalline powder, m. p. 205° (decomp.). It is probably the *cis*-form, because it does not absorb bromine, and it does yield an imide. The *ammonium* salt and the *silver* salt,  $C_{16}H_5O_5N_2Ag$ , were prepared. *N-Naphthalimidomaleinimide*,  $C_{12}H_6O_2 \cdot N \cdot N : C_4H_4O_2$ , is obtained with some difficulty; it is necessary to boil the acid for some minutes with a large excess of acetyl chloride. It forms minute, acicular, colourless crystals, m. p. 118—120°; if the heating is continued, it resolidifies at 150° and melts again at 215°. The authors suppose that the treatment with acetyl chloride yields the unsymmetrical imide (annexed formula), which when heated above its melting point is transformed into the symmetrical imide; in one preparation this



isomeride was obtained direct, crystallising in small, colourless needles, m. p. 240°. *N-Naphthalimidomaleinimide* gives Piutti's reaction (with sodium methoxide or ethoxide) for substituted unsaturated imides.

*N-Naphthalimidocitraconamic acid*,  $C_{12}H_6O_2 \cdot N \cdot NH \cdot C_5H_5O_3$ , forms colourless, prismatic crystals. Like the corresponding maleinamic acid, it dissolves in alkalis, and is reprecipitated by dilute hydrochloric acid or sulphuric acid, but not by acetic acid. The ammonium and silver salts were prepared. *N-Naphthalimidocitraconimide*,



is obtained by heating the acid for some time at  $140^\circ$ , or by boiling it with glacial acetic acid. On heating it begins to soften at  $250^\circ$ , and melts at  $254-255^\circ$ . The imide can also be obtained by boiling *N*-aminonaphthalimide with an excess of citraconic anhydride. It gives Piutti's reaction.

*N-Naphthalimidophthalimide*,  $C_{12}H_6O_2 \cdot N \cdot N \cdot C_8H_4O_2$ , is obtained by the interaction of *N*-aminonaphthalimide and phthalic anhydride in presence of glacial acetic acid or chloroform in the cold. It crystallises in colourless scales, m. p. about  $320^\circ$ . It dissolves readily in alkali hydroxides, and is reprecipitated by carbon dioxide.

*N-Naphthalimidonaphthalimide*,  $C_{12}H_6O_2 \cdot N \cdot N \cdot C_{12}H_6O_2$ , is prepared by heating together equimolecular quantities of *N*-aminonaphthalimide and naphthalic anhydride at  $240-260^\circ$ . After cooling, the reaction product is dissolved in concentrated sulphuric acid, and the solution poured into an excess of water. It is a white, crystalline powder, m. p. about  $330^\circ$ . It dissolves in alkali hydroxides, and is reprecipitated by carbon dioxide. Neither this nor the preceding imide is attacked by hydrochloric acid; concentrated sulphuric acid hydrolyses them in the warm, yielding *N*-aminonaphthalimide.

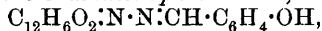
Aldehydes react with *N*-aminonaphthalimide, giving in general the Schiff's bases resulting from the elimination of the elements of water. In the case of the aromatic aldehydes containing a *p*-hydroxy-group (*p*-hydroxybenzaldehyde, protocatechualdehyde, and vanillin) an intermediate additive product is formed, which can then be dehydrated. When the *p*-hydroxy-group is substituted, however (as in anisaldehyde, veratraldehyde, and piperonaldehyde), the condensation product is obtained direct. It was not possible to isolate a formaldehyde derivative.

*Ethylidene-N-aminonaphthalimide*,  $C_{12}H_6O_2 \cdot N \cdot N \cdot CHMe$ , is obtained on mixing acetaldehyde with *N*-aminonaphthalimide; it forms small, colourless needles, m. p.  $172^\circ$ , and is readily hydrolysed.

*Benzylidene-N-aminonaphthalimide*,  $C_{12}H_6O_2 \cdot N \cdot N \cdot CHPh$  (obtained in presence of acetic acid or on warming with an excess of benzaldehyde), crystallises in colourless needles, m. p.  $206-207^\circ$ .

*Cinnamylidene-N-aminonaphthalimide*,  $C_{12}H_6O_2 \cdot N \cdot N \cdot CH \cdot CH \cdot CHPh$ , prepared in the same manner as the preceding derivative, forms small, colourless needles, m. p.  $195-196^\circ$ .

*o-Hydroxybenzylidene-N-aminonaphthalimide*,



crystallises in thin, colourless needles, m. p.  $230-231^\circ$ .

When a mixture of *N*-aminonaphthalimide and *p*-hydroxybenzaldehyde is kept in the presence of glacial acetic acid, the *additive product*,  $C_{12}H_8O_2N_2 \cdot C_7H_6O_2$ , is obtained in the form of thin, colourless needles. If it is boiled with glacial acetic acid, *p-hydroxybenzylidene-N-aminonaphthalimide*,  $C_{12}H_6O_2 \cdot N \cdot N \cdot CH \cdot C_6H_4 \cdot OH$ , is obtained; it

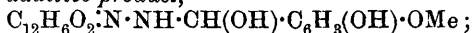
crystallises in slightly yellow prisms, which begin to soften at  $270^{\circ}$ , and melt at  $283\text{--}284^{\circ}$  (decomp.).

*p*-Methoxybenzylidene-*N*-aminonaphthalimide,  $\text{C}_{12}\text{H}_6\text{O}_2\text{:N:N:C}_8\text{H}_8\text{O}$ , crystallises in colourless needles, which begin to ball together at  $210^{\circ}$ , and melt at  $216\text{--}217^{\circ}$ .

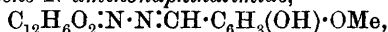
When resorcilaldehyde reacts with *N*-aminonaphthalimide, a mixture of the *additive product* and the imide is formed, which, on boiling with glacial acetic acid, yields 2:4-dihydroxybenzylidene-*N*-aminonaphthalimide,  $\text{C}_{12}\text{H}_6\text{O}_2\text{:N:N:CH}\cdot\text{C}_6\text{H}_3(\text{OH})_2$ , which crystallises in slightly yellow prisms, which become red about  $180^{\circ}$ , and then almost black, and melt at  $289\text{--}290^{\circ}$  (with slow heating); when placed in a bath at  $285^{\circ}$ , the substance becomes reddish-purple, balls together, and melts at  $288\text{--}289^{\circ}$  (decomp.).

*N*-Aminonaphthalimide and protocatechualdehyde, in presence of glacial acetic acid, yield an *additive product*,  $\text{C}_{12}\text{H}_6\text{O}_2\text{:N:N:C}_7\text{H}_6\text{O}_3$ , a slightly yellow, microcrystalline powder, which, on heating, becomes brown at  $260^{\circ}$  and black at  $280^{\circ}$ . When it is boiled with glacial acetic acid, 3:4-dihydroxybenzylidene-*N*-aminonaphthalimide,  $\text{C}_{12}\text{H}_6\text{O}_2\text{:N:N:CH}\cdot\text{C}_6\text{H}_3(\text{OH})_2$ , is obtained; it crystallises in small, pale yellow prisms.

*N*-Aminonaphthalimide and vanillin in presence of glacial acetic acid yield the *additive product*,

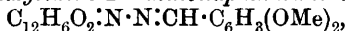


it crystallises in tufts of yellow needles, which soften and ball together about  $220^{\circ}$ , and melt at  $226\text{--}227^{\circ}$ . When it is heated at  $130\text{--}140^{\circ}$  (or at  $160^{\circ}$ ), or boiled with glacial acetic acid, it yields 4-hydroxy-3-methoxybenzylidene-*N*-aminonaphthalimide,



which crystallises in long, colourless needles, softens about  $228^{\circ}$ , and melts at  $231\text{--}232^{\circ}$ .

3:4-Dimethoxybenzylidene-*N*-aminonaphthalimide,



is obtained by keeping an alcoholic solution of *N*-aminonaphthalimide and veratraldehyde for two days; it forms colourless needles, m. p.  $229\text{--}230^{\circ}$ .

Piperonylidene-*N*-aminonaphthalimide,



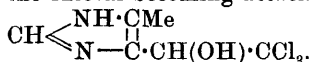
obtained from piperonaldehyde in glacial acetic acid at the ordinary temperature, forms small, colourless needles, m. p.  $256\text{--}257^{\circ}$ .

When *N*-aminonaphthalimide is boiled with an excess of *p*-benzoquinone in glacial acetic acid, *N*-naphthalimido-*p*-benzoquinonemonoimine,  $\text{C}_{12}\text{H}_6\text{O}_2\text{:N:N:C}_6\text{H}_4\text{:O}$ , is obtained as a slightly brown, microcrystalline precipitate. The compound is soluble in alkali hydroxides, giving an orange or red coloration, and is reprecipitated by dilute hydrochloric acid or carbon dioxide. The substance dissolves in concentrated sulphuric acid, giving a red solution with a violet tinge, and is precipitated unaltered on addition of water.

R. V. S.

Condensation of 5(4)-Methylglyoxaline with Chloral. OTTO GERNGROSS (*Ber.*, 1912, 45, 509—526. Compare Abstr., 1909, i, 189).—The condensation of 4-methylglyoxaline with chloral is

analogous to that with formaldehyde (Windaus, Abstr., 1909, i, 258), the chloral becoming attached to the ring in position 5 (or 4), namely,



The ester hydrochloride,  $\text{HCl}, \text{CH} \begin{array}{c} \text{NH} \cdot \text{CMe} \\ \diagup \quad | \\ \text{N} - \text{C} \cdot \text{CHCl} \cdot \text{CO}_2\text{Me} \end{array}$ , and the hydrochloride of the corresponding acid contain an extremely labile chlorine atom. In aqueous solution at  $0^\circ$  the chlorine is precipitated completely by silver nitrate; when the aqueous solution is evaporated the hydrochloride of the hydroxy-acid is formed quantitatively. This chlorine atom reacts with sodium methoxide with the formation of the methoxy-compound,  $\text{HCl}, \text{CH} \begin{array}{c} \text{NH} \cdot \text{CMe} \\ \diagup \quad | \\ \text{N} - \text{C} \cdot \text{CH}(\text{OMe}) \cdot \text{CO}_2\text{Me} \end{array}$ .

When the hydroxy-acid is warmed with dilute nitric acid, a mixture of two nitrates is obtained, which are separated by boiling with 90% alcohol. The faintly basic nitrate of the  $\alpha$ -ketonic acid is hydrolysed, whereas the more basic nitrate of 4-methylglyoxaline-5-carboxylic acid remains in solution.

The ketonic acid,  $\text{CH} \begin{array}{c} \text{NH} \cdot \text{CMe} \\ \diagup \quad | \\ \text{N} - \text{C} \cdot \text{CO} \cdot \text{CO}_2\text{H} \end{array}$ , forms a crystalline oxime with a characteristic sodium salt. When heated with aniline, carbon dioxide is eliminated, and the base,  $\text{CH} \begin{array}{c} \text{NH} \cdot \text{CMe} \\ \diagup \quad | \\ \text{N} - \text{C} \cdot \text{CH} \cdot \text{NPh} \end{array}$ , formed. When reduced with aluminium amalgam the hydroxy-acid is reformed.

5(4)-Methylglyoxaline-4(5)-carboxylic acid,  $\text{CH} \begin{array}{c} \text{NH} \cdot \text{CMe} \\ \diagup \quad | \\ \text{N} - \text{C} \cdot \text{CO}_2\text{H} \end{array}$ , is the main product of the oxidation of methylglyoxalineglycollic acid with concentrated nitric acid. The ethyl ester of this acid is obtained synthetically on boiling thioglyoxaline with 10% nitric acid.

The *hydrobromide* of 5(4)-methylglyoxalineglycollic acid crystallises in short, pointed needles, m. p.  $184-185^\circ$  (decomp.). The *hydrobromide* of the *ester* is obtained in lancet-shaped crystals pointed at both sides, which sinter at  $160^\circ$ , m. p.  $166^\circ$  (decomp.); the *hydrochloride* of the acid crystallises in four-sided prisms, m. p.  $183-184^\circ$  (decomp.); that of the *ester* forms rhombic and lancet-shaped platelets, which sinter at  $147^\circ$ , m. p.  $150.5^\circ$ .

5(4)-Methylglyoxaline-4(5)-glycollic acid crystallises in well-formed, lustrous plates and stunted prisms, which become brown at  $205^\circ$ , m. p.  $215^\circ$ , to a reddish-brown foam. The *nitrate* crystallises in long, six-sided plates, decomp.  $150^\circ$ ; the *phosphotungstate* separates in microscopic needles; the *sodium* salt forms plates. The *copper* salt yields narrow, four-sided rods of a pale blue colour.

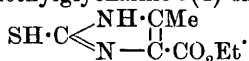
5(4)-Methylglyoxaline-4(5)-chloroacetic acid *hydrochloride*, prepared by the action of acetyl chloride on methyl methylglyoxalineglycollate hydrochloride, and isolated first in the form of the *methyl ester hydrochloride*, which crystallises in crossed needles sintering at  $165^\circ$ , m. p.  $167^\circ$  (decomp.), crystallises in stout, lustrous, four-sided, rhombic plates, which becomes yellow at  $190^\circ$ , m. p.  $204^\circ$  (decomp.).

5(4)-Methylglyoxaline-4(5)-glyoxylic acid crystallises in short rods and needles, which become brown at 230° and begin to decompose at 240°. The *sodium* salt forms transparent, four-sided plates with oblique ends; the *nitrate* has pointed crystals, which begin to decompose at 200°; the *hydrochloride* crystallises in six-sided plates, which become brown at 235° and decomp. at 242°. The *oxime* crystallises in needles, which sinter at 225°, m. p. 228° (decomp.); it forms a characteristic *sodium* salt, crystallising in thin, flat needles, m. p. 210° (decomp. to a black mass).

Methylglyoxalineglyoxylic acid, when reduced by aluminium amalgam in alcoholic aqueous sodium hydroxide solution, is converted into methylglyoxalineglycollic acid.

The *anil* of 5(4)-methylglyoxaline-4(5)-aldehyde crystallises in sharp needles, m. p. 224° (decomp. to blackish-brown drops).

5(4)-Methylglyoxaline-4(5)-carboxylic acid, prepared by oxidation of methylglyoxalineglycollic acid with concentrated nitric acid, crystallises in long, thin, matted needles, m. p. 223° (decomp.), and sublimes in flat needles when heated above 200°. At the melting point carbon dioxide is eliminated, and methylglyoxaline formed. The *ammonium* salt is not stable; the *potassium* salt has decomp. 238°. The *hydrochloride* crystallises in lustrous platelets, m. p. 230° (decomp.); the *phosphotungstate* is obtained in small, thin, four-sided plates. The *ethyl* ester, prepared by heating the potassium salt with ethyl alcohol and ethyliodide, crystallises in long rods with oblique ends, m. p. 205—206°, and is identical with the product obtained synthetically from ethyl 2-thiol-4(5)-methylglyoxaline-5(4)-carboxylate,



The *sodium* salt crystallises in long, slender needles, m. p. 240°; the *nitrate* forms four-sided plates, m. p. 167° (decomp.); the *hydrochloride* has m. p. 183° (some decomp.). The ester is hydrolysed on prolonged boiling with concentrated hydrochloric acid to 5(4)-methylglyoxaline-4(5)-carboxylic acid.

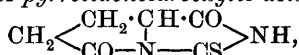
E. F. A.

**Constitution of the Supposed Pyrazolinecarboxylic Acid.** CARL BÜLOW (*Ber.*, 1912, 45, 528—533. Compare Bülow, this vol., i, 134).—Polemical. A reply to Buchner (this vol., i, 213). Pyrazoline compounds which contain no carboxyl group distil without decomposition, whereas Buchner's compound very readily loses nitrogen when heated; it is not believed possible for the carboxyl group to make this difference. Buchner's pyrazolidine from ethyl phenylpyrazolidinecarboxylate boils without decomposition, whereas the known pyrazolidines are very unstable. These and other reasons are quoted against assigning a pyrazoline structure to Buchner's compound. E. F. A.

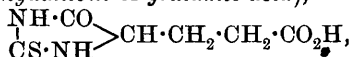
**Hydantoins. X. Action of Potassium Thiocyanate on Pyrrolidonecarboxylic Acid. 2-Thiohydantoin-4-propionic Acid.** TREAT B. JOHNSON and HERBERT H. GUEST (*Amer. Chem. J.*, 1912, 47, 242—251).—Johnson and Nicolet (this vol., i, 53) have

shown that by the action of potassium thiocyanate on either glycine or acetylglycine in presence of acetic anhydride, the same 2-thio-3-acetylhydantoin is produced, and Johnson (*J. Biol. Chem.*, 1912, 11, 97) has found that, under similar conditions, alanine and acetylalanine both yield the same 2-thio-3-acetyl-4-methylhydantoin. A study has now been made of the behaviour of potassium thiocyanate towards pyrrolidonecarboxylic acid in presence of acetic anhydride, and it has been found that the corresponding cyclic thiohydantoin is produced.

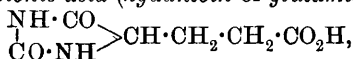
The thiohydantoin of pyrrolidonecarboxylic acid,



m. p. 206° (decomp.), forms long, prismatic crystals, and is hydrolysed by dilute hydrochloric acid with production of 2-thiohydantoin-4-propionic acid (thiohydantoin of glutamic acid),



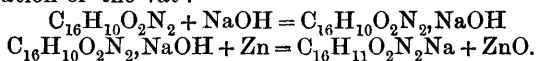
m. p. 122°, which crystallises in rhombic plates. The latter thiohydantoin is readily desulphurised by chloroacetic acid with formation of hydantoin-4-propionic acid (hydantoin of glutamic acid),



m. p. 165°, which crystallises in hexagonal, tabular prisms; this compound is also produced, but in smaller yield, by the action of chloroacetic acid on pyrrolidonecarboxylic acid thiohydantoin.

Attempts were made to synthesise 2-thiohydantoin-4-propionic acid by the action of potassium thiocyanate on glutamic acid dissolved in water, alcohol, or acetic anhydride, but without success. E. G.

**Theory of the Indigo Vat.** ARTHUR BINZ and KURT SCHÄDEL (*Ber.*, 1912, 45, 586—597. Compare Abstr., 1911, i, 497).—The authors summarise the results of previous work in support of the view that in the formation of the indigo-vat, the indigotin is not directly reduced to indigo-white, but first combines with one or two molecules of sodium hydroxide (or other alkali hydroxide) to form an additive compound (compare Abstr., 1906, i, 749), from which oxygen is then removed by the reducing agent (for example, zinc) employed in the preparation of the vat:



If this interpretation is correct, the velocity of vat formation should be increased by replacing the free indigotin by the above-mentioned additive compound, and this is found to be the case. Zinc, iron, and magnesium react much more rapidly on the additive compound with sodium hydroxide than on indigotin in the presence of the same amount of free alkali.

Bromindigotin and dibromindigotin react with sodium ethoxide in alcoholic solution, yielding the compounds,  $\text{C}_{16}\text{H}_9\text{O}_2\text{N}_2\text{Br}, \text{NaOH}$  and  $\text{C}_{16}\text{H}_8\text{O}_2\text{N}_2\text{Br}_2, \text{NaOH}$ , which are decomposed by washing with alcohol more readily than the corresponding compound of indigotin. The

alkali derivatives of the tetrahalogenoindigotins, on the other hand, are very stable.

With respect to the fixation of indigotin in the fibre, the authors consider that the first stage consists in the chemical union of the fibre with the indigo-white, and that this union remains intact during the subsequent oxidation. It is very improbable that a colloidal complex with the fibre is first produced, since it is found that colloidal indigotin cannot be fixed on the fibre.

F. B.

**Bromo- and Methoxy-derivatives of Indigotin.** PAUL FRIEDLÄNDER, S. BRUCKNER, and G. DEUTSCH (*Annalen*, 1912, 388, 23—49). —Dibromo- and dimethoxy-indigotins containing the substituents in positions 4:4', 5:5', 7:7', and 6:6' have been synthesised from the corresponding *o*-nitrobenzaldehydes or anthranilic acids with the object of ascertaining the influence of the substituents on the colours of the dyes. The colours of the first three dyes, in solution or on the fibre, do not markedly differ from that of indigotin itself; 6:6'-dichloro-, 6:6'-dibromo-, and 6:6'-dimethoxy-indigotin, however, exhibit a very different, reddish-violet shade.

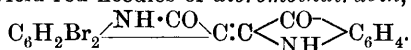
6-Bromo-2-nitrotoluene, m. p. 38°, obtained from 2-nitro-*o*-toluidine by the Gattermann method in the cold, is reduced by tin, stannous chloride, and hydrochloric acid to 6-bromo-*o*-toluidine, a yellow oil, the *acetyl* derivative, m. p. 163°, of which is oxidised to *bromoacetyl-anthranilic acid*,  $\text{NHAc} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CO}_2\text{H}$ , m. p. 224°, by potassium permanganate at 80° in the presence of magnesium sulphate. This acid is converted by boiling sulphuric acid (1:1) into *m*-bromoaniline (*acetyl* derivative, m. p. 84°), but when hydrolysed by 10% sodium hydroxide yields 6-bromoanthranilic acid, m. p. 136°. The latter is boiled with an excess of chloroacetic acid in aqueous sodium carbonate, and the resulting 3-bromophenylglycine-2-carboxylic acid is converted in the usual manner into 4:4'-dibromoindigotin, which crystallises from chloroform in blue needles with a copper lustre, exhibits pronounced dichroism in solution, and yields a normal vat with alkaline hyposulphite.

5:5'-Dibromoindigotin has already been prepared by Baeyer (*Ber.*, 1879, 12, 1315). It is obtained by the direct bromination of indigotin in anhydrous solvents, and can also be produced from 5-bromoanthranilic acid. 4-Bromophenylglycine-2-carboxylic acid has m. p. 227—228° (decomp.).

6:6'-Dibromoindigotin, a constituent of the antique purple dye obtained from *Murex brandaris* (Abstr., 1909, ii, 262), has been prepared by Sachs from *p*-bromo-*o*-nitrobenzaldehyde (Abstr., 1904, i, 593). The authors prepare it in larger quantity from the bromoanthranilic acid (*acetyl* derivative, m. p. 217°). 5-Bromophenylglycine-2-carboxylic acid, m. p. about 236°, is a yellow, crystalline powder, and yields 6-bromoacetylindoxyl, m. p. 118·5°, by boiling with acetic anhydride and sodium acetate. Attempts to prepare 7:7'-dibromoindigotin from the bromoanthranilic acid have been unsuccessful. It has been obtained in very small yield by an application of Bauer's isatin synthesis (Abstr., 1907, i, 603). *o*-Bromo-oxanilide, m. p. 205°, is

boiled with phosphorus pentachloride in toluene, and the resulting *di-o-bromophenylloxaliminochloride*,  $\begin{matrix} \text{CCl:N}\cdot\text{C}_6\text{H}_4\text{Br} \\ \text{CCl:N}\cdot\text{C}_6\text{H}_4\text{Br}' \end{matrix}$  m. p. 110°, yellow needles, is heated at 100° with 100% sulphuric acid, whereby *7-bromoisatin*,  $\text{C}_6\text{H}_3\text{Br}\cdot\text{C}\begin{matrix} \text{NH} \\ \text{CO} \end{matrix}\text{CO}$ , m. p. 192°, reddish-yellow needles, is obtained. 7-Bromoisatin responds to the indophenin test, and by warming in benzene with phosphorus pentachloride and subsequently treating the solution with hydrogen sulphide, yields *7:7'-dibromoindigotin*, which crystallises in needles with a copper lustre.

Indoxyl condenses with 5:7-dibromoisatin chloride in benzene to form *5:7-dibromoindigotin*, blue needles, and with 5:7-dibromoisatin in acetic acid to yield red needles of *dibromoindirubin*,



*2-Amino-6-methoxybenzonitrile*, m. p. 141°, colourless needles, obtained by the reduction of 2-nitro-6-methoxybenzonitrile by tin, stannous chloride, and hydrochloric acid, forms an *acetyl* derivative, m. p. 176°, and is not hydrolysed by acids or alkalis, dilute or concentrated, hot or cold, but is slowly attacked by very concentrated sodium hydroxide at 160—170°, yielding *2-amino-6-methoxybenzamide*, m. p. 150°. This substance, unlike the nitrile, reacts readily with chloroacetic acid in boiling, concentrated sodium carbonate, yielding *3-methoxyphenylglycine-2-carboxylamide*,  $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p. 208° (decomp.), yellow crystals, from which sodium hydroxide at 170—190° or boiling acetic anhydride and sodium acetate (and atmospheric oxygen) produce *4:4'-dimethoxyindigotin*, needles with a copper lustre.

*5:5'-Dimethoxyindigotin*, blue needles with a copper lustre, is obtained from 2-nitro-5-methoxybenzaldehyde, acetone, and dilute sodium hydroxide in the usual manner.

2-Acetylamino-*p*-cresol and methyl sulphate in alkaline solution yield the *methyl ether*,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NHAc}$ , m. p. 95° (the corresponding *ethyl ether* has m. p. 126°). These ethers are oxidised to the corresponding acids by boiling aqueous potassium permanganate and magnesium sulphate. *4-Methoxyacetylanthranilic acid*, m. p. 199° (decomp.), and *4-ethoxyacetylanthranilic acid*, m. p. 182—183°, yield by hydrolysis with dilute sulphuric acid (1:1) *4-methoxyanthranilic acid*, m. p. 166° (decomp.) (*methyl ester*, m. p. 75°), and *4-ethoxyanthranilic acid*, m. p. 174° respectively. These acids react with chloroacetic acid in boiling 10% sodium hydroxide, the products yielding, after acidification, *5-methoxyphenylglycine-2-carboxylic acid*,

$\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p. 159—161° (decomp.), brown, microscopic needles, and *5-ethoxyphenylglycine-2-carboxylic acid*, m. p. 166—167°, red, microscopic needles respectively, from which the *6:6'-dialkyloxyindigotins* are obtained in the usual manner.

*7:7'-Dimethoxyindigotin*, needles with a copper lustre, is prepared from the nitromethoxybenzaldehyde, acetone, and sodium hydroxide.

C. S.

**Action of Thioacetic Acid on Cyanoguanidine (Synthesis of Thioliminomethyltriazine).** ADRIANO OSTROGOVICH (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 213—217. Compare Abstr., 1911, i, 1036).—When cyanoguanidine is heated with an ethereal solution of thioacetic acid for about two hours until the evolution of hydrogen sulphide ceases, 6-thiol-2-imino-4-methyl-1:3:5-triazine,  $C_4H_6N_4S$ , is precipitated. A further portion can be obtained from the solution, so that the total yield is 93%. The pure substance forms small, colourless crystals, which decompose without melting; for it the formula:  $N \begin{smallmatrix} \text{CMe}=\text{N} \\ \text{C}(\text{SH})\cdot\text{NH} \end{smallmatrix} > \text{C}\cdot\text{NH}$ , or the tautomeric thionic form, is suggested. The compound is soluble in acids, in alkali hydroxides, and in ammonia.

R. V. S.

**Researches on Purines. V. 2-Oxy-1-methylpurine.** CARL O. JOHNS (*J. Biol. Chem.*, 1912, 11, 73—79).—Five of the six isomerides of 2-oxymethylpurine have been already described. The sixth, 2-oxy-1-methylpurine, can be obtained from 5:6-diamino-3-methyldihydro-2-pyrimidone. The potassium salt of nitrocytosine (5-nitro-6-amino-dihydro-2-pyrimidone) is methylated by methyl iodide, and the product is found to be 5-nitro-6-amino-3-methyldihydro-2-pyrimidone, crystallising in slender prisms, m. p. 274° (decomp.). When this is reduced with freshly precipitated ferrous hydroxide, it gives a good yield of 5:6-diamino-3-methyldihydro-2-pyrimidone, which in turn reacts with formic acid to give a *formyl* derivative, the potassium salt of which when heated lost water and so formed the potassium salt of 2-oxy-1-methylpurine. This purine crystallises in flat prisms containing  $2H_2O$ ; decomp. 280°. They effloresce in the air and become anhydrous over sulphuric acid. An aqueous solution gives sparingly soluble precipitates with platinum chloride and picric acid. The *picrate* has m. p. 214° (decomp.).

W. D. H.

**A Purine-Hexose Compound.** JOHN A. MANDEL and EDWARD K. DUNHAM (*J. Biol. Chem.*, 1912, 11, 85—86).—A preliminary note on a compound of adenine and hexose separated from an extract of yeast. It forms sheaves of delicate acicular crystals, and melts at 206°. Analysis shows close agreement with the figures calculated from the formula  $C_{11}H_{15}O_5N_5$ . A phenylosazone obtained from it yielded 15.3% nitrogen. The hexose has not yet been identified.

W. D. H.

**Existence of Complexes between Purine Substances and Sodium Salicylate.** GIOVANNI PELLINI and MARIO AMADORI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 290—295. Compare Abstr., 1910, i, 525).—By measurements of the depression of the freezing point of aqueous solutions of sodium salicylate to which caffeine and theobromine, respectively, are added, the authors establish the existence of complexes similar to those formerly described. The tendency to their formation is more marked than in the case of sodium benzoate, and it is greater for caffeine than for theobromine.

Measurements of the solubility in water at 25° and at 40° of

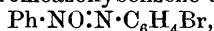
pharmaceutical "sodium salicylate and caffeine" show that the product is not a mixture, as in the case of "sodium benzoate and caffeine," but on this point further experiments are needed. R. V. S.

**Xanthine Derivatives from Uric Acid. IV. Preparation of Xanthine and Hypoxanthine.** ERNST E. SUNDWIK (*Zeitsch. physiol. Chem.*, 1912, **76**, 486—488. Compare Abstr., 1911, i, 584).—Xanthine is formed to the extent of 30—33% when uric acid is heated at 200° with oxalic acid in presence of much glycerol.

Xanthine is converted into hypoxanthine by dissolving in excess of sodium hydroxide and shaking with chloroform at 60—70° during two hours. E. F. A.

**Azoxy-compounds.** ANGELO ANGELI and BRUNO VALORI (*Atti R. Accad. Lincei*, 1912, [v], **21**, i, 155—165. Compare Angeli and Alessandri, Abstr., 1911, i, 1045).—In the present paper two more pairs of isomeric azoxy-compounds are described, namely,  $\alpha$ - and  $\beta$ -*p*-bromoazoxybenzene and  $\alpha$ - and  $\beta$ -4-bromo-4'-nitroazoxybenzene.

When azoxybenzene is treated with bromine without a solvent,  $\alpha$ -*p*-bromoazoxybenzene,  $C_{12}H_9ON_2Br$ , is obtained; it forms straw-yellow crystals, m. p. 73° (previously given as 75°). Oxidation of *p*-bromoazobenzene with hydrogen peroxide in glacial acetic acid solution, the mixture being kept at 40—50° for some days, yields  $\alpha$ -*p*-bromoazoxybenzene, m. p. 73°, identical with that above described, and, in addition,  $\beta$ -*p*-bromoazoxybenzene, which forms yellow crystals, m. p. 92°. It is not possible to convert the two *p*-bromoazoxybenzenes into each other directly, and therefore they do not resemble the stereoisomeric azoxy-compounds of Reissert (Abstr., 1909, i, 435), but both the isomerides now described yield *p*-bromoazobenzene again on reduction with aluminium amalgam.  $\alpha$ -*p*-Bromoazoxybenzene is not acted on by bromine, but  $\beta$ -*p*-bromoazoxybenzene when treated with bromine yields 4:4'-dibromoazoxybenzene. The constitutions of the two substances may be derived from this fact, because it is probable (in view of the formation of the bromo-derivatives about to be described, and of others already known) that a bromine atom attaches itself in the para-position in the nucleus in every NPh· group. The authors therefore ascribe to  $\alpha$ -*p*-bromoazoxybenzene the formula



whilst  $\beta$ -*p*-bromoazoxybenzene is  $NPh \cdot NO \cdot C_6H_4Br$ .

When bromine is added to *p*-nitroazobenzene in the presence of traces of iodine, 4-bromo-4'-nitroazobenzene,  $C_{12}H_8O_2N_3Br$ , is obtained; it forms dark red crystals, m. p. 203°. The bromination cannot be effected in glacial acetic acid even in sunlight. The action of nitric acid (D 1·45) on *p*-bromoazobenzene yields the same 4-bromo-4'-nitroazobenzene.

When  $\alpha$ -*p*-bromoazoxybenzene is greatly warmed with nitric acid (D 1·45) a compound,  $C_{12}H_8O_3N_3Br$ , m. p. 99°, is obtained; in this substance the bromine and the nitro-group are probably attached to the same benzene nucleus. Treatment of  $\alpha$ -*p*-bromoazoxybenzene with concentrated sulphuric acid for an hour on the water-bath leads to the production of *p*-bromoazobenzene and 4-bromo-4'-hydroxyazobenzene.

The addition of bromine to *p*-bromoazobenzene yields 4:4'-dibromoazobenzene,  $C_{12}H_8N_2Br_2$ , which forms dark orange-yellow crystals, m. p. 204°. If this substance is kept at 100° for twelve hours with hydrogen peroxide, 4:4'-dibromoazoxybenzene is obtained, identical with that prepared by brominating  $\beta$ -*p*-bromoazoxybenzene.

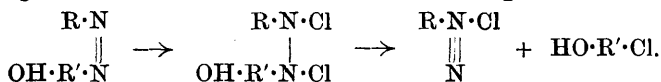
$\alpha$ -4-Bromo-4'-nitroazoxybenzene,  $C_6H_4Br \cdot N \cdot NO \cdot C_6H_4 \cdot NO_2$ , m. p. 194°, is obtained by keeping 4-bromo-4'-nitroazobenzene in glacial acetic acid solution with hydrogen peroxide at 100° for a day.  $\beta$ -4-Bromo-4'-nitroazoxybenzene,  $C_6H_4Br \cdot N \cdot NO \cdot C_6H_4 \cdot NO_2$ , is formed by treating  $\beta$ -*p*-nitroazoxybenzene,  $NPh \cdot NO \cdot C_6H_4 \cdot NO_2$  (compare Angelo and Alessandri, *loc. cit.*), with bromine in the presence of iodine in the warm; it crystallises in minute, pale yellow prisms, m. p. 203°. Nitric acid (D 1.45) reacts with  $\beta$ -*p*-bromoazoxybenzene, yielding  $\alpha$ -4-bromo-4'-nitroazoxybenzene, identical with that above described.

R. V. S.

**Scission of Azo-dyes by Halogens.** MAXIMILIAN P. SCHMIDT (*J. pr. Chem.*, 1912, [ii], 85, 235—240).—*p*-Hydroxyazobenzene is converted by the action of chlorine or hypochlorous acid in aqueous solution into benzenediazonium chloride and 2:4:6-trichlorophenol, and by bromine into benzenediazonium bromide and 2:4:6-tribromophenol.

Sodium diazobenzenesulphonate when subjected to the same treatment also yields benzenediazonium salts (compare Fischer, *Abstr.*, 1878, 302), and a similar decomposition has been observed in the case of a large number of azo-dyes.

With respect to the mechanism of the reaction, it is imagined that an additive compound with the halogen is first produced, which then undergoes decomposition as shown in the following scheme:



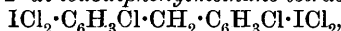
F. B.

**Aromatic Substances Containing Multivalent Iodine.** LUIGI MASCARELLI and B. TOSCHI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 145—151. Compare Mascarelli and Cerasoli, *Abstr.*, 1910, i, 725; Mascarelli, Toschi, and Zambonini, *ibid.*, 831).—Attempts to prepare six-membered rings containing iodine have not been successful. Only in one case, namely, from the tetrazo-compound from 2:2'-diamino-4:4'-tetramethyldiaminodiphenylmethane, was a small quantity of a yellow powder obtained, which had m. p. 220—225°, and showed the properties of an *iodonium base*. In the present paper some *endo-bisazo-derivatives* (compare Duval, *Abstr.*, 1910, i, 703, 781) are described, which were obtained during the course of the work.

When 2:2'-diamino-4:4'-dichlorodiphenylmethane is treated with nitrous acid, the tetrazo-compound is obtained. This reacts with potassium iodide, yielding 4:4'-dichloro-2:2'-di-iododiphenylmethane and a substance,  $C_{13}H_8N_4Cl_2$ , which crystallises in golden-yellow scales decomposing at 260—265°. To it is assigned the constitution

of *pp'*-dichloroendobisazodiphenylmethane,  $\text{C}_6\text{H}_3\text{Cl} \begin{array}{c} \diagup \\ \text{N}_2 \end{array} \text{C} \begin{array}{c} \diagdown \\ \text{N}_2 \end{array} \text{C}_6\text{H}_3\text{Cl}$ . This compound when treated with sulphuric acid yields a crystalline substance (not analysed) which decomposes at  $249\text{--}252^\circ$ . Its alcoholic solution gives an intense green coloration with ferric chloride, and to it the constitution of 4 : 4'-dichloro-2-hydroxyendoazodiphenylmethane  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Cl}\cdot\text{CH} \begin{array}{c} \diagup \\ \text{N}_2 \end{array} \text{C}_6\text{H}_3\text{Cl}$ , is ascribed.

4 : 4'-Dichloro-2 : 2'-di-iododiphenylmethane tetrachloride,



is obtained in yellow crystals, m. p. about  $102^\circ$  (evolving chlorine), when chlorine is passed through a chloroform solution of 4 : 4'-dichloro-2 : 2'-di-iododiphenylmethane. It is a very stable substance, and does not form iodoso- and iodoxy-derivatives when treated with the reagents which usually effect that change, and it was also impossible to obtain the di-iodoxy-derivative by oxidation with chlorine or with Caro's acid.

R. V. S.

**Azo dyes from Substituted Pyrroles.** HANS FISCHER and E. BARTHOLOMÄUS (*Zeitsch. physiol. Chem.*, 1912, 76, 478--485).—In view of their importance for recognising and characterising blood and bile pigments, the azo-dyes from a number of substituted pyrroles have been prepared by interaction with diazobenzenesulphonic acid. Monoazo-compounds were obtained in all cases.

The compound,  $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_4\text{NHMe}_2\cdot\text{COMe}$ , from 2 : 4-dimethyl-3-acetylpyrrole crystallises in long, lustrous, red needles.

The compound,  $\text{C}_{15}\text{H}_{17}\text{O}_5\text{N}_3\text{S}$ , from ethyl 2 : 5-dimethylpyrrole-3-carboxylate crystallises in long, greenish-olive, rhombic needles.

The compound,  $\text{C}_{18}\text{H}_{19}\text{O}_5\text{N}_3\text{S}$ , from 2 : 5-dimethylpyrrole-3-carboxylic acid separates in yellowish-brown needles.

The compound,  $\text{C}_{12}\text{H}_{13}\text{O}_5\text{N}_3\text{S}$ , from 2 : 5-dimethylpyrrole is obtained in tiny, microscopic, orange needles. The corresponding dye from 2 : 4-dimethylpyrrole crystallises in yellowish-brown needles.

Hæmopyrrole picrate has m. p.  $125^\circ$  (corr.); it does not readily condense with diazobenzenesulphonic acid. The free hæmopyrrole couples very readily, however, forming orange-yellow needles of the compound,  $\text{C}_{14}\text{H}_{17}\text{O}_3\text{N}_3\text{S}$ ; it dissolves in concentrated sulphuric acid with a greenish-yellow coloration, and is totally different from the azo-dye obtained from 2 : 4-dimethyl-3-ethylpyrrole.

E. F. A.

**Losses in the Isolation of the Monoamino-acids [from Proteins] by the Ester Method.** II. EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1912, 77, 59--74. Compare *Abstr.*, 1911, i, 1049).—The pure amino-acids either singly or mixed were esterified, distilled, and hydrolysed, the amount recovered and the losses at each stage of the operation being determined. In this way the proportion recovered was from glycine 62.5%, from *d*-alanine 70%, and *dl*-leucine 80%. From a mixture of all five amino-acids there was obtained 50% of the glycine, 57% of the alanine, 66% of the leucine, 58% of the glutamic acid, and 40% of the *l*-aspartic acid. *d*-Valine is

recovered to the extent of 68%, *l*-phenylalanine only to the extent of 54%. In presence of protein the yields are still less.

It is considered that if these losses by the isolation of the monoamino-acids are taken into account, the proteins are almost entirely composed of the already known constituents.

E. F. A.

**Introduction of Iodine into Protein Derivatives.** HERMANN PAULY (*Zeitsch. physiol. Chem.*, 1912, 76, 291—292).—Basic nitrogenous substances exposed to the action of excess of iodine form brown periodides, in which the iodine is only loosely attached. Iodo-protein compounds must be colourless, and retain their iodine after treatment for a short time with sulphurous acid. The iodotryptophan described by Neuberg (Abstr., 1907, i, 955) is considered to be a periodide; it is not possible to introduce iodine into tryptophan or monobenzoyltryptophan.

E. F. A.

**Estimation of Amino-groups in the Oxyproteic Acids of Normal Urines.** JÓZEF BROWINSKI and STEPHANE DĄBROWSKI (*Bull. Acad. Sci. Cracow*, 1911, A, 587—595; *Zeitsch. physiol. Chem.*, 1912, 77, 92—106).—Determinations have been made of the ammonia and amino-nitrogen in the oxyproteic acids both before and after hydrolysis, using Sørensen's method of titration with formaldehyde.

Urochrome and *allooxyproteic acid* before hydrolysis contain about 2.7% of ammonia nitrogen and 2.4%, and 6.4% respectively of amino-nitrogen. *antiOxyproteic* and *oxyproteic acids*, which are not precipitated by basic lead acetate, contain no ammonia, but 11.2% and 38.8% respectively of amino-nitrogen. It is believed that the last two acids constitute the greater proportion of the oxyproteic acids of urine.

Hydrolysis with boiling hydrochloric acid leads to the formation of melanins and secondary products; hydrofluoric acid can be used to effect hydrolysis at the temperature of a boiling water-bath, and with it a much larger proportion of amino-acid nitrogen is obtained.

Melanin is formed from urochrome when hydrolysis with hydrofluoric acid is prolonged, but not from any other of the oxyproteic acids. This is taken to indicate that the oxyproteic acids are not to be regarded as the mother substances of the urinary pigment.

The proportions of ammonia and amino-nitrogen given by the four acids when decomposed with hydrofluoric acid for twenty-four hours are as follows: urochrome,  $\text{NH}_3$  8.7%,  $\text{NH}_2$  26.4%; *allooxyproteic acid*,  $\text{NH}_3$  4.2%,  $\text{NH}_2$  76.9%; *antioxyproteic acid*,  $\text{NH}_3$  3.2%,  $\text{NH}_2$  33.9%; *oxyproteic acid*,  $\text{NH}_3$  8.3%,  $\text{NH}_2$  80.5%.

E. F. A.

**Hæmoglobin.** EUGEN LETSCHE (*Zeitsch. physiol. Chem.*, 1912, 76, 243—257. Compare Abstr., 1910, i, 599).—The absorption number (*A*) of hæmoglobin solutions, that is, the ratio of concentration (*c*) to the extinction coefficient (*e*), should be a constant independent of the apparatus used and the observer, if the method is to be used to measure the concentration of hæmoglobin solutions. Measurements made to test this indicate the value  $2.081 \times 10^{-3}$  for *A*, in agreement with Hüfner's original determinations, but differing from the value

$1.87 \times 10^{-3}$  determined by Butterfield, and previously used by the writer (Abstr., 1910, i, 599), whose values must be corrected accordingly. The amount of carbon monoxide fixed per gram of hæmoglobin is 1.36 c.c., which is in excellent agreement with the value 1.34 determined by Hüfner and by Butterfield. E. F. A.

**The Behaviour of Carbon Monoxide Blood to Certain Precipitating Agents.** KURT GESTEWITZ (*Zeitsch. exp. Path. Ther.*, 1911, Reprint 15 pp.).—Vegetable agglutinins, such as ricin and phasin, precipitate from carbon monoxide blood, the carboxyhæmoglobin in the corpuscles; zinc and copper salts precipitate it free from the corpuscles. The copper precipitate (produced by adding 1% copper sulphate solution) in normal blood is brown in colour, in carbon monoxide blood red, which is quite characteristic to the eye; no spectroscopic investigation is necessary. The colour difference with zinc salts is not so striking. The zinc carboxyhæmoglobin can be readily dried, and then remains undecomposed for weeks. W. D. H.

**The Cleavage of Nucleic Acid by Organ Enzymes.** ALFRED SCHITTENHELM and KARL WIENER (*Zeitsch. physiol. Chem.*, 1912, 77, 77—85).—The experiments confirm on the whole the results of Levene and Medigreceanu, and relate to the enzymes concerned in nucleic acid cleavage in various tissue extracts; the products of cleavage inhibit the activity of the enzymes concerned. W. D. H.

**Yeast Nucleic Acids. V. Structure of Pyrimidine Nucleosides.** PHŒBUS A. LEVENE and FREDERICK B. LA FORGE (*Ber.*, 1912, 45, 608—620. Compare Levene and Jacobs, Abstr., 1911, i, 96, 510).—The pyrimidine complexes in nucleic acid are very resistant towards the hydrolytic action of dilute mineral acids. When distilled with hydrochloric acid (D 1.06) for thirty-six hours, furfuraldehyde is liberated slowly, corresponding in amount with equimolecular proportions of ribose and base in the complex. When hydrolysed by hydrobromic acid in presence of bromine, cytidine is converted into 5-bromouracil and *d*-ribonic acid. Uridine or cytidine when treated with bromine in aqueous solution yields a solution which reduces Fehling's solution and forms a crystalline precipitate when heated with phenylhydrazine; this behaviour indicates that the double bond has remained intact.

When uridine is evaporated with concentrated nitric acid, an anhydride of two molecules of nitrouridinecarboxylic acid is obtained, which is readily converted into its ethyl or butyl esters, and when hydrolysed gives nitrouracil.

Alkyl derivatives of uridine or cytidine could not be obtained.

Both compounds are fairly easily reduced to dihydro-compounds, which are very easily hydrolysed by mineral acids, giving ribose and dihydro-derivatives of the bases. It is assumed that the glucoside formation between ribose and the base involves position 5 in the base, and that the contiguity of this to the double bond conditions the resistance to hydrolysis.

The preparation of uridine has been simplified by conversion of the

ribose into glucoside, which prevents its precipitation together with the base with lead acetate or barium hydroxide.

Cytidine is conveniently isolated as the sparingly soluble nitrate, m. p. 197°. The *free base* crystallises in long needles, which sinter at 220°, m. p. 230° (decomp.),  $[\alpha]_D^{21} + 29.63^\circ$ .

5-Bromouridine is very similar to uridine; it has m. p. 181—184°,  $[\alpha]_D^{21} - 15.4^\circ$ .

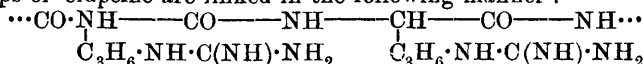
Hydroxyuridine (corresponding with 5-bromo-4-hydroxydihydro-uracil) has m. p. 222—223°; the phenylhydrazide forms long, citron-yellow needles, m. p. 209°.

The *anhydride* of *nitrouridinecarboxylic acid*,  $C_{18}H_{16}O_{17}N_6$ , crystallises in short, thick prisms, decomp. above 200°; the *silver* salt is amorphous. The *ethyl* ester forms slender needles, decomp. above 200°; the *n-butyl* ester sinters at 185°, m. p. 190—192°.

Dihydrouridine is a colourless syrup,  $[\alpha]_D + 39.1^\circ$ .

E. F. A.

**Free Amino-groups of the Simplest Proteins.** ALBRECHT KOSSEL and ALEXANDER T. CAMERON (*Zeitsch. physiol. Chem.*, 1912, **76**, 457—463. Compare Kossel and Kennaway, *Abstr.*, 1911, i, 667).—Nitroclupeine, obtained by nitration of clupeine, yields a nitroarginine on hydrolysis. This nitroarginine when treated with nitrous acid by van Slyke's process yields nitrogen corresponding with the decomposition of one amino-group. Since the amino-groups of guanidine and nitroguanidine are not decomposed by this reagent, the reactive amino-group can only be that of the ornithine residue, and the arginine groups of clupeine are linked in the following manner:



In further support of this formula it is shown that clupeine behaves similarly to guanidine when nitrated, it has the same acid-fixing power as the guanidine-groups in the molecule, and, lastly, unchanged clupeine gives no nitrogen by van Slyke's process.

Cyprinine, the protamine of carp sperm, contains at least 30.3% of its total nitrogen in the form of lysine; 23.6% of the total nitrogen is set free by nitrous acid.

In sturine about 6.9% of the total nitrogen is liberated; this roughly corresponds to the total amount of lysine present, but this quantity is not enough to make up all the acid-fixing groups of sturin.

E. F. A.

**Electrical Transport of Colloids.** LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Zeitsch. physiol. Chem.*, 1912, **76**, 385—387. Compare Pekelharing and Ringer, *Abstr.*, 1911, i, 1051).—A criticism of the arrangement adopted by Pekelharing and Ringer in measuring the electrical transport of pepsin. It is regarded as important that the middle and side vessels should have exactly the same hydrogen ion concentration.

E. F. A.

**Compounds of Amino-acids and Ammonia.** VII. PETER BERGELL and PAUL BOLL (*Zeitsch. physiol. Chem.*, 1912, **76**, 464—467).—To establish whether the asymmetric hydrolysis of leucinamide was

brought about by a special enzyme or by the usual protein- or peptide-splitting enzymes, the effect of the addition of *N*-hydrochloric acid to the enzyme solution has been studied. The enzyme hydrolysing silk peptone was but little affected, those digesting casein and fibrin were only partly destroyed, but that acting on leucinamide was entirely killed, unchanged optically inactive leucinamide being recovered. Accordingly, the last change is attributed to a specific enzyme.

E. F. A.

**Comparative Hydrolysis of Sucrose by Various Acids in Presence of Invertase.** GABRIEL BERTRAND, M. ROSENBLATT, and (Mme.) M. ROSENBLATT (*Bull. Soc. chim.*, 1912, [iv], 11, 176—186. Compare Abstr., 1898, ii, 128; 1909, i, 272; Sørensen, Abstr., 1910, i, 147; Euler and Ugglas, Abstr., 1910, i, 345, 796; Michaelis and Davidsohn, Abstr., 1911, i, 1051, 1052).—Previous investigations beginning with those of Kjeldahl in 1881 have shown that the activity of invertase and other enzymes is modified by the presence of acids or alkalis, but the conclusions arrived at as to the quantities of acids or alkalis that are most effective and as to the general laws governing these actions have been very variable.

In the present investigation account has been taken of the alkalinity of the yeast extract and of the sucrose solutions employed and disturbing influences due to these causes, and to variation in the yeast and the sucrose employed have been avoided. The results are summarised and tabulated in the original. They show that the acids, grouped according to their basicity, arrange themselves for activity at optimum concentrations, taking hydrochloric acid as 100, in the same order as for their catalytic activity on sucrose. Among the monobasic acids, trichloroacetic, dichloroacetic, and lactic acids are exceptional in their behaviour. The monobasic acids become more active as catalysts in presence of invertase, and this is also true, but to a less extent, for dibasic acids, whilst for tribasic acid the inverse holds. No explanation can be given at present of the exceptional behaviour of the three acids referred to already, or of the great increase in catalytic activity shown by aromatic sulphonic acids in presence of invertase.

T. A. H.

**Cellulase.** HANS VON EULER (*Zeitsch. angew. Chem.*, 1912, 25, 250—251).—A brief account of the work of earlier investigators on the action of bacteria and fungi on cellulose is given, and the conclusion is drawn that the hydrolysis of pure cellulose by enzymes derived from fungi or higher forms of plant life has not yet been demonstrated.

It is shown in the present communication that cellulose-dextrins, obtained by the action of strong sulphuric acid on cellulose, are converted under the influence of an enzyme (*cellulose-dextrinase*) occurring in the extract obtained by pressing *Merulius lacrimans* into substances having a greater reducing action on Fehling solution; that the change is brought about by an enzyme is demonstrated by the fact that very little change takes place if the extract is heated before being added to the cellulose-dextrin solution.

W. H. G.

**Synthetic Action of Enzymes.** WILLIAM M. BAYLISS (*Proc. physiol. Soc.*, 1911-12, xl-xli; *J. Physiol.*, 43).—Using glycerol to reduce the water content, the synthesis by emulsin of quinol and dextrose to form arbutin can readily be observed in a week or less. A small degree of synthesis can readily be detected polarimetrically. This experiment lends itself well to class work. W. D. H.

**The Nature of Enzyme Action. II. The Synthetic Properties of Anti-Emulsin.** WILLIAM M. BAYLISS (*J. Physiol.*, 1912, 43, 455-466).—Intraperitoneal injection of emulsin does not give rise to any true anti-enzyme, although precipitins for the proteins contained in the solution are produced. The inhibitory action of serum so obtained on emulsin is no greater than that of normal serum, and is merely due to diminution of optimal acidity. Neither normal serum nor the immune serum has any synthetic action. Emulsin, on the other hand, will synthesise lactose and also the glucoside of glycerol. This synthesis is retarded by serum, probably owing to diminution of acidity. Emulsin is not a protein. W. D. H.

**Influence of Protoplasmic Poisons on Reductase.** D. FRASER HARRIS (*Bio-Chem. J.*, 1912, 6, 200-202).—The activity of this intracellular enzyme is not affected by reagents, such as chloroform, sodium fluoride, etc., which lessen the activity of, or destroy, protoplasm. W. D. H.

**The Nitration of Arsanilic Acid.** LUDWIG BENDA (*Ber.*, 1912, 45, 53-58).—The brownish-yellow substance obtained in addition to diazoarsanilic acid, mononitroarsanilic acid, and *s*-trinitroaniline in the nitration of arsanilic acid has the composition  $C_6H_6O_7N_3As$ .

As the action of bromine in alkaline solution gives 4-bromo-2:6-dinitroaniline (m. p.  $158^\circ$ , compare Austen, this Journ., 1876, ii, 513), and the action of potassium hydroxide yields 3:5-dinitro-4-hydroxyphenyl-arsinic acid (Benda and Bertheim, this vol., i, 63), the compound must be 3:5-dinitro-4-aminophenylarsinic acid. In the fact that it resists diazotisation, it resembles *s*-trinitroaniline. D. F. T.

**Preparation of Aromatic Stibines.** LUDWIG KAUFMANN (D.R.-P. 240316).—Triphenylstibine can be obtained in 80-90% yield and m. p.  $53^\circ$  (Michaelis and Reese give m. p.  $48^\circ$ ) by boiling triphenylstibine sulphide (100 parts) with absolute alcohol (450 parts) and benzene (50 parts) during half an hour, adding copper powder, and continuing the heating during three hours; on cooling, the product separates in a pure condition. The copper can be replaced by iron in the presence of ferric chloride, or the mixture left at the ordinary temperature during about fifteen hours, and finally boiled for one hour. F. M. G. M.

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## Organic Chemistry.

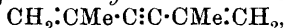
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**Asphalt Theory of Naphtha-formation: New Work on the Genesis of Naphtha.** K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 354—359. Compare Abstr., 1904, ii, 180; 1905, ii, 43; 1907, i, 269; ii, 361; 1909, i, 39).—The naphtha synthesised by the method of Sabatier and Senderens (Abstr., 1907 i, 269) consists of unsaturated liquid hydrocarbons which have a high iodine number, and readily oxidise and become tarry. If, however, the catalytic substance is insufficiently heated, instead of a liquid product, a black, polymerised tarry substance resembling natural asphalt is obtained. The qualitative and quantitative resemblance between some of the fractions obtained on distilling naphtha and natural asphalt has already been pointed out by the author, and a similar resemblance is now found with the distillation products of this artificial asphalt.

The conclusion is drawn that the formation of naphtha is a more complex process than is assumed by the theories of Mendeléeff, Berthelot, and Cloëz, these only dealing with the initial stage of the process, namely, the formation of unsaturated hydrocarbons from carbides. These hydrocarbons, by a process of polymerisation, give solid natural bitumen (asphalt), which, on decomposition by heat or on spontaneous decomposition occupying countless years, yield liquid naphtha. This process is probably reversible, since naphtha, by oxidation or other processes, may be converted into more complex products similar to asphalt, and undoubtedly possessing a cyclic structure. Destructive distillation of the tarry matter formed by the condensation of naphtha gives a naphtha rich in paraffins. The author regards the asphalt theory of the formation of naphtha as definitely established.

T. H. P.

**Preparation of Hydrocarbons with Two Double and One Triple Linking.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 241424).— $\beta$ *ε*-Dimethylhexa- $\Delta^{\alpha\epsilon}$ -dien- $\Delta^{\gamma}$ -inene,



a colourless oil, b. p. 32°/17 mm., was obtained by distilling the tetramethylglycol,  $\text{OH}\cdot\text{CMe}_2\cdot\text{C}:\text{C}\cdot\text{CMe}_2\cdot\text{OH}$  (142 parts), with potassium hydrogen sulphate (50 parts) at 140—150° under atmospheric pressure, whilst  $\gamma$ *η*-dimethyl- $\Delta^{\delta}$ -octinen- $\gamma$ *η*-diol,  $\text{OH}\cdot\text{CMeEt}\cdot\text{C}:\text{C}\cdot\text{CMeEt}\cdot\text{OH}$ , colourless crystals, m. p. 53°, b. p. 126°/20 mm., when distilled with anhydrous oxalic acid furnished  $\gamma$ *η*-dimethylocta- $\Delta^{\alpha\alpha}$ -dien- $\Delta^{\delta}$ -inene,  $\text{CHMe}\cdot\text{CMe}\cdot\text{C}:\text{C}\cdot\text{CMe}\cdot\text{CHMe}$ , an oil, b. p. 71°/20·5 mm.

F. M. G. M.

**The Inflammable Capacity of Mixtures of Methyl Chloride and Air.** SAPOSHNIKOFF (*Zeitsch. ges. Schiess. Sprengstoffwesen*, 1911, 6, 384).—A study of the combustion of mixtures of methyl chloride and air in varying proportions and at different temperatures. The heat of combustion of one kilo. of methyl chloride is 3099 calories, whereas

the corresponding figure for methane is 13,000; the conditions under which methyl chloride explodes are also considered in the original.

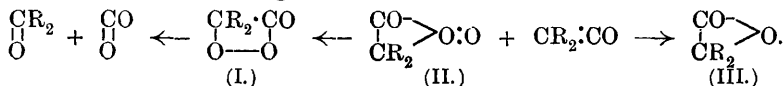
F. M. G. M.

**Thermal Analysis of Hexachloroethane and of its Binary Mixtures.** PAUL PASCAL (*Compt. rend.*, 1912, 154, 883—886).—The ordinary cooling curve for hexachloroethane reveals the existence of three modifications, the  $\alpha$ -variety stable above  $125^\circ$ , the  $\beta$ -variety existing between  $71.6^\circ$  and  $125^\circ$ , and the  $\gamma$ -form, stable below  $71.6^\circ$ . The transition point  $125^\circ$  being ill defined on the curve, the accurate value was found from the curves for mixtures of the hexachloride with naphthalene and phenanthrene. Mixtures containing not more than 8% of naphthalene or 13% of phenanthrene show the unusual property of remaining solid at  $71.6^\circ$ , but undergoing partial liquefaction when the temperature falls slightly. The curves are reproduced and fully discussed in the original.

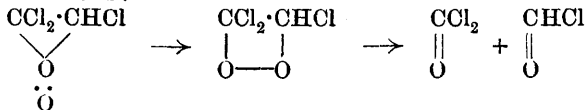
The cryoscopic constant for hexachloroethane is 560. W. O. W.

**Autoxidation of Trichloroethylene.** HERMANN STAUDINGER (*J. pr. Chem.*, 1912, [ii], 85, 330—333).—Remarks on Erdmann's paper on this subject (this vol., i, 65). From investigations on the autoxidation of the ketens, the author has come to the conclusion that the addition of oxygen to an autoxidisable substance, A, takes place unsymmetrically, thus:  $A + >O:O \rightarrow A:O:O$ , and not symmetrically,  $A < \begin{smallmatrix} O \\ | \\ O \end{smallmatrix}$ , as hitherto imagined.

The autoxidation products of ketens consist of oxides of the type (I), which, in some cases, may be isolated, but readily decompose into ketones and carbon dioxide, together with oxides of the type (III), produced by the decomposition of the initial product (II), as shown in the following scheme:



The author agrees on the whole with the views expressed by Erdmann on the autoxidation of trichloroethylene, but represents the formation of carbon monoxide, carbonyl chloride, and hydrogen chloride as follows:



F. B.

**Ethylenic Isomerism of Acetylene Dichloride.** GEORGES CHAVANNE (*Compt. rend.*, 1912, 154, 776—777).—Commercial acetylene dichloride consists of a mixture of two isomerides which can be separated by fractional distillation. The two compounds have b. p.  $49^\circ/760$  mm. and  $60.2^\circ/760$  mm. respectively. Both unite with bromine, yielding the same dibromide, m. p.  $-26^\circ$ , b. p.  $195^\circ/760$  mm.

W. O. W.

**Action of Potassium Hydroxide on Tertiary Alcohols: New Method for the Diagnosis of Alcohols.** MARCEL GUERBET (*Compt. rend.*, 1912, 154, 713—715. Compare this vol., i, 67, 154).—Tertiary alcohols are scarcely attacked by potassium hydroxide below 230°. Above this temperature, oxidation slowly occurs, and the acids produced contain fewer carbon atoms than the original alcohol. Formic and propionic acids were recognised amongst the products from dimethylethylcarbinol, whilst a small amount of butyric acid was obtained from  $\beta$ -methylpentan- $\beta$ -ol. W. O. W.

**Catalytic Dehydration of Aliphatic Alcohols in the Wet Way by Sulphuric Acid.** JEAN B. SENDERENS (*Compt. rend.*, 1912, 154, 777—779. Compare Abstr., 1910, i, 649; 1911, i, 600—637).—Tertiary alcohols, even the lowest in the series, readily yield the corresponding ethylenic hydrocarbons when boiled with 3 to 4% of their volume of sulphuric acid. In the case of the secondary alcohols, this decomposition does not occur below the  $C_5$  term, whilst with primary alcohols dehydration is inappreciable below the  $C_8$  term. The function of the sulphuric acid appears to be purely catalytic, and not to depend merely on its capacity to absorb water. Its efficiency as a catalyst depends on the boiling point of the mixture, the low boiling alcohols only undergoing decomposition in presence of a relatively large amount of acid, whilst the high boiling, tertiary alcohols lose water equally readily in the presence of a much smaller proportion of acid. W. O. W.

$\Delta^{\alpha}$ -Penten- $\delta$ -ol,  $CH_3:CH:CH_2\cdot CHMe\cdot OH$ . HENRI PARISELLE (*Compt. rend.*, 1912, 154, 710—712).—Magnesium turnings (24 grams) are treated successively with allyl bromide (10 grams) and acetaldehyde (4 grams). On treating the product in the usual way,  $\Delta^{\alpha}$ -penten- $\delta$ -ol is obtained as a colourless liquid, b. p. 115—116°,  $D^{20}_D$  0.840,  $n^{20}_D$  1.425; the *acetyl* derivative has b. p. 132—135°. Phosphorus pentachloride converts it into a mixture of  $\beta\delta$ -dichloropentane and  $\delta$ -chloro- $\Delta^{\alpha}$ -pentene, b. p. 97—100°. W. O. W.

$\alpha$ -Dimethoxy- $\Delta^{\beta}$ -pentinene and its Hydrogenation. ROBERT LESPIEAU (*Compt. rend.*, 1912, 154, 886—888).— $\alpha$ -Dimethoxy- $\Delta^{\beta}$ -pentinene,  $OMe\cdot CH_2\cdot C:C\cdot CH_2\cdot CH_2\cdot OMe$ , prepared from the magnesium derivative of  $\delta$ -methoxy- $\Delta^{\alpha}$ -butinene (Abstr., 1907, i, 581), has b. p. 176—177°/760 mm.,  $D^{16}_D$  0.9385,  $n^{16}_D$  1.442. By addition of bromine it yields  $\beta\gamma$ -dibromo- $\alpha$ -dimethoxy- $\Delta^{\beta}$ -pentene, b. p. 132—133°/15 mm. Hydrogenation in presence of platinum black leads to the formation of  $\alpha$ -dimethoxypentane and  $\alpha$ -methoxypentane, the latter being formed with loss of methyl alcohol. W. O. W.

**Hydrolysis and Constitution of Lecithin.** FERNAND MALENGREAU and GEORGES PRIGENT (*Zeitsch. physiol. Chem.*, 1912, 77, 107—120. Compare Abstr., 1911, ii, 795).—Lecithin is hydrolysed by acids in the same manner as glycerolphosphoric acid; fatty acid and phosphoric acid are eliminated simultaneously, although the fatty acid is split off much more quickly, the difference being the more marked as the catalytic activity of the acid increases.

The choline group in lecithin does not behave as if it were an ester group attached to phosphoric acid. It is rapidly eliminated at the same rate as the fatty acids.

After two hours' heating of lecithin-cadmium chloride with *N*/10-sulphuric acid, hydrolysis is incomplete; nearly all the choline has been eliminated, but only 3.9% of the glycerolphosphoric acid has been resolved. As heating is continued, the glycerolphosphoric acid is progressively hydrolysed, and after seventy-two hours' heating this has occurred to about the extent of three-fourths.

With *N*/10-hydrochloric acid, the fatty acids are completely eliminated from lecithin in eight hours, but only 12.8% of the glycerolphosphoric acid is hydrolysed.

E. F. A.

**Action of Phosphorus Trichloride on Organic Acids: Monoacetylphosphorous Acid.** BENJAMIN T. BROOKE (*J. Amer. Chem. Soc.*, 1912, **34**, 492—499).—The reaction between phosphorus trichloride and acetic acid is represented in certain text-books by the equation (1)  $3\text{CH}_3\cdot\text{CO}_2\text{H} + 2\text{PCl}_3 \rightarrow 3\text{CH}_3\cdot\text{COCl} + \text{P}_2\text{O}_3 + 3\text{HCl}$ , and in others by the equation (2)  $3\text{CH}_3\cdot\text{CO}_2\text{H} + \text{PCl}_3 \rightarrow 3\text{CH}_3\cdot\text{COCl} + \text{P}(\text{OH})_3$ . A study of this reaction has now been made, and has shown that equation (2) is correct, whilst equation (1), indicating the formation of phosphorous oxide, is entirely wrong.

Two secondary reactions take place, the more important of which is expressed thus:  $\text{CH}_3\cdot\text{CO}_2\text{H} + \text{CH}_3\cdot\text{COCl} \rightleftharpoons (\text{CH}_3\cdot\text{CO})_2\text{O} + \text{HCl}$ . It has been found that when the preparation is carried out in the usual way under a reflux condenser, the hydrogen chloride required to convert the acetic anhydride into the chloride escapes from the reaction mixture. If, however, the mixture of glacial acetic acid and phosphorus trichloride is left at 18° for six hours under a slight pressure (equivalent to 10 cm. of concentrated sulphuric acid), only a small amount of hydrogen chloride escapes, and the formation of acetic anhydride is almost completely obviated.

The other secondary reaction results in the formation of acetylphosphorous acid, thus:  $\text{P}(\text{OH})_3 + \text{CH}_3\cdot\text{COCl} = \text{P}(\text{OH})_2\cdot\text{OAc} + \text{HCl}$ . *Acetylphosphorous acid* can be prepared in a pure state by adding 40 c.c. of acetic anhydride to 5 grams of phosphorous acid at the ordinary temperature, treating the mixture with 10 c.c. of acetyl chloride, and warming to 50°. The compound separates in white crystals, and, after the supernatant liquid has been decanted, is washed with ether and dried under a pressure of 10 mm.

When acetyl chloride is prepared by using the quantities of acetic acid and phosphorus trichloride indicated by equation (1), phosphorous oxide is not produced, but the residue consists of phosphorous acid and a small amount of the acetyl derivative. The phosphorus trichloride in excess of that required by equation (2) can be recovered.

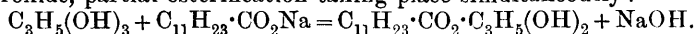
The quantity of hydrogen chloride evolved by the action of acetyl chloride on phosphorous acid has been estimated, and the results indicate that a diacetyl derivative may possibly be formed, although it could not be isolated.

E. G.

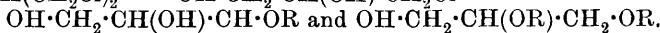
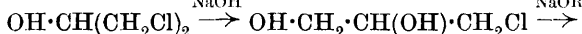
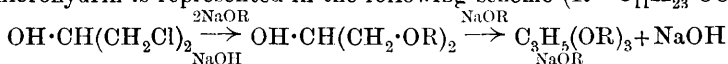
**Ethyl Dinitroacetate.** ANDRÉ WAHL (*Ann. Chim. Phys.*, 1912, [viii], 25, 421—430).—A more detailed account of work already published (Abstr., 1903, i, 225; 1904, i, 795). In the action of nitric acid on ethyl hydrogen malonate there is formed, in addition to ethyl dinitroacetate, some ethyl furoxandicarboxylate. In general, ethyl dinitroacetate is formed by the action of nitric acid on compounds of the following types:  $\text{CHR}:\text{CH}\cdot\text{CO}_2\text{Et}$ ;  $\text{CRR}:\text{CH}\cdot\text{CO}_2\text{Et}$ ;  $\text{CHR}:\text{C}(\text{COMe})\cdot\text{CO}_2\text{Et}$ . Ethyl dinitroacetate decomposes slowly when kept, or at once when heated, forming nitric acid and ethyl furoxandicarboxylate (compare Jovitschitsch, Abstr., 1902, i, 202).

T. A. H.

**Action of Concentrated Sulphuric Acid on Trilaurin.** B. W. VAN ELDIK THIEME (*J. pr. Chem.*, 1912, [ii], 85, 284—307).—The preparation of mono- and di-glycerides by the action of alkali salts of aliphatic acids on glycerol mono- and di-chlorohydrins (Guth, *Diss.*, Rostock, 1902; Krafft, Abstr., 1904, i, 136) is not recommended by the author, as it is found that a mixture of glycerides is produced; thus, sodium laurate and glycerol  $\alpha$ -monochlorohydrin yield a mixture of monolaurin, dilaurin, and trilaurin, whilst with glycerol  $\alpha\gamma$ -dichlorohydrin the product consists mainly of dilaurin and trilaurin. An explanation of these results was obtained from the behaviour of glycerol towards sodium laurate; when heated at  $100^\circ$ , a mixture of these substances becomes alkaline, owing to the formation of sodium hydroxide, partial esterification taking place simultaneously:



A similar esterification, resulting in the formation of a mixture of glycerides, occurs with the glycerol chlorohydrins; the production of monolaurin,  $\alpha\beta$ - and  $\alpha\gamma$ -dilaurin, and trilaurin from glycerol  $\alpha\gamma$ -dichlorohydrin is represented in the following scheme ( $\text{R} = \text{C}_{11}\text{H}_{23}\cdot\text{CO}$ ).



These results also afford an explanation of the widely divergent values given in the literature for the m. p.'s of mono- and di-glycerides.  $\beta$ -Monolaurin (compare Grün and Skopnik, Abstr., 1910, i, 356) is obtained in a pure condition as follows: glycerol  $\alpha\gamma$ -dichlorohydrin is converted by means of chlorosulphonic acid into  $\text{SO}_3\text{H}\cdot\text{O}\cdot\text{CH}(\text{CH}_2\text{Cl})_2$ , which reacts with lauric acid at  $45^\circ$ , yielding  $\beta$ -laurio- $\alpha\gamma$ -dichlorohydrin,  $\text{C}_{11}\text{H}_{23}\cdot\text{CO}_2\cdot\text{CH}(\text{CH}_2\text{Cl})_2$ , a pale yellow liquid, b. p.  $180\text{—}181^\circ/4$  mm.; this is transformed into the corresponding *iodohydrin* by means of sodium iodide in alcoholic solution, the iodohydrin heated with silver nitrite, and the resulting ester of nitrous acid hydrolysed with hydrochloric acid.  $\beta$ -Monolaurin has m. p.  $60.5^\circ$ .  $\alpha$ -Monolaurin, prepared from  $\alpha\beta$ -dibromohydrin in a similar manner, has m. p.  $58.9^\circ$ ; Grün and Skopnik (*loc. cit.*) give  $52^\circ$ .

$\alpha$ -Laurio- $\beta\gamma$ -dibromohydrin has b. p.  $197\text{—}198^\circ/3$  mm.

$\alpha\beta$ -Dilaurio- $\gamma$ -chlorohydrin, prepared by the successive action of chlorosulphonic acid and lauric acid on glycerol  $\alpha$ -chlorohydrin, has

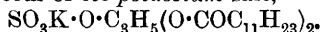
b. p. 185—195°/5 mm., m. p. 30°; Grün and Schacht (Abstr., 1907, i, 462) give 24°. It is converted by the method described above into  $\alpha\beta$ -dilaurin,  $\text{OH}\cdot\text{C}_3\text{H}_5(\text{O}\cdot\text{CO}\cdot\text{C}_{11}\text{H}_{23})_2$ , m. p. 56·3°.

$\alpha\alpha$ -Dilaurin, obtained together with  $\alpha\beta$ -dilaurin by heating glycerol with lauric acid, is an oil; the product obtained by Grün and Schacht (*loc. cit.*) by the interaction of sodium laurate and  $\alpha\alpha$ -dichlorohydrin, and described by them as  $\alpha\alpha$ -dilaurin, consists mainly of  $\alpha\beta$ -dilaurin and trilaurin.

Lauric acid forms with sulphuric acid a crystalline compound of the composition  $\text{C}_{11}\text{H}_{23}\cdot\text{CO}_2\text{H}, 1\frac{1}{2}\text{H}_2\text{SO}_4$ ; a similar compound is also formed from  $\beta$ -lauro- $\alpha\gamma$ -dichlorohydrin.

The action of strong sulphuric acid on trilaurin has also been studied. It is found that an additive compound is first produced, which then undergoes decomposition, the lauryl groups being replaced by  $\text{SO}_3\text{H}$ . By partly hydrolysing the product,  $\beta$ -monolaurin and  $\alpha\beta$ -dilaurin, together with a small amount of  $\alpha\alpha$ -dilaurin, were obtained. For complete decomposition of trilaurin into glyceryltrisulphuric acid, a large excess of sulphuric acid and a low temperature are necessary.

The first product of the decomposition,  $\alpha\beta$ -dilaurosulphuric acid, has been isolated in the form of its *potassium* salt,

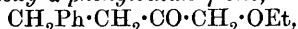


Glyceroltrisulphuric acid is not readily hydrolysed by water to glycerol and sulphuric acid as stated by Klason (*J. pr. Chem.*, 1879, [ii], 20, 1); glycerolmonosulphuric acid is produced, which is readily isolated in the form of its *barium* salt, and is hydrolysed by water only after prolonged boiling.

F. B.

**Ethyl  $\gamma$ -Ethoxyacetoacetate.** MARCEL SOMMELET (*Compt. rend.*, 1912, 154, 706—708).—Although ethyl acetate reacts with ethyl bromoacetate in presence of zinc to give only a trace of ketone, yet ethyl ethoxyacetate under the same conditions readily forms ethyl  $\gamma$ -ethoxyacetoacetate,  $\text{OEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , b. p. 105—106°/11 mm., 116—117°/20 mm. When freshly prepared, this substance is colourless, but rapidly alters on exposure to air. An alcoholic solution gives a bright red coloration with ferric chloride. The *copper* salt crystallises in green needles, m. p. 145—146°. Hydrazine hydrate forms 3-ethoxymethylpyrazolone,  $\text{C}_6\text{H}_{10}\text{O}_2\text{N}_2$ , m. p. 148—149·5°. The *sodium* salt reacts with benzyl chloride, giving a mixture of mono- and di-benzyl derivatives.

*Ethyl  $\gamma$ -ethoxy- $\alpha$ -benzylacetoacetate*,  $\text{OEt}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CH}_2\text{Ph})\cdot\text{CO}_2\text{Et}$ , b. p. 185—187°/14 mm., forms a *pyrazolone*, m. p. 119—120°, and on hydrolysis yields  $\delta$ -ethoxy- $\alpha$ -phenylbutan- $\gamma$ -one,



b. p. 157°/19—20 mm. (*semicarbazone*, m. p. 103—105°). *Ethyl  $\gamma$ -ethoxy- $\alpha\alpha$ -dibenzylacetoacetate* is an oil, b. p. 243—247°/14 mm.

W. O. W.

**The Action of Ammonium Cyanide (Potassium Cyanide and Ammonium Chloride) on Chlorinated Aldehydes.** KARL RASKE (*Ber.*, 1912, 45, 725—734).—When an ethereal solution of chloroacetaldehyde is shaken with an aqueous solution of ammonium chloride

and potassium cyanide and the product treated with hydrochloric acid,  $\beta$ -chlorolactic acid is formed. When  $\beta$ -chloropropaldehyde is similarly treated,  $\gamma$ -chloro- $\alpha$ -hydroxybutyric acid, m. p.  $58^\circ$ , is obtained. Its ammonium and silver salts were examined. When its aqueous solution is boiled, or the solid acid preserved at the ordinary temperature, the lactone of  $\alpha$ -dihydroxybutyric acid is formed. The ammonium and calcium salts of the latter acid were investigated.

Chloralacetamide, when acted on successively by hydrocyanic and hydrochloric acids, yielded a *product*, the analyses of which agreed with the formula  $\text{CCl}_3 \cdot \text{CH}(\text{NH}_2\text{Ac}) \cdot \text{CO} \cdot \text{NH}_2, \text{H}_2\text{O}$ , m. p.  $88-89^\circ$ . This appears, however, to be a compound of trichlorolactamide and acetamide, since it is readily resolved into these substances by the action of hydrochloric acid, and it can also be obtained by crystallising a mixture of these substances from chloroform or benzene. Attempts to obtain pure crystalline compounds of trichlorolactamide with benzamide, formamide, and pyridine respectively were unsuccessful. H. W.

**Cystine.** JULIUS MAUTHNER (*Zeitsch. physiol. Chem.*, 1912, 78, 28—36).—The cystine obtained from a case of cystinuria had  $[\alpha]_D - 205.28^\circ$ . By treatment with ammonia and zinc dust at the ordinary temperature the sulphur was removed and about half the theoretical quantity of alanine was obtained. This proved to be *dl*-alanine.

Cystine interacts with potassium cyanide, forming  $\alpha$ -amino- $\beta$ -thiocyanopropionic acid,  $\text{SCN} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ ; this crystallises in short, stout, lustrous prisms, also in flat prisms and six-sided platelets. On heating it becomes brown at  $180^\circ$ , m. p.  $220^\circ$  (decomp.),  $[\alpha]_D^{18} - 83.17^\circ$ . The copper salt separates in rosettes of microscopic platelets, or when quickly precipitated in tiny needles; the hydrochloride forms long prisms and needles. E. F. A.

**Dichloroacetaldehyde and the Formation of Vinyl Acetates from Bromoacetaldehydes.** BRUNO MYLO (*Ber.*, 1912, 45, 645—651).— $\beta$ -Bromovinyl acetate,  $\text{CHBr} \cdot \text{CH} \cdot \text{OAc}$ , b. p.  $146-149^\circ$ , is obtained by treating dibromoacetaldehyde (1 mol.) and acetyl bromide (about 5 mols.) with finely divided copper (1 atom) and heating the mixture at the b. p. for sixteen hours.  $\alpha\beta$ -Tribromoethyl acetate,  $\text{CHBr}_2 \cdot \text{CHBr} \cdot \text{OAc}$ , b. p.  $114-117/15.5$  mm., is prepared by heating equal molecular quantities of dibromoacetaldehyde and acetyl bromide.  $\beta\beta$ -Dibromovinyl acetate,  $\text{CBr}_2 \cdot \text{CH} \cdot \text{OAc}$ , b. p.  $70-71.5/7$  mm., is prepared from bromal, acetyl bromide, and finely divided copper. Equal molecular quantities of dichloroacetaldehyde and acetaldehyde are converted, after the addition of a little aqueous zinc chloride, into dichlorotrimethyltrioxin,  $\text{CHCl}_2 \cdot \text{CH} \begin{smallmatrix} \text{O} \cdot \text{CHMe} \\ \text{O} \cdot \text{CHMe} \end{smallmatrix} \text{O}$ , m. p.  $73-74.5^\circ$ , colourless prisms, and bisdichlorotrimethyltrioxin,  $\text{CHMe} \begin{smallmatrix} \text{O} \cdot \text{CH}(\text{CHCl}_2) \\ \text{O} \cdot \text{CH}(\text{CHCl}_2) \end{smallmatrix} \text{O}$ , m. p.  $53-54.5^\circ$ , tufted needles; both have an intense odour, somewhat resembling that of paraldehyde.

C. S.

**Hydrolysis of Carbohydratephosphoric Acid Esters.** HANS VON EULER and YNGVE FUNKE (*Zeitsch. physiol. Chem.*, 1912, 77, 488—496).—Sodium hexosephosphate is not hydrolysed by trypsin, pepsin, defibrinated blood, or by a kidney extract. When fed to a rabbit, three-quarters of the hexosephosphate were hydrolysed.

E. F. A.

**Specific Rotatory Power of Lævulose.** BERNHARD TOLLENS (*Zeitsch. Ver. deut. Zuckerind.*, 1912, 360—361).—Herzfeld and Winter (Abstr., 1886, 438) have found values between  $-71^{\circ}$  and  $-77^{\circ}$  for the rotatory power of lævulose. It is pointed out that both observers used lævulose syrups, and omitted to allow for the moisture in these when calculating the experimental results. When recalculated a value of  $-92^{\circ}$  to  $-93^{\circ}$  is obtained in each case, agreeing with that generally accepted.

E. F. A.

**Saccharification of Starch by Dilute Acids.** AUGUSTE FERNBACH and MARCEL SCHOEN (*Bull. Soc. chim.*, 1912, [iv], 11, 303—308).—The balance of existing evidence is in favour of the view that whilst malt diastase hydrolyses starch to dextrins and maltose, dilute acids convert it into dextrose, although in recent years Weber and Macpherson (Abstr., ii, 296) and others have found maltose in the commercial glucose prepared by acid hydrolysis of starch. The authors have prepared phenylosazones from the products obtained by the hydrolysis of starch mucilage under pressure with hydrochloric acid, oxalic acid, and sulphuric acid, and in each case have obtained notable quantities of maltosazone, which was identified by its crystalline form and melting point. The latter was generally low, owing to the difficulty of freeing the substance from small quantities of dextrins (compare Grueters, *Compt. rend.*, 1890, 110, 1204).

T. A. H.

**Humic Acid of Sphagnum Peat.** SVEN ODÉN (*Ber.*, 1912, 45, 651—660).—The object of the research is to ascertain whether or not the non-colloidal alkali compounds obtained by the action of alkalis on the humous substances of sphagnum peat are true salts. Reasons are stated for the belief that such alkali compounds are non-colloidal. The preparation from peat of a solution of ammonium humate free from colloids is described. By ultramicroscopical examination, the solution exhibits very feeble internal luminescence, which is due probably to the high molecular weight of ammonium humate (compare Lobry de Bruyn, Abstr., 1904, ii, 470). By suitable treatment with hydrochloric acid and centrifugalising, the free humic acid can be isolated. The fact that the electrical conductivity of 0.182*N*-ammonia is increased by the addition of a suspension of humic acid, shows that the latter is a true acid, and forms an ammonium salt, which is electrolytically dissociated. The equivalent weight of the acid is about 339 as determined by Kohlrausch's conductivity method; 0.00520*N*-sodium hydroxide is treated with successive small quantities of a suspension of humic acid (containing 0.0042 gram per c.c.) until the equivalent conductivity reaches a minimal value. As determined by the analysis of the calcium salt, the equivalent weight of humic acid is 345. The

variation with the dilution of the equivalent conductivity of solutions of sodium humate indicates that humic acid is tribasic.

When humic acid is heated at  $100^{\circ}$ , the gelatinous mass loses water and is changed to a hard, brittle substance, which forms a black, glistening powder. This modification does not form a suspension in water, and is not directly soluble in alkalis. By the prolonged action of alkalis, however, it swells and partly dissolves as the brown alkali humate; the change is by no means complete, even after forty-six days. C. S.

**Coal and Carbonised Residues.** EDUARD DONATH and FRITZ BRÄUNLICH (*Chem. Zeit.*, 1912, 36, 373—376).—The study of coals by means of the reaction with dilute nitric acid (*ibid.*, 1904, 28, 180) has now been extended to include other reagents. Fusion with alkali hydroxide at  $250^{\circ}$  and extraction with water gives dark brown solutions with brown coal, charcoal, and carbonised organic material, and much of the coloured matter is precipitated by acids. True coal, coke, graphite, and acetylene soot yield colourless solutions. Brown coals are almost completely converted into humic acids, and these acids may be separated into two fractions, one of which is completely soluble in the concentrated alkali (I), whilst the second remains insoluble, but is dissolved by very dilute alkali hydroxide (II). After precipitation with acid, the two substances may be distinguished by their behaviour towards a 10% solution of ammonium carbonate, in which (I) is completely soluble and (II) insoluble. The acid (I) is insoluble in cold water, whilst (II) yields a dark brown solution. True coal may be rendered soluble by repeated fusion with alkali at  $400^{\circ}$ .

The humic acids (I) from brown coal are mixed with oxalic acid and an acid which sublimates at  $300^{\circ}$ , and also with a crystalline substance which gives a red coloration with ferric chloride. A fatty acid is also present. If ferric oxide is added to the alkali fusion, a clear solution is obtained with water, and acids no longer produce a precipitate. Much oxalic acid is present, as well as substances which give a coloration with ferric chloride.

A mixture of equal volumes of concentrated nitric and sulphuric acids reacts violently with brown coal and wood, but only slowly with coal. Those materials which yield humic acids with alkali are converted by the acid mixture into substances soluble in acetone or alcohol, and this furnishes a ready means of distinguishing between the two classes of coal. C. H. D.

**Alkylation of Amino-acids with Alkyl Sulphates.** JON. NOVÁK (*Ber.*, 1912, 45, 834—850).—An endeavour to improve the esterification method for the estimation of amino-acids. Methyl sulphate applied in the cold with an aqueous solution of an alkali gives, in general, excellent yields of a product methylated at both the carboxyl group and the nitrogen atom. The analogous reaction with ethyl sulphate is far from complete even when assisted by warming. The reaction product, after neutralisation with sulphuric acid, is evaporated to a syrup and extracted with alcohol; after again evaporating, warming with dilute hydrochloric acid to decompose any

alkylsulphuric acid, and then removing sulphuric acid by barium chloride, the hydrochloride of the amino-ester is extracted with alcohol and examined by conversion into various derivatives.

Glycine gave with methyl sulphate a 93% yield of betaine hydrochloride, together with a small quantity of the methyl ester of betaine hydrochloride. With ethyl sulphate, triethylbetaine was obtained (platinichloride, m. p. 217—218.5° corr.), together with diethylaminoacetic acid; the latter results from the hydrolysis of its ethyl ester (platinichloride, tablets, m. p. 140—142° corr.), which is also produced.

*dl*-Alanine with methyl sulphate produced only methylbetaine ( $\alpha$ -trimethylpropiobetaine) (83.6% theory), the platinichloride of which melts at 210—212° (corr.). No betaine compound was obtained with ethyl sulphate, the products being  $\alpha$ -diethylaminopropionic acid (copper salt, violet-red leaflets), the corresponding ethyl ester, b. p. 86°/18 mm. (platinichloride, tablets, m. p. 114—116° corr.), and a little  $\alpha$ -ethylaminopropionic acid (the copper salt was prepared).

*dl*-Leucine on methylation gave 87% of the theoretical yield of the betaine of  $\alpha$ -trimethylammoniumisohexzoic acid; platinichloride, leaflets, m. p. 217—218° (corr.); aurichloride, leaflets, m. p. 164—165° (corr.). Ethyl sulphate left most of the leucine unaffected, but a little  $\alpha$ -ethylaminoisobutylacetic acid was obtained (copper salt, violet powder).

*dl*-Phenylalanine was methylated to the betaine of  $\alpha$ -trimethylammoniumphenylpropionic acid; platinichloride, tablets, m. p. 195.5—196.5° (corr.); aurichloride, leaflets, m. p. 93—94° (corr.). The yield was 96%.

*l*-Aspartic acid, when methylation was attempted, gave a practically quantitative yield of fumaric acid, the rest of the molecule appearing as a mixture of tetramethylammonium chloride, trimethylamine, and dimethylamine. In the treatment with ethyl sulphate, a small amount of fumaric acid and diethylamine was obtained.

*d*-Glutamic acid gave on methylation a 92% yield of a pentamethyl derivative, probably the chloride of the dimethyl ester of *N*-trimethylglutamic acid ( $\text{CO}_2\text{Me}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{NMe}_3\text{Cl}\cdot\text{CO}_2\text{Me}$ ); platinichloride, needles, m. p. 201° (decomp.); aurichloride, needles, m. p. 125—128°. A small quantity of a dimethyl derivative, probably *N*-dimethylglutamic acid, was also obtained (aurichloride, leaflets). The action of ethyl sulphate on glutamic acid gave no satisfactory result.

D. F. T.

**Polypeptides Containing *d*-Aminobutyric Acid.** EMIL ABDERHALDEN and HSING LANG CHANG (*Zeitsch. physiol. Chem.*, 1912, 77, 471—487. Compare Abderhalden, Chang and Wurm, Abstr., 1911, i, 526).—Several new dipeptides have been prepared containing *d*-aminobutyric acid, also three of the possible tripeptides containing glycine, alanine, and aminobutyric acid. Attention is called to the great alteration in physical and biochemical properties caused by the alteration in the order in which these three units are united.

Glycyl-*dl*-aminobutyric anhydride, prepared from glycyl-*dl*-aminobutyric acid, crystallises in rhombic plates, m. p. 238°, and is identical with the anhydride prepared from  $\alpha$ -aminobutyrylglycine (Fischer and Raske, Abstr., 1906, i, 457).

*l*-Aminobutyric acid is converted by nitrosyl bromide into *d*- $\alpha$ -bromobutyric acid,  $[\alpha]_D^{20} + 15.43^\circ$ . On treatment with ammonia partly racemised *d*- $\alpha$ -aminobutyric acid is obtained.

*d*-Bromobutyryl chloride, prepared by the action of thionyl chloride on the acid, has b. p.  $65-69^\circ/15$  mm.

*d*-Bromobutyryl-glycyl-*d*-aminobutyric acid, prepared from glycyl-*d*-aminobutyric acid and *d*-bromobutyryl chloride, crystallises in very minute needles, m. p.  $141^\circ$  (corr.),  $[\alpha]_D^{20} + 5.55^\circ$ . When set aside with 25% ammonia, *d*-aminobutyryl-glycyl-*d*-aminobutyric acid is formed; it has m. p.  $241^\circ$  (decomp.),  $[\alpha]_D^{20} + 12.75^\circ$ .

*d*-Bromobutyryl-glycyl-*d*-alanine sinters at  $80^\circ$ , m. p.  $148^\circ$ ,  $[\alpha]_D^{20} - 21.32^\circ$ . *d*-Aminobutyryl-glycyl-*d*-alanine reacts acid with litmus in aqueous solution; it has m. p.  $239^\circ$  (corr.),  $[\alpha]_D^{20} - 7.8^\circ$ .

*d*-Bromobutyryl-*d*-alanine crystallises in cubes or in teeth-like branched platelets, which soften at  $112^\circ$  (corr.), m. p.  $132^\circ$  (corr.),  $[\alpha]_D^{20} - 20.08^\circ$ .

*d*-Aminobutyryl-*d*-alanine has m. p.  $266^\circ$  (corr.),  $[\alpha]_D^{20} - 12.55^\circ$ .

Chloroacetyl-*d*-aminobutyryl-*d*-alanine crystallises in needles, m. p.  $195^\circ$  (corr.),  $[\alpha]_D^{20} - 61.94^\circ$ . Glycyl-*d*-aminobutyryl-*d*-alanine is neutral to litmus in aqueous solution, m. p.  $247^\circ$  (corr.),  $[\alpha]_D^{20} - 76.62^\circ$ .

*d*-Bromobutyrylglycine has m. p.  $93^\circ$  (corr.),  $[\alpha]_D^{20} + 32.44^\circ$ . *d*-Aminobutyrylglycine is a crystalline powder, m. p.  $226^\circ$  (corr.),  $[\alpha]_D^{20} + 26.83^\circ$ .

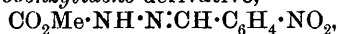
*d*-Bromopropionyl-*d*-aminobutyrylglycine separates in long needles, m. p.  $166^\circ$  (corr.),  $[\alpha]_D^{20} - 12.83^\circ$ . *d*-Alanyl-*d*-aminobutyrylglycine has m. p.  $214^\circ$  (corr.),  $[\alpha]_D^{20} + 13.86^\circ$ .

Glycyl-*d*-aminobutyric acid has  $[\alpha]_D^{20} - 20.33^\circ$ .

E. F. A.

**Electrochemical Reductions. I. Reduction of Primary Nitroamines into Hydrazines.** H. J. BACKER (*Rec. trav. chim.*, 1912, 31, 1—29).—The author has reduced a number of primary nitroamines by electrical methods, using a cathode of tin or of copper coated with tin (compare Boehringer & Söhne, Abstr., 1906, i, 637). The cathode liquid was varied according to the stability of the substances worked with, using either dilute sulphuric or acetic acids or a mixture of the two, a solution of sodium sulphate, or as an alkaline medium a solution of sodium carbonate. The anode liquid was sulphuric acid (20%) for acid reductions, and a saturated solution of sodium carbonate for alkaline reductions. The hydrazines obtained by the reductions invariably were characterised by preparing condensation products with aldehydes.

Methyl nitrourethane is best reduced in a dilute solution of acetic acid containing sodium acetate, methyl hydrazinecarboxylate hydrochloride being obtained (yield 88%), and characterised by its benzylidene derivative (compare Diels and Fritzsche, Abstr., 1911, i, 957). The *p*-nitrobenzylidene derivative,



crystallises in pale yellow needles, m. p.  $212^\circ$ . By reduction in alkaline solution, contrary to expectation, free hydrazine itself is formed. Ethyl nitrourethane gives a yield of 70% on similar reduction in acid solution.

Nitrocarbamide is best reduced in a mixture of dilute acetic and

sulphuric acids, the semicarbazide hydrochloride being subsequently obtained to the extent of 74% of theory (compare Holroyd, *Trans.*, 1901, 79, 1326). By condensation with pyruvic acid, the *semicarbazone*,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} : \text{CMe} \cdot \text{CO}_2\text{H}$ , is obtained in white needles, which melt and decompose at  $200^\circ$ . From it a *potassium* and *barium* salt have been prepared.

W. G.

**Constitution of the Fulminuric Acids. III. CELSIO ULPIONI** (*Gazzetta*, 1912, 42, i, 209—227).—The author calls attention to two papers (Abstr., 1905, i, 750; *Rend. Soc. Chim. Roma*, 26th Nov., 1905) in which he described previously to the work of Jovitschitsch (Abstr., 1906, i, 732) the gradual decomposition of ethyl furoxandicarboxylate, although with results differing substantially from those of Jovitschitsch. In the present paper an account is given of the action of boiling water on ethyl furoxandicarboxylate (previously recorded in the second of the papers above-mentioned), and the results so obtained are discussed in connexion with those of Wieland (Abstr., 1909, i, 610), who observed a different series of reactions when the hydrolysis was effected with barium hydroxide.

When ethyl furoxandicarboxylate is boiled with water for four or five days, and the aqueous liquid then neutralised with ammonia, *ethyl ammonionitrocynoacetate*,  $\text{CO}_2\text{Et} \cdot \text{C}(\text{CN}) \cdot \text{NO} \cdot \text{OH} \cdot \text{NH}_3$ , is obtained in crystalline form after evaporation. When potassium carbonate is used instead of ammonia, the potassium derivative is obtained, and is identical with that of Conrad and Schulze (Abstr., 1909, i, 211). The *silver* derivative,  $\text{C}_5\text{H}_5\text{O}_4\text{N}_2\text{Ag}$ , crystallises in heavy needles. When it is treated with hydrogen sulphide and filtered, the filtrate yields on evaporation in a vacuum, transparent, prismatic crystals, which consist probably of impure *ethyl nitrocynoacetate*. On reduction with sodium amalgam, ethyl ammonionitrocynoacetate yields the sodium oximinocynoacetate, whilst when it is treated in alcoholic solution with hydrogen chloride, the ammonium salt of ethyl nitromalonate is produced. This shows that the middle carbon atom of the product obtained by the author by the destruction of ethyl furoxandicarboxylate is linked with a nitro-group, whilst in Wieland's products there is an oximino-group. An aqueous solution of ethyl ammonionitrocynoacetate treated with an ammoniacal copper solution slowly deposits the compound  $(\text{C}_3\text{H}_2\text{O}_3\text{N}_3)_2\text{Cu} \cdot 4\text{NH}_3$ , identical with that obtained from ammoniacal copper solutions of ammonium fulminurate (compare Conrad and Schulze, *loc. cit.*). Saponification of ethyl ammonionitrocynoacetate with barium hydroxide yields the *barium* derivative,  $\text{C}_3\text{O}_4\text{N}_2\text{Ba} \cdot 2\text{H}_2\text{O}$ , but it is not possible to isolate the free acid, because it decomposes quantitatively in solution, forming nitroacetonitrile and carbon dioxide. The *ammonium* salt of nitroacetonitrile,  $\text{C}_2\text{N}_2\text{O}_2\text{H}_2\text{NH}_3$ , has m. p. about  $135^\circ$ .

R. V. S.

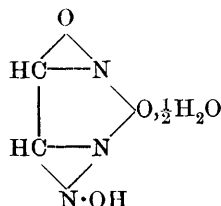
**Constitution of the Fulminuric Acids. IV. CELSIO ULPIONI** (*Gazzetta*, 1912, 42, i, 243—263).—The paper records attempts which have been made to prepare (or to ascertain the structure of) some of

the seven different substances  $C_2H_2O_2N_2$ , which have at least one oxygen atom linked with nitrogen.

By the action of boiling water on ethyl furoxandicarboxylate the author obtained (compare preceding abstract) nitrocyanoacetic acid (of which the constitution was established by Conrad and Schulze, Abstr., 1909, i, 211) and nitroacetonitrile (of which the constitution was settled by Steinkopf and Bohrmann, Abstr., 1908, i, 327). The substance of m. p.  $40^\circ$  described by Steiner (Trans., 1876, ii, 288) as nitroacetonitrile, the author finds to have the composition  $C_4O_2N_4$ , and to be, consequently, *furoxandicarboxylonitrile*,  

$$\begin{array}{c} \text{CN}\cdot\text{C}\cdot\text{N}\cdot\text{O} \\ | \quad | \\ \text{CN}\cdot\text{C}\cdot\text{N}\cdot\text{O} \end{array}$$

[With A. DE DOMINICIS].—From the oxidation of glyoxime with sodium hypochlorite or with concentrated nitric acid, no individual product could be isolated. Oxidation of glyoxime with permanganate yields a compound (C 25.91%, H 4.08%, N 30.64%), which crystallises in needles and decomposes at  $97^\circ$ . When glyoxime is oxidised with nitrogen peroxide in ethereal solution, a yellow, crystalline substance,  $C_2H_3O_3N_3\cdot\frac{1}{2}H_2O$ , is obtained; it has m. p.  $104^\circ$ . It forms an ammonium salt,  $C_2H_3O_3N_3\cdot NH_3\cdot\frac{1}{2}H_2O$ . For this substance of m. p.  $104^\circ$  the annexed formula is suggested.



[With N. SCIACCA].—The interaction of equimolecular quantities of ethyl cyanocarboxylate and hydroxylamine in alcoholic solution yields a crystalline substance,  $C_4H_8O_3N_2$ , m. p.  $99\text{--}100^\circ$ . It gives a green precipitate with copper acetate, and an intense reddish-violet coloration with ferric chloride. The substance is assigned the structure of the ethyl ester of *oxalmonoamido-oxime*,  $CO_2Et\cdot C(N\cdot OH)\cdot NH_2$ . When it is saponified with sodium hydroxide, a crystalline substance, m. p.  $141^\circ$  (decomp.), is obtained, which is probably *oxalmonoamido-oxime*. The silver salt,  $C_2H_3O_3N_2Ag$ , forms acicular crystals. R. V. S.

**Sodium Pentacyanohydrazinoferrite** [**Hydrazinoferrpentacyanide**]. E. BIESALSKI and OTTO HAUSER (*Zeitsch. anorg. Chem.*, 1912, 74, 384—388).—If a concentrated solution of 6 grams of hydrazine hydrate is added, drop by drop, to an ice-cold alkaline solution of 12 grams of sodium nitroprusside in ethyl and methyl alcohol, a yellow, crystalline precipitate is obtained, which is washed with alcohol and ether and dried over sulphuric acid, and has the composition  $Na_3N_5H_4(CN)_5\cdot H_2O$ . It gives the characteristic reaction of ferropentacyanides, a red coloration when boiled with hydroxylamine. It readily decomposes, becoming green and evolving cyanogen.

At least one more cyanogen group may be replaced by using an excess of hydrazine. Similar reactions occur, but less readily, with phenylhydrazine, ethylamine, and diethylamine (compare Hofmann, Abstr., 1900, i, 591). C. H. D.

**New Silicanes.** ARTUR BYGDÉN (*Ber.*, 1912, 45, 707—713. Compare Abstr., 1911, i, 845).—The author has extended his work on

tetra-alkylsilicanes, and has prepared compounds containing 9, 10, and 11 atoms of carbon, and a derivative of silicoethane, as well as silicanes containing the phenyl group. The following substances are described:

*Triethyl-n-propylsilicane*, b. p. 172·8—173·2° (corr.)/761·4 mm.,  $D_4^{15}$  0·775, from trichloro-*n*-propylsilicane and magnesium methyl bromide (4·5 mols.); *triethyl-n-butylsilicane*, b. p. 190·6—191·6°/762·2 mm.,  $D_4^{15}$  0·782, from trichlorobutylsilicane and magnesium ethyl bromide (4·2 mols.); *triethylisobutylsilicane*, b. p. 187·0—187·2° (corr.)/762 mm.,  $D_4^{15}$  0·784, from trichloroisobutylsilicane and magnesium ethyl bromide (4·5 mols.); *triethylisoamylsilicane*, b. p. 204·6—205·6° (corr.)/757·3 mm.,  $D_4^{15}$  0·785, from trichloroisoamylsilicane and magnesium ethyl bromide (4·5 mols.).

*Hexamethylsilicoethane*,  $Si_2Me_6$ , prepared from silicon hexachloride and magnesium methyl bromide (6·2 mols.), has b. p. 112—114° (corr.)/756·9 mm., m. p. 12·5—14°.

Trichlorophenylsilicane, isolated from the product obtained by the gradual addition of magnesium phenyl bromide to a solution of silicon tetrachloride in ether, has b. p. 200·5—201·5° (corr.)/740·4 mm., whereas Ladenburg (Abstr., 1873, 1026) found 197°. Magnesium methyl bromide (3·3 mols.) and magnesium ethyl bromide (4·2 mols.) convert it respectively into *phenyltrimethylsilicane*, b. p. 171·5—171·7° (corr.)/759·4 mm.,  $D_4^{15}$  0·873, and *phenyltriethylsilicane*, b. p. 238·2—238·4° (corr.)/763·1 mm.,  $D_4^{15}$  0·894.

An attempt to prepare dichlorophenylethylsilicane by the interaction of magnesium ethyl bromide (1·1 mols.), and trichlorophenylsilicane was not completely successful (compare Kipping, Trans., 1907, 91, 215), but the product so obtained, when acted on by magnesium methyl bromide (2·3 mols.), yielded *phenyldimethylethylsilicane*, b. p. 197·6—198·6° (corr.)/758·7 mm.,  $D_4^{15}$  0·881.

*Benzyltrimethylsilicane*, prepared from trichlorobenzylsilicane and magnesium methyl bromide (3·3 mols.), has b. p. 191·2—191·4° (corr.)/759·5 mm.,  $D_4^{15}$  0·872.

H. W.

**Proposals for a Nomenclature of Heterocyclic Substances and its Extension to Cyclic Substances in General and to Acyclic Compounds.** AUGUSTE BÉHAL (*Bull. Soc. chim.*, 1912, [iv], 11, 264—275).—The nomenclature proposed is a literal rendering of formulæ without reference to the functions of the characteristic groups in the substance, and it is suggested that it would be especially useful for indexing purposes.

Greek prefixes are to be used to indicate the number of links in a closed chain, and the nature of the links will be indicated by the words oxo, azo, thio for rings containing O, N or S, or oxonio, azonio, sulphinio, etc., in the case of oxonium, azonium or sulphinium compounds. The residue :SO will be called thion, and  $SO_2$  will be named sulphone. The names of closed saturated chains will end in -ane, and unsaturation will be indicated by the terminations -ene, -diene, -triene, etc.; thus, dihydropyrrole will be *cyclopentazene*, and pyridine becomes *cyclohexazotriene*. The numbering of the links composing the ring will begin with the atom of lowest atomic weight. In polyheterocyclic compounds, Latin prefixes will be used to indicate the number

of rings, and numbers appended indicating the points of attachment; thus quinoline would be bicyclo-5:10-decazo-1-pentene-1:3:5:6:8. The same system could be used for polyhomocyclic substances; thus anthracene would be tetracyclo-1:8:2:7:9:14-tetradecahexene-2:3:5:9:10:12. In the case of bridged rings, the linking atoms forming the bridge would be indicated by letters *a*, *b*, *c*, etc., and the position of the bridge by the numbers of the atoms in the primary ring, at which it is attached; thus pinene would be bicyclo-*a*:6:4-heptene-1-trimethyl-*a*:*a*:1. In general, the longest possible chain is to be taken as the basis of the name, and where two chains are of equal length the more complex is to be taken as a basis. The dioxide formula for quinone would be called bicyclo-*a*:*b*:1:4-octodioxotriene-1:3:5, or, if preferred, the nature of the linking bridge atoms may be indicated thus: bicyclo-*a*:*b*(O.O):1:4-octodioxotriene-1:3:5.

The system is applied to acyclic compounds with the addition of the Geneva system of numbering atoms in side-chains, and the convention that oxygen doubly linked to carbon is to be indicated by the suffix -one; thus diethyl ether becomes pentoxane-3, the acid anhydride,  $\text{CH}_3\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{CH}_3$ , becomes octoxane-4-dione-3:5-dimethyl-2:7, and sulphonal,  $\text{CH}_2\text{Me}\cdot\text{SO}_2\cdot\text{CMe}_2\cdot\text{SO}_2\cdot\text{CH}_2\text{Me}$ , would be called heptadisulphone-3:5-dimethyl-4:4.

The names may be shortened by using numerals and letters in place of prefixes, thus 3C for tricyclo- and so on, different kinds of type being used for numerals and letters serving different purposes in the name, thus  $\beta$ -naphthol tetrahydride could be written 2C-1:6-1O-triene-2:4:6-ol-3 (bicyclo-1:6-decatriene-2:4:6-ol-3).

A large number of examples of the application of this system to the naming of complex substances are given in the original.

T. A. H.

$\Delta^{13}$ -*cyclo*Hexadiene. CARL D. HARRIES (*Ber.*, 1912, 45, 809—816. Compare *Abstr.*, 1909, i, 218; Crossley, *Trans.*, 1904, 85, 1403).—The formation of *cyclo*hexene as well as *cyclo*hexadiene on elimination of hydrogen bromide from 1:2-dibromocyclohexane by means of quinoline is confirmed, contrary to the results of Zelinsky and Gorsky (*Abstr.*, 1911, i, 847), by the following new investigation. When dibromocyclohexane is treated in alcoholic solution with trimethylamine, an *additive product*,  $\text{C}_6\text{H}_{18}\text{NBr}$ , of trimethylamine with a monobromide is obtained, m. p.  $181^\circ$  (decomp.). When heated, this decomposes into trimethylamine and a hydrocarbon,  $\text{C}_6\text{H}_8$ ,  $D_{20}^{20}$  0.8421,  $n_D^{20}$  1.475. It gives an intense dark red coloration with concentrated sulphuric acid. On prolonged treatment with ozone a mixture of *mono*- and *di*-ozonide is obtained, from which, on decomposition, succindialdehyde and other products resulted.

The hydrocarbon when brominated yields a tetrabromide crystallising in thick, colourless prisms, m. p.  $87$ — $89^\circ$ . On brominating the mixture of hydrocarbons obtained by the method of Zelinsky and Gorsky, two tetrabromides, m. p.  $87$ — $89^\circ$  and  $155$ — $156^\circ$ , possibly corresponding with *cis*- and *trans*-isomerides, as well as an oily fraction,

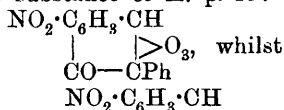
were obtained ; the last contained 1 : 2-dibromocyclohexane, corresponding with about 25% of cyclohexene in the original hydrocarbon.

E. F. A.

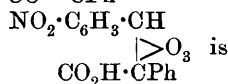
**Indones and their Transformation Products in Sunlight. Behaviour with Ozone.** MARUSSIA BAKUNIN (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iii], 17, 379—386. Compare Bakunin and Lanis, *Abstr.*, 1911, i, 992).—The present paper deals with 4-nitro-2-phenylindone and with the product, m. p. about 320°, obtained when it is kept in sunlight. The latter does not react with phenylhydrazine or semicarbazide. 4-Nitro-2-phenylindone, however, yields with semicarbazide a substance,  $C_{16}H_{12}O_3N_4$ , which has m. p. 210°, and crystallises in yellow needles.

The action of ozone on the nitrophenylindone and on the substance of m. p. 320° has also been investigated, the dilute ozone employed being obtained by passing oxygen through a Berthelot tube connected with an induction coil. 4-Nitro-2-phenylindone when ozonised in chloroform solution at 0° yielded (1) benzoic acid ; (2) a substance, m. p. 128° (obtained in some experiments only) ; (3) a well-crystallised, stable substance, m. p. 157—158°. The last-named product reacts with phenylhydrazine, and is not affected by sodium carbonate or by boiling water. When boiled with barium hydroxide, it dissolves, and from the solution, on addition of acid, benzoic acid can be obtained, and also a substance, m. p. 136—137°. The substance of m. p. 157°

is assigned the constitution of an ozonide,



for the compound of m. p. 136° the formula



suggested. Analyses were made in both cases.

The transformation product (of m. p. 320°) of 4-nitro-2-phenylindone was unaffected by ozone under the conditions of experiment.

R. V. S.

**Explosiveness of the Residues from Ethereal Solutions of Nitrophenylindones Exposed to Light.** III. MARUSSIA BAKUNIN (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iii], 17, 375—378. Compare Bakunin and Lanis, *Abstr.*, 1911, i, 992).—Ethereal solutions of nitrophenylindones which have been exposed to light yield on distillation an explosive residue. Ether and ethereal solutions of cinnamic acid did not yield an explosive residue after exposure to light in the same circumstances ; if the explosive properties are due to ethyl peroxide, therefore, it is possible that the dissolved nitro-derivative favours its formation.

R. V. S.

**Molecular Compounds of Aromatic Amines with Nitro-derivatives.** DEMETRIUS E. TSAKALOTOS (*Bull. Soc. chim.*, 1912, [iv], 11, 284—288. Compare *Abstr.*, 1908, i, 498).—Mixtures of aromatic amines with nitro-derivatives are intensely coloured, and Ostromisslensky (*Abstr.*, 1911, ii, 195) has obtained spectroscopic evidence of

the formation of a definite molecular compound between aniline and nitrobenzene, although Kremann (Abstr., 1905, ii, 77) had shown that the fusion curve for mixtures of these two substances did not indicate the formation of such a compound. The author's previous work (*loc. cit.*) has shown that such compounds may only exist in the liquid state, and he has therefore examined viscosity and density curves for mixtures of (1) aniline and nitrobenzene, (2) dimethylaniline and nitrobenzene, and the fusion curve for  $\alpha$ -mononitronaphthalene and  $\alpha$ -naphthylamine, and finds that in these cases there is no indication of the formation of molecular compounds, so that the latter must be almost entirely dissociated even in the liquid state. Kremann (*loc. cit.*), however, has shown that stable compounds of this kind are formed between the aromatic amines and di- and tri-nitro-compounds.

T. A. H.

**Preparation of Diarylamines.** KNOLL & Co. (D.R.-P. 241853).—Diarylamines have previously been prepared by heating arylamine hydrochlorides with elimination of ammonium chloride; the condensation of the bases is now found to take place readily in the presence of iodine.

2:2'-Dinaphthylamine (m. p. 170.5°) was obtained in quantitative yield by heating  $\beta$ -naphthylamine in the presence of 0.5% of iodine during four hours at 230°; in the absence of iodine a 10% yield only was obtained; this reaction also takes place in boiling aniline solution.

The following compounds were also prepared in the presence of iodine: 4:4'-Dihydroxydiphenylamine, m. p. 169°, in 70% yield at 200° from *p*-aminophenol; the triacetyl derivative has m. p. 132.5° (the previously recorded m. p.'s are 174.5° and 128.5° respectively).

$\alpha$ -Phenyl-naphthylamine, m. p. 60°, b. p. 223°/10 mm., in 85% yield from aniline, and  $\alpha$ -naphthylamine at 230—250° during eight hours.

$\alpha$ -o-Methoxyphenyl-naphthylamine, m. p. 99.5°, b. p. 226—228°/11 mm.; the *p*-methoxy-compound has b. p. 250—252°/13 mm.  $\alpha$ -o-Tolyl-naphthylamine has b. p. 198—202°/9 mm.; the *m*-tolyl derivative, b. p. 234—237°/11 mm.; the *p*-tolyl derivative, m. p. 78°, b. p. 230°/10 mm.; the *m*-xylyl derivative, b. p. 227—232°/9 mm.; the *p*-chlorophenyl derivative, m. p. 102—103°, and the *m*-chlorophenyl derivative, m. p. 72.5°, b. p. 238—241°/12 mm.

$\beta$ -Phenyl-naphthylamine has m. p. 108°, b. p. 237°/15 mm.; the *p*-chlorophenyl derivative, m. p. 101°, b. p. 251.5°/13 mm., being obtained in 90% yield from  $\beta$ -naphthol and *p*-chloroaniline.

$\beta$ -*m*-Tolyl-naphthylamine has m. p. 68—69°, b. p. 243—246°/15 mm., yield 90% (previously recorded, m. p. 67°); the *o*-tolyl derivative, m. p. 95°, b. p. 235—237°/14 mm.; the *o*-chlorophenyl derivative, m. p. 89°, b. p. 236—238°/13.5 mm.; the *m*-chlorophenyl derivative, m. p. 101°, b. p. 250—253°/11 mm., and the *p*-chloro-*o*-tolyl derivative, m. p. 75°, b. p. 262—264°/15.5 mm.

Di-2 naphthyl-*m*-phenylenediamine, m. p. 234°, from  $\beta$ -naphthol and *m*-phenylenediamine at 200—260°, is obtained in quantitative yield.

F. M. G. M.

**The Action of Iodine on Phenols. II. The Catalytic Decomposition of Triiodophenol.** JOHN M. WILKIE (*J. Soc. Chem. Ind.*, 1912, 31, 208—210. Compare Abstr., 1911, ii, 546).—The author has found that the addition of one drop of *N*/10-solution of iodine to a saturated solution of sodium tri-iodophenol produces a striking colour effect, the solution finally becoming semi-solid owing to the precipitation of tetraiododiphenylenequinone (compare Abstr., 1911, ii, 546). Investigation of this reaction has shown that (1) the reaction is truly catalytic, since no iodine is lost, the iodine in the final phase corresponding exactly with that added initially; (2) the acid liberated in the reaction is hydriodic acid, and (3) the weight of the tetraiododiphenylenequinone produced corresponds with that of the tri-iodophenol taken.

The reaction has a high initial velocity, and, in some cases, is practically complete in one hour. It does not proceed in neutral solution, the presence of a small quantity of free alkali being necessary. Excess of alkali, however, completely inhibits the reaction, it being difficult to obtain a satisfactory conversion if the alkali exceeds two mols. of sodium hydroxide per mol. of tri-iodophenol, and under such conditions the iodine is not recoverable. With solutions containing inhibitive amounts of alkali, reaction occurs if dilute acid is added cautiously to restore the optimum condition; carbon dioxide acts similarly if slowly bubbled through the solution. The addition of considerable amounts of iodine will also overcome the inhibitory effects of alkali.

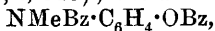
The author considers that hypiodous acid is the real catalyst, acting in accordance with the equations:  $2\text{I}_2 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{HI} + 2\text{HOI}$ ;  $2\text{C}_6\text{H}_2\text{I}_3\text{ONa} + 2\text{HOI} = \text{C}_{12}\text{H}_4\text{I}_4\text{O}_2 + 2\text{I}_2 + 2\text{NaOH}$ . T. S. P.

**Nitro-derivatives of Diphenyl Ether.** ALPHONSE MAILHE and MARCEL MURAT (*Compt. rend.*, 1912, 154, 715—716).—When diphenyl ether is treated with fuming nitric acid in acetic acid solution at 50°, *o*- and *p*-nitrodiphenyl ether,  $\text{C}_6\text{H}_5\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , are formed. The former is an oil, b. p. 185°/55 mm., whilst the latter crystallises in clinorhombic prisms, m. p. 56°; on reduction, it yields *p*-aminodiphenyl ether,  $\text{C}_{12}\text{H}_{11}\text{ON}$ , m. p. 82°. This amine develops an intense and persistent red coloration with bleaching powder.

A mixture is obtained when diphenyl ether is added to cold fuming nitric acid. Extraction of the product with boiling alcohol yields 2:4:2':4'-tetranitrodiphenyl ether,  $\text{C}_6\text{H}_3(\text{NO}_2)_2\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$ , m. p. 95°, and a more soluble trinitro-derivative, m. p. 108—110°. A second extraction yields a pentanitro-derivative, m. p. 86—88°. Extraction with carbon tetrachloride gives an ill-defined mixture, m. p. 110—120°, but subsequent treatment of the residue with ether removes the 4:4'-dinitro-derivative, m. p. 138—139°, and a very soluble 2:4:6:2':4':6'-hexanitro-derivative, m. p. 67°. If the original mixture of nitro-compounds is treated with sulphuric and nitric acids, an octanitro-derivative, m. p. 195°, is formed. The orientation of the compounds mentioned has not been definitely established

W. O. W.

***m*-Methylaminophenol.** JOACHIM BIEHRINGER and A. TANZEN (*Chem. Zeit.*, 1912, 36, 389).—*m*-Methylaminophenol can be satisfactorily prepared by methylating *m*-aminophenol with methyl iodide in the presence of potassium hydroxide solution at 100° in a sealed tube. It was obtained as a viscous oil, b. p. 169·5°/12 mm. (compare Gnehm and Scheutz, Abstr., 1901, i, 519); the *dibenzoyl* derivative,



forms colourless needles, m. p. 150°.

D. F. T.

**New Derivatives of Phenyl Sulphide.** EDOUARD BOURGEOIS and P. HUBER (*Rec. trav. chim.*, 1912, 31, 30—32).—*o*- and *p*-Aminophenyl sulphides are obtained by reduction of the corresponding nitro-compounds with tin and hydrochloric acid. The *o*-aminophenyl sulphide,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SPh}$ , crystallises from alcohol in colourless, transparent tablets, m. p. 35·5°, b. p. 212°/25 mm., 257·5°/100 mm. The para-compound crystallises in white needles, m. 96° (Kehrmann and Bauer, Abstr., 1897, i, 27, give 93°). These two bases on diazotisation and boiling with water give the corresponding hydroxy-compounds. *o*-Hydroxyphenyl sulphide,  $\text{SPh} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , is a viscous, yellow liquid, b. p. 219°/66 mm., and the para-compound a white solid, m. p. 25°.

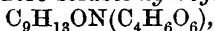
W. G.

**Trinitroanisoles.** H. VERMEULEN (*Rec. trav. chim.*, 1912, 31, 101—104. Compare Abstr., 1906, i, 256; and Blanksma, Abstr., 1904, i, 577; 1908, i, 979).—The trinitroanisoles were all obtained from the dinitroanisoles, using for nitration a mixture of nitric acid (D 1·5) and sulphuric acid in equal volumes.

2:3-Dinitroanisole yields 2:3:4-trinitroanisole, m. p. 155° (compare Meldola and Eyre, Trans., 1902, 81, 993), which when acted on by sodium methoxide gives 2:4-dinitro-1:3-dimethoxybenzene. 3:6-Dinitroanisole is converted into 3:4:6-trinitroanisole, m. p. 106—107°, which gives 4:6-dinitro-1:3-dimethoxybenzene with sodium methoxide, thus orientating the third nitro-group. 3:4-Dinitroanisole yields a mixture of 2:3:4- and 3:4:6-trinitroanisoles. 3:5-Dinitroanisole on nitration gives 2:3:5-trinitroanisole, m. p. 104°, and a small quantity of 3:4:5-trinitroanisole, m. p. 119—120°. With sodium methoxide, the former yields 3:5-dinitroveratrole, and the latter, 4:5-dinitro-1:3-dimethoxybenzene.

W. G.

***a*-*p*-Methoxyphenylethylamine [*a*-Anisylethylamine].** MARIO BETTI and GIUSEPPE DEL RIO (*Gazzetta*, 1912, 42, i, 283—288).—The authors have resolved the base into the optical isomerides by crystallisation of the hydrogen tartrates from alcohol. The less soluble *hydrogen tartrate*,  $\text{C}_9\text{H}_{13}\text{ON}(\text{C}_4\text{H}_6\text{O}_6)$ , forms large, lustrous crystals. It has  $\alpha^{20} + 1·66^\circ$  in 5% aqueous solution (200 mm. tube). The free base liberated from it has  $[\alpha]_{\text{D}}^{23} + 22·68^\circ$  in light petroleum (concentration 3·704%). Its *benzoyl* derivative crystallises in long needles, m. p. 129°, and has  $\alpha + 0·80^\circ$  in 1% alcoholic solution and in 400 mm. tube at about 20°. The more soluble *hydrogen tartrate*,



has  $\alpha + 1·12$ — $1·16^\circ$  in 5% aqueous solution in a 200 mm. tube at about

20°. The free base has  $[a]_D - 19.13^\circ$ . Its *benzoyl* derivative has m. p.  $138^\circ$ , and  $\alpha - 0.74^\circ$  in 1% alcoholic solution in a 400 mm. tube at about  $20^\circ$ .

R. V. S.

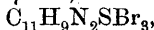
**Haloid Derivatives of Ditolyl Ethers.** ALPHONSE MAILHE and MARCEL MURAT (*Bull. Soc. chim.*, 1912, [iv], 11, 288—294).—A more detailed account of work published already (this vol., i, 254), in the course of which some further compounds are described. The mono-halogenated substances have the halogen atom in the para-position with respect to the ether linking, and the di-halogenated compounds have a halogen atom in the para-position in each of the two rings, except in the di-*p*-tolyl ethers, where the ortho-positions are occupied by the halogen atoms.

Chlorodi-*o*-tolyl ether has  $D^{10} 1.1741$ ,  $n_D 1.590$ . Dichlorodi-*o*-tolyl ether has  $D^9 1.2980$ ,  $n_D 1.611$ . *Bromo-di-o-tolyl ether*, b. p.  $323-325^\circ$ ,  $D^9 1.4090$ ,  $n_D 1.613$ , is a viscous liquid. The *dibromo*-derivative boils at  $250^\circ/15$  mm.

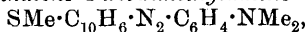
*Chlorodi-m-tolyl ether*, b. p.  $312^\circ$ ,  $D^{13} 1.1630$ ,  $n_D 1.588$ , and the corresponding *dichloro*-compound, b. p.  $336-338^\circ$ ,  $D^{13} 1.2882$ ,  $n_D 1.606$ , are both very viscous liquids. *Bromodi-m-tolyl ether*, b. p.  $330^\circ/755$  mm.,  $n_D 1.624$ , is liquid, whilst the *dibromo*-compound, already described by Cook (*Abstr.*, 1910, i, 731), is solid, m. p.  $120^\circ$ .

Chlorodi-*p*-tolyl ether,  $D^{10} 1.18$ ,  $n_D 1.602$ , and the *dichloro*-derivative are both liquid. *Bromo-di-p-tolyl ether* has  $n_D 1.620$ . T. A. H.

**4-Amino- $\alpha$ -naphthyl Mercaptan.** II. THEODOR ZINCKE and FRANZ SCHÜTZ (*Ber.*, 1912, 45, 636—645. Compare this vol., i, 257).—4-Amino- $\alpha$ -naphthyl methyl sulphide in alcoholic solution reacts with amyl nitrite and concentrated hydrochloric acid to form 1-methylthiol-naphthalene-4-diazonium chloride,  $\text{SMe} \cdot \text{C}_{10}\text{H}_6 \cdot \text{N}_2\text{Cl}$ , decomp.  $120^\circ$ , green needles or leaflets. The diazo-compound is stable, forms a *platini-chloride*, *chromate*, *nitrate*, *sulphate*, *bromide*, and *perbromide*,



decomp.  $135^\circ$ , and condenses normally with  $\beta$ -naphthol and with dimethylaniline to form respectively 1-methylthiolnaphthalene-4-azo- $\beta$ -naphthol,  $\text{SMe} \cdot \text{C}_{10}\text{H}_6 \cdot \text{N}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$ , green crystals with red fracture, and 1-methylthiolnaphthalene-4-azodimethylaminobenzene,



m. p.  $155^\circ$ , purple-red leaflets (*hydrochloride*, green powder). The diazo-compound is reconverted into 4-amino- $\alpha$ -naphthyl methyl sulphide by stannous chloride or sulphurous acid, but is changed by cold 10% potassium sulphite to 1 : 1'-dimethylthiol-4 : 4'-azonaphthalene,  $\text{N}_2(\text{C}_{10}\text{H}_6 \cdot \text{SMe})_2$ , dark red prisms with a green lustre, and by a mixture of 40% potassium hydrogen sulphite and cold saturated aqueous potassium chloride to *potassium* 1-methylthiolnaphthalene-4-diazosulphonate,  $\text{SMe} \cdot \text{C}_{10}\text{H}_6 \cdot \text{N}_2 \cdot \text{SO}_3\text{K}$ , m. p. about  $220^\circ$  (decomp.), yellow leaflets. The *sodium* salt, decomp.  $200^\circ$ , and the *barium* and the *silver* salts of the latter are described. The diazosulphonate is converted into the diazonium chloride by concentrated hydrochloric acid, and reacts in boiling water with zinc dust and acetic acid to form, after the addition of hot saturated potassium chloride, *potassium* 1-methylthiol-

*naphthalene-4-hydrazinesulphonate*,  $\text{SMe} \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH} \cdot \text{NH} \cdot \text{SO}_3\text{K}$ , decomp. 199—200°, colourless needles, which is decomposed by hydrochloric acid, yielding nitrogen, ammonia, sulphuric and sulphurous acids, and 4-amino- $\alpha$ -naphthyl methyl sulphide. The impure *hydrazine* has been obtained as an oil from the *barium hydrazinesulphonate*; by acetylation it yields the *acetyl* derivative,  $\text{SMe} \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH} \cdot \text{NHAc}$ , m. p. 216°, glistening leaflets.

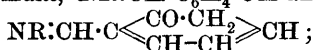
4-Dimethylamino- $\alpha$ -naphthyl methyl sulphide reacts with amyl nitrite and formic acid (D 1:2) to form 4-methylthiol- $\beta$ -naphthaquinone,  $\text{SMe}\cdot\text{C}_{10}\text{H}_5\text{O}_2$ , m. p.  $197^\circ$ , brownish-red needles, which is reduced to a colourless, unstable *quinol*, yields  $\beta$ -naphthaquinoneanilide or dianilide by treatment with aniline under suitable conditions, dichloro- $\beta$ -naphthaquinone by treatment with chlorine, 2-hydroxy- $\alpha$ -naphthaquinone by treatment with alkalis, and reacts with *o*-phenylenediamine to form the *naphthaphenazine*,  $\text{SMe}\cdot\text{C}_{10}\text{H}_5\text{N}_2\text{C}_6\text{H}_4$ , m. p.  $170^\circ$ , yellow needles.

C. S.

**Phenol-Quinone Isomerism of the Schiff's Bases of Aromatic Hydroxyaldehydes.** WILHELM MANCHOT and BERTIL PALMBERG (*Annalen*, 1912, 388, 103—135).—The mutually interchangeable "yellow" and "red" modifications of *p*-homosalicylidene-aniline and of ethyl salicylidene-*p*-aminobenzoate have been already described (Abstr., 1909, i, 805; 1910, i, 33; 1911, i, 36). Two new examples are now given. *α*-2-Hydroxynaphthylidene-*p*-aminophenol,  $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , when prepared by the rapid cooling of a concentrated alcoholic solution of its components, is obtained in yellow needles, m. p. 222°. When prepared by slow crystallisation or by keeping the yellow needles in contact with their mother liquor, the substance is obtained in the "red" modification, orange-yellow prisms, m. p. 226°; this form is converted into the "yellow" modification by rapid crystallisation from alcohol. In a similar manner, ethyl *p*-homosalicylidene-*p*-aminobenzoate,

has been obtained in a "yellow" modification (individual crystals appear as almost colourless, six-sided plates under the microscope) and a "red" modification, m. p. 101° (individual crystals appear as yellow or orange-red prisms); the "yellow" form becomes red at about 80°, melts at 90°, resolidifies, and melts again at 101°.

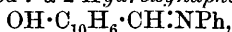
The isomerism in each of the preceding four cases is somehow connected with the hydroxyl group in the aldehyde, because only one compound is obtained in each case when the methyl or ethyl ether of the hydroxyaldehyde is condensed with the amine. It is suggested that the "yellow" and the "red" modifications may be represented by the respective formulæ,  $\text{NR}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$  and



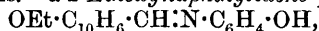
the "yellow" modification reacts more rapidly with cold alcoholic ferric chloride. Attempts have been made to prepare, from the "yellow" and the "red" modifications of an anil, derivatives corresponding with each of these formulæ, but they have been unsuccessful

on account of the ease with which the "yellow" and the "red" modifications change into one another; only in the case of ethyl *p*-homosalicylidene-*p*-aminobenzoate has the "yellow" modification been converted into a *hydrobromide*,  $C_{17}H_{17}O_3N, HBr$ , m. p.  $207^\circ$ , and the "red" modification into a *hydrobromide*, m. p.  $215-216^\circ$ .

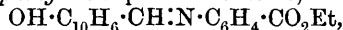
The following compounds, each of which occurs in only one modification, are described:  *$\alpha$ -2-Hydroxynaphthylideneaniline*,



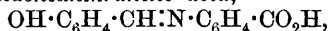
m. p.  $92^\circ$ , almost colourless, six-sided leaflets; by crystallisation from aqueous alcohol, the substance is obtained in hydrated, yellow needles, m. p.  $90-100^\circ$ , but the red leaflets described by Knoevenagel and Schröter are shown to be a mixture of the anil and a red oxidation product, m. p.  $265^\circ$ , the composition of which could not be settled definitely by analysis.  *$\alpha$ -2-Ethoxynaphthylidene-*p*-aminophenol*,



m. p.  $188^\circ$ , almost colourless prisms;  *$\alpha$ -2-hydroxynaphthylidene-*p*-anisidine*,  $OH \cdot C_{10}H_6 \cdot CH : N \cdot C_6H_4 \cdot OMe$ , yellow needles, m. p.  $108^\circ$ ; *ethyl  $\alpha$ -2-hydroxynaphthylidene-*p*-aminobenzoate*,



m. p.  $140^\circ$ , slender needles, and its *ethyl ether*, m. p.  $103.5^\circ$ , colourless crystals;  *$\alpha$ -2-hydroxynaphthylidene- $\alpha$ -naphthylamine*, m. p.  $178^\circ$ , orange-red crystals;  *$\alpha$ -2-hydroxynaphthylidene- $\beta$ -naphthylamine*, m. p.  $140^\circ$ , orange-yellow needles; *methyl *p*-homosalicylidene-*p*-aminobenzoate*,  $OH \cdot C_6H_3Me \cdot CH : N \cdot C_6H_4 \cdot CO_2Me$ , m. p.  $162^\circ$ ; **p*-homosalicylidene-*p*-aminobenzoic acid*, m. p.  $265^\circ$ ; **p*-homosalicylidene-*p*-aminophenol*, m. p.  $171^\circ$ , orange-red crystals; **p*-homosalicylidene-*p*-anisidine*, m. p.  $122^\circ$ ; *2-methoxy-5-methylbenzylidene-*p*-aminophenol*, m. p.  $190.5^\circ$ , colourless crystals; *2-methoxy-5-methylbenzylidene-*p*-anisidine*, m. p.  $90^\circ$ , colourless needles; *salicylideneanthranilic acid*,



has been obtained as a light yellow, crystalline mass, m. p.  $196-197^\circ$ , and as red crystals, m. p.  $202-203^\circ$ , but the evidence is not conclusive that these are "yellow" and "red" modifications respectively; *salicylidene-*p*-aminophenol*, m. p.  $140^\circ$ , yellow plates; *salicylidene-*p*-anisidine*, m. p.  $84^\circ$ , colourless, hexagonal leaflets; *o-methoxybenzylidene-*p*-aminophenol*, m. p.  $168^\circ$ , colourless leaflets.

C. S.

**The Action of Polyhydric Phenols on Uranium Salts.** J. A. SIEMSSSEN (*Chem. Zeit.*, 1912, 36, 353-354).—The addition of resorcinol, quinol, catechol, pyrogallol, phloroglucinol, etc., to the yellow solutions of uranium salts gives intensely red solutions, the tone of which varies from a light red to a purple-red, according to the concentration (compare Weinland and Binder, *ibid.*, 208). Experiments in which resorcinol was chiefly used showed that cotton is not dyed by such solutions, even in the presence of potassium hydrogen sulphate. Wool is dyed yellow, the colour becoming more intense on treatment with ammonia, and being very resistant towards cold alkalis and acids and towards warm soap and soda solutions; it is also completely fast to light. The compound to which the colour is due has not been isolated.

T. S. P.

**Triphenylcarbinols. III.** HUGO KAUFFMANN and PAUL PANNWITZ (*Ber.*, 1912, 45, 766—776).—Certain triphenylcarbinols containing methoxy-groups can be reduced to the corresponding triphenylmethane derivatives by alcoholic hydrogen chloride (*Abstr.*, 1905, i, 773; 1909, i, 99). However, the acetaldehyde which is also produced frequently reacts with the product to form tarry substances. The reduction of the carbinol is effected far more conveniently by boiling formic acid. It is found that under conditions in which triphenylcarbinol itself is extremely slowly reduced, (i) the presence of a methoxyl group in the ortho-position to the methane carbon atom greatly facilitates the reduction; in the meta-position it has very little influence; in the para-position it has a slight facilitating influence. Several methoxy-groups in para-positions render the reduction more easy; (ii) the influence of hydroxyl groups is similar to that of methoxyl groups; (iii) halogen atoms in the benzene nuclei do not markedly affect the reducibility; (iv) chloroanil, malachite-green, rosolic acid, fluorescein, and triphenylmethane-dyes, such as magenta, are reduced extremely slightly or not at all; (v) the reducibility does not run *pari passu* with the basicity of the triphenylcarbinols.

The following new compounds are described: *m*-Methoxytriphenylmethane, leaflets, m. p. 86°. *op'*-Dimethoxytriphenylcarbinol, m. p. 115°, is prepared from *p*-methoxybenzophenone and magnesium *o*-anisyl iodide, and yields *op'*-dimethoxytriphenylmethane, m. p. 94°, by reduction, best by zinc dust and acetic acid. *oo'p'*-Trimethoxytriphenylcarbinol, m. p. 119°, prepared from magnesium *o*-anisyl iodide and 2:4-dimethoxybenzophenone, is easily reduced to *oo'p'*-trimethoxytriphenylmethane, m. p. 118°. 5-Bromo-2:4-dimethoxytriphenylcarbinol, m. p. 186°, is obtained by the bromination of 2:4-dimethoxytriphenylcarbinol in carbon disulphide or concentrated sulphuric acid, and yields 5-bromo-2:4-dimethoxytriphenylmethane, m. p. 176°, by reduction. 5-Chloro-2:4-dimethoxytriphenylcarbinol, m. p. 182°, obtained by treating 2:4-dimethoxytriphenylcarbinol in chloroform with phosphorus pentachloride and subsequently with water, is reduced, as easily as the preceding bromo-compound, to 5-chloro-2:4-dimethoxytriphenylmethane, m. p. 159°.

Michael's salicylresorcinol is shown to be resorcinylic salicylate, not 2:2'-4'-trihydroxybenzophenone as has hitherto been supposed.

C. S.

**Action of Magnesium Phenyl Bromide on Methylpinacolin.** (Mme.) PAULINE RAMART-LUCAS (*Compt. rend.*, 1912, 154, 708—710).—The tertiary alcohols obtained by applying the Grignard reaction to trialkylacetophenones (*Abstr.*, 1910, i, 378) undergo dehydration when heated with acetyl chloride and acetic anhydride, giving the corresponding hydrocarbons. The constitution of  $\gamma$ -phenyl- $\beta\beta$ -dimethylbutan- $\gamma$ -ol (*loc. cit.*) and of the corresponding pentanol has been completely established by their synthesis from pinacolin and methylpinacolin respectively by the action of magnesium phenyl bromide. The occurrence of acetophenone amongst the products formed by the action of chromic acid on  $\gamma$ -phenyl- $\beta\beta$ -dimethylbutan- $\gamma$ -ol is probably due to the intermediate formation of a hydrocarbon containing the

trimethylene ring, arising through a dehydrating action of the oxidising mixture. W. O. W.

**Dipterocarpol.** LEOPOLD VAN ITALLIE (*Pharm. Weekblad*, 1912, 49, 314—321).—*Dipterocarpol* is a phytosterol isolated from the balsam of *Dipterocarpus Hasseltii* and *D. trinervis* by extracting with boiling alcohol the part insoluble in light petroleum. It forms colourless plates, m. p. 134—135°,  $[\alpha]_D + 64.6^\circ$ , molecular formula  $C_{27}H_{46}O_2$ . It answers the phytosterol tests of Liebermann, Hesse, Mach, Hirschsohn, and Tschugaeff.

When heated at 160° under pressure with anhydrous sodium acetate and acetic anhydride, it yields, by elimination of  $H_2O$ , *dipterocarpol anhydride*,  $C_{27}H_{44}O$ , colourless, doubly refracting crystals, m. p. 69—70°, which answers to the same tests as the parent substance. Phenyl-carbimide also reacts, forming the anhydride, but no product was obtained with either benzoyl chloride or benzoic anhydride.

Oxidation with Kiliani's chromic acid mixture converts the phytosterol into the corresponding ketone, *dipterocarphone*,  $C_{27}H_{44}O_3$ , colourless, columnar, rhombic crystals, m. p. 183—184°,  $[\alpha]_D + 71.03^\circ$ , which answers the phytosterol tests. Its formation indicates the presence of a  $CH\cdot OH$ -group in dipterocarpol. *Dipterocarpoxyime*,  $C_{27}H_{44}O_2\cdot NOH$ , forms microscopic, colourless crystals, m. p. 249—250°.

With halogens, dipterocarpol forms additive products, which could not be obtained crystalline. Reduction with sodium and amyl alcohol did not yield any crystalline product. A. J. W.

**Olivil.** WILHELM KOERNER and BARTOLO L. VANZETTI (*Mem. R. Accad. Lincei*, 1911, [v], 8, 749—792. Compare Abstr., 1903, i, 430).—The authors give a full account of the work on this subject previously reported (*loc. cit.*), and some new derivatives are described. Olivil ethyl alcoholate has m. p. about 120°, and  $[\alpha]_D^{25} - 23.8^\circ$  (in ethyl alcohol). Olivil hydrate has m. p. about 105°, and  $[\alpha]_D^{25} - 127^\circ$  (in water). Olivil methyl alcoholate has m. p. about 97°, and  $[\alpha]_D^{25} - 48.9^\circ$  (in methyl alcohol). Olivil propyl alcoholate has m. p. about 104°. Olivil isopropyl alcoholate has m. p. 101.5°. Olivil allyl alcoholate has m. p. 99.5—106°.

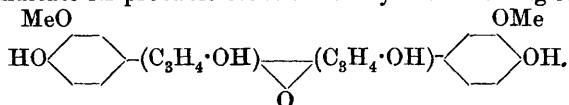
Dimethylolivil,  $C_{18}H_{16}O_8(OMe)_4$ , crystallises in small, silky needles, m. p. 156°,  $[\alpha]_D^{25} - 56.4^\circ$  (in alcohol). When treated with bromine in glacial acetic acid solution, dimethylolivil yields a *monobromo*-derivative,  $C_{22}H_{27}O_7Br$ , which crystallises in colourless scales, m. p. 128°, and also a *di*bromo-derivative,  $C_{22}H_{26}O_7Br_2$ , which forms (with 1 mol. of benzene) silky needles, m. p. about 85°, or (anhydrous) spherical aggregates of needles, m. p. 132°. Dimethylolivil also yields a derivative with *mercuric acetate*,  $C_{22}H_{26}O_6(HgAc)_2$ , and with *mercuric chloride*,  $C_{22}H_{26}O_6(HgCl)_2$ . *Monomethylolivil*,  $C_{21}H_{26}O_7$ , is obtained when olivil is treated with about three-fourths of the amount of methyl iodide calculated for complete methylation; it crystallises in woolly needles, m. p. 218° (if the bath is previously heated to 200°). *Diethylolivil*,  $C_{24}H_{32}O_7$ , crystallises in needles, m. p. 182°. *Monoethylolivil*,  $C_{22}H_{28}O_7$ , has m. p. 145°. *Methylethylolivil*,  $C_{23}H_{30}O_7$ , can be prepared either from monoethylolivil or from monomethylolivil; it crystallises in needles, m. p. about 169°. *Dipropylolivil*,  $C_{26}H_{36}O_7$ ,

forms long, thin needles, m. p.  $135.5^\circ$  *Dibenzylolivil*,  $C_{34}H_{36}O_7$ , crystallises in silky needles, m. p.  $150-157^\circ$ , according to the mode of heating.

*isoOlivil*,  $C_{18}H_{16}O_3(OH)_2(OMe)_2$ , forms prismatic crystals, m. p.  $167^\circ$ ; it has  $[\alpha]_D^{25} + 352^\circ$  (in water),  $[\alpha]_D^{15} + 118^\circ$  (in acetic acid),  $[\alpha]_D^{25} + 61.1^\circ$  (in alcohol). With concentrated sulphuric acid it gives a deep orange-red coloration, which becomes violet on addition of water, and with ferric chloride it yields a fugitive blue coloration, which becomes green and finally brown. With ethyl alcohol, *isoolivil* yields an *alcoholate*,  $C_{20}H_{24}O_7, \frac{1}{2}EtOH$ , which forms tabular crystals. The *methyl alcoholate*,  $C_{20}H_{24}O_7, 2MeOH$ , crystallises in tablets. The compound with ethyl ether,  $C_{20}H_{24}O_7, Et_2O$ , and the compound with acetone,  $C_{20}H_{24}O_7, COMe_2$ , are also crystalline.

*Dimethylisoolivil*,  $C_{18}H_{16}O_3(OMe)_4$ , crystallises in silky needles, m. p.  $184.5^\circ$ ,  $[\alpha]_D^{22.5} + 33.58^\circ$ . *Monomethylisoolivil*,  $C_{18}H_{16}O_3(OH)(OMe)_3$ , forms prismatic crystals (with methyl alcohol) or thin needles (with  $2H_2O$ ) [Repossi: the hydrate crystallises in the tetragonal system,  $\alpha:c = 1:0.91654$ ]; the anhydrous substance has m. p.  $208^\circ$ . *Diethylisoolivil*,  $C_{24}H_{32}O_7$ , crystallises in needles, m. p.  $179-179.5^\circ$ ,  $[\alpha]_D^{22.5} + 38.22^\circ$  (in alcohol). *Monoethylisoolivil*,  $C_{22}H_{28}O_7$ , crystallises with  $2H_2O$ , and has m. p.  $148-150^\circ$  with subsequent partial solidification; the anhydrous substance is very hygroscopic. *Ethylmethylisoolivil*,  $C_{23}H_{30}O_7$  (prepared by ethylating monomethylisoolivil), crystallises in groups of needles, m. p. about  $189^\circ$ ,  $[\alpha]_D^{25} + 50.35^\circ$  (in alcohol). *Methylethylisoolivil*,  $C_{23}H_{30}O_7$  (prepared by methylating monoethylisoolivil), has m. p.  $168^\circ$ ,  $[\alpha]_D^{25} + 46.3^\circ$  (in alcohol). *Benzylmethylisoolivil*,  $C_{28}H_{32}O_7$  (from monomethylisoolivil), crystallises in soapy needles, m. p.  $173-174^\circ$ .

In view of the reactions of olivil now and formerly described, the authors indicate its probable constitution by the following formula:



*isoOlivil* would differ from this only in regard to the arrangement of atoms in the side-chain.

R. V. S.

**Direct Hydrogenation of Alkyl Benzoates by Catalysis: Preparation of Alkyl cycloHexanecarboxylates.** PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1912, 154, 922-925).—Benzoic acid and its esters, which are the aromatic compounds most easily hydrogenated by the ordinary method, have hitherto proved the most difficult to attack by the catalytic method in presence of reduced nickel. Very small quantities of cyclohexanecarboxylic acid are formed when benzoic acid and a large excess of hydrogen are passed over nickel below  $200^\circ$ .

When methyl benzoate and hydrogen are passed over nickel at  $210-225^\circ$ , the metal rapidly loses all activity as a catalyst, owing to the formation of a film of nickel benzoate. By operating at  $180^\circ$ , however, with a large excess of hydrogen, the action proceeds readily in the normal way. From ethyl benzoate at  $180^\circ$ , a good yield of

ethyl cyclohexanecarboxylate,  $D^{16}$  0.962,  $n_D^{16}$  1.452, is obtained. *iso*-Amyl benzoate gave an 80% yield of *iso*amyl cyclohexanecarboxylate, b. p. 247°,  $D^{18}$  0.934,  $n_D^{18}$  1.458. W. O. W.

[Preparation of 2:4-Dichlorophenylthiolacetic Acid.] KALLE & Co. (D.R.-P. 241839).—2:4-Dichlorophenylthiolacetic acid, colourless needles, is prepared from 2:4-dichloroaniline by successive diazotisation, xanthogenation, followed by treatment with sodium hydroxide and chloroacetic acid; after treatment with concentrated sulphuric acid, it yields a vat dye (violet powder), which dyes cotton a fast violet-red. F. M. G. M.

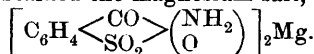
[Preparation of  $\psi$ -Cumylthiolacetic Acid.] KALLE & Co. (D.R.-P. 241910).— $\psi$ -Cumylthiolacetic acid, colourless needles, is prepared by known methods from 5-chloro-*o*-toluidine. The patent contains a tabulated summary of the properties of numerous vat dyes prepared from arylthiolacetic acid obtained from toluidines, xylydines,  $\psi$ -cumidines, anisidines, phenetidines, naphthylamines, and their halogen and nitrated derivatives. F. M. G. M.

Two Compounds Formed by Iodine and Tyrosine obtained by the Tryptic Hydrolysis of Proteins. PAUL MACQUAIRE (*Compt. rend.*, 1912, 154, 938—939).—Analyses confirm the identity of di-iodotyrosine from peptone (this vol., i, 58) and that prepared by the action of iodine on tyrosine. On prolonged boiling of di-iodotyrosine with water, a portion of the iodine is eliminated, and a more stable, coloured, amorphous substance formed. W. O. W.

Further Study of Two of the Products of the Transformation of *p*-Sulphamidobenzoic Acid when Heated to 220°. JOSEPH S. CHAMBERLAIN (*Amer. Chem. J.*, 1912, 47, 318—333).—Stoddard (this vol., i, 111) has investigated the products obtained by Remsen and Muckenfuss (*Abstr.*, 1896, i, 481) by heating *p*-sulphamidobenzoic acid at 220°. An account is now given of a further study of these substances.

When the product obtained by heating the acid at 220° for eight hours is extracted with hot alcohol, the ammonium salt of *p*-benzoic sulphinide,  $C_6H_4\langle\begin{smallmatrix} CO \\ SO_2 \end{smallmatrix}\rangle N\cdot NH_4$ , separates on cooling. The barium salt,  $(C_6H_4\langle\begin{smallmatrix} CO \\ SO_2 \end{smallmatrix}\rangle N)_2Ba\cdot 3H_2O$ , copper salt,  $(C_6H_4\langle\begin{smallmatrix} CO \\ SO_2 \end{smallmatrix}\rangle N)_2Cu$ , and lead salt,  $(C_6H_4\langle\begin{smallmatrix} CO \\ SO_2 \end{smallmatrix}\rangle N)_2Pb\cdot 3H_2O$ , are also described.

By the action of magnesium hydroxide on the "infusible diamide," Stoddard (*loc. cit.*) obtained the magnesium salt,



On treating the diamide with barium hydroxide, however, the whole of the nitrogen is expelled as ammonia, and barium *p*-sulphobenzoate is produced, and an intermediate salt containing one atom of nitrogen cannot be obtained.

On heating a mixture of potassium hydrogen *p*-sulphobenzoate

and ammonium thiocyanate at 200°, a salt was obtained which was probably *potassium p-carbamidobenzenesulphonate*; the corresponding *sodium* salt was also prepared.

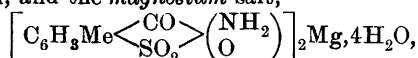
E. G.

**Study of the Products Formed by the Action of Heat on *p*-Sulphamido-*m*-toluic Acid.** CAMPBELL E. WATERS (*Amer. Chem. J.*, 1912, 47, 333—351).—In view of the results obtained on heating *p*-sulphamidobenzoic acid at 220° (Remsen and Muckenfuss, *Abstr.*, 1896, i, 481; Stoddard, *this vol.*, i, 111; Chamberlain, preceding abstract), a study has been made of the effect of heat on *p*-sulphamido-*m*-toluic acid.

Remsen and Iles have stated that this acid has m. p. 254·5—255°, but it is now found that the m. p. varies greatly with the rate of heating.

When the acid is heated for five to seven hours at 220°, it undergoes a similar change to that which takes place in the case of *p*-sulphamidobenzoic acid; the products of the change are *p*-sulpho-*m*-toluic acid, ammonium hydrogen *p*-sulphotoluate, and an infusible diamide of *p*-sulpho-*m*-toluic acid, but no evidence was obtained of the existence of an acid analogous to Remsen and Muckenfuss' *iso-p*-sulphamidobenzoic acid.

The *infusible diamide*,  $C_6H_3Me<\begin{smallmatrix} CO \\ SO_2 \end{smallmatrix}>(NH_2)_2$ , crystallises in orthorhombic plates. Both nitrogen atoms are eliminated as ammonia by the action of sodium hydroxide or barium hydroxide, thus indicating that a sulphamido-group is not present. On boiling the compound with magnesium hydroxide, however, only one nitrogen atom is expelled, and the *magnesium salt*,



of an acid isomeric with *p*-sulphamido-*m*-toluic acid is produced; the corresponding *barium* and *potassium* salts crystallise with 1H<sub>2</sub>O, the *zinc* salt with 5½H<sub>2</sub>O, and the *copper* salt with 3H<sub>2</sub>O; the *ammonium* salt forms rectangular prisms.

*Barium p-sulpho-m-toluate* crystallises in needles containing 2H<sub>2</sub>O; the *barium hydrogen* and *sodium hydrogen* salts crystallise with 5H<sub>2</sub>O and 2½H<sub>2</sub>O respectively. The *ammonium hydrogen* salt, prepared from the *barium* salt, or by the hydrolysis of *p*-sulphamido-*m*-toluic acid, was not identical with that obtained from the product of the prolonged fusion of the sulphamido-acid.

E. G.

**Preparation of Carboxylic Acids of Aromatic Ammonium Compounds or their Derivatives.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 240835. Compare *Abstr.*, 1911, i, 627; *this vol.*, i, 176).—When *ω*-chloro-*p*-toluic acid, m. p. 195° (*loc. cit.* gives 190—192°), is heated at 60—70° during seven to eight hours with dimethylaniline, it yields the *compound*, C<sub>6</sub>H<sub>4</sub>·C<sub>6</sub>H<sub>4</sub>·CH<sub>2</sub>·NClMe<sub>2</sub>Ph, needles, m. p. 151° (decomp.). Similar products are formed when other tertiary bases are employed.

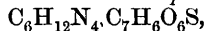
*ω*-Chloro-*p*-toluonitrile, colourless crystals, m. p. 78°, is prepared by chlorinating *p*-toluonitrile; when treated with pyridine it yields the *compound*, C<sub>5</sub>H<sub>5</sub>NCl·CH<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>·CN, colourless needles readily soluble in alcohol or water.

F. M. G. M.

**Action of the Ultra-violet Rays on Stereoisomerides of the Cinnamic Series.** II. MARUSSIA BAKUNIN (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iii], 17, 372—375. Compare Bakunin and Parlati, *Abstr.*, 1907, i, 415; Bakunin and Lanis, *Abstr.*, 1911, i, 992; Stoermer, *ibid.*, i, 295).—The most favourable results were obtained by keeping alcoholic solutions of the substances at a distance of a few centimetres from an uviol lamp for about 190 hours. The phenyl-cinnamic acid of m. p.  $172^{\circ}$  is unaffected. After twenty-four hours, the phenyl-*p*-nitrocinnamic acid of m. p.  $143^{\circ}$  is completely converted into that of m. p.  $214^{\circ}$ . The reverse change could not be effected. The phenyl-*m*-nitrocinnamic acid of m. p.  $181^{\circ}$  is converted slowly and partially into that of m. p.  $195^{\circ}$ , and the inverse change also occurs, but less readily. The phenyl-*o*-nitrocinnamic acid of m. p.  $196^{\circ}$  apparently yields traces of the isomeride of m. p.  $147^{\circ}$ .

4-Nitro-2-phenylindone and 6-nitro-2-phenylindone are very slightly affected by the ultra-violet rays. R. V. S.

**Preparation of Hexamethylenetetramine Sulphosalicylates.** J. D. RIEDEL (D.R.-P. 240612. Compare *Abstr.*, 1893, i, 298; this vol., i, 168).—*Hexamethylenetetramine sulphosalicylate*



prismatic crystals, is prepared by treating an aqueous solution of hexamethylenetetramine (1 part) with an alcoholic solution of sulphosalicylic acid (2 parts); it is of therapeutic value, and is decomposed by hot dilute mineral acids with evolution of formaldehyde.

F. M. G. M

**Some Derivatives of Benzoylpropionic Acid.** (Attempted Synthesis of Hydroxyl Derivatives of Naphthalene.) GUIDO BARGELLINI and MICHELE GIUA (*Gazzetta*, 1912, 42, i, 197—209).—The authors have attempted to obtain naphthalene derivatives: (1) by withdrawing  $\text{H}_2\text{O}$  from derivatives of benzoylpropionic acid, such as the lactone resulting from the reduction of anisoylpropionic acid with sodium amalgam; (2) by removing  $\text{H}_2\text{O}$  from benzoylpropionic acid, or  $\text{MeOH}$  from its methyl ester. In the present paper a number of methoxyl-derivatives of benzoylpropionic acid are described; they were obtained by condensing succinic anhydride with anisole and with other aromatic methoxy-compounds.

Anisoylpropionic acid,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , is obtained when anisole is treated with succinic anhydride in the presence of aluminium chloride, and is identical with that prepared by Poppenberg (*Abstr.*, 1902, i, 60). On reduction with sodium amalgam it yields *anisyl- $\gamma$ -butyrolactone*, which has m. p. about  $45^{\circ}$ . *Methyl anisoyl-propionate*,  $\text{C}_{12}\text{H}_{14}\text{O}_4$ , forms white needles, m. p.  $46-47^{\circ}$ . *3:4-Dimethoxybenzoylpropionic acid*,  $\text{C}_{12}\text{H}_{14}\text{O}_5$  (from veratrole and succinic anhydride in the presence of aluminium chloride), crystallises in colourless needles, m. p.  $160-161^{\circ}$ . It gives a yellow coloration with concentrated sulphuric acid. *2:4-Dimethoxybenzoyl-propionic acid*,  $\text{C}_{12}\text{H}_{14}\text{O}_5$  (from resorcinol dimethyl ether and succinic anhydride), has m. p.  $146^{\circ}$ . It gives a yellow coloration with concentrated sulphuric acid. *2:5-Dimethoxybenzoylpropionic acid*,  $\text{C}_{12}\text{H}_{14}\text{O}_5$  (from quinol dimethyl ether and succinic anhydride), forms

lustrous needles, m. p. 99—100°; it gives an orange-yellow coloration with concentrated sulphuric acid. 2:4:5-*Trimethoxybenzoylpropionic acid*,  $C_{13}H_{16}O_6$  (from hydroxyquinol trimethyl ether and succinic anhydride), crystallises in colourless needles, m. p. 168—169°; it gives a yellowish-green coloration with concentrated sulphuric acid. Its *methyl ester*,  $C_{14}H_{18}O_6$ , forms colourless plates, m. p. 110—111°; it gives a pale yellow coloration with concentrated sulphuric acid.

When pyrogallol trimethyl ether is treated with succinic anhydride in the presence of aluminium chloride, 2-*hydroxy-3:4-dimethoxybenzoylpropionic acid*,  $C_{12}H_{14}O_6$ , is produced; it crystallises in colourless needles, m. p. 152°. With concentrated sulphuric acid the substance gives a yellow coloration, which becomes dark red on warming. With ferric chloride it gives a red coloration. It is not possible to esterify the free hydroxyl-group in this acid. *Methyl 2-hydroxy-3:4-dimethoxybenzoylpropionate*,  $C_{13}H_{16}O_6$ , forms colourless needles, m. p. 106°; it gives a yellowish-green coloration with concentrated sulphuric acid.

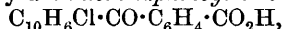
R. V. S.

**Friedel-Crafts' Reaction.** II. GUSTAV HELLER (*Ber.*, 1912, 45, 665—673. Compare *Abstr.*, 1908, i, 994).—To ascertain whether the complex, intermediate product, the existence of which is assumed in the formation of benzoylbenzoic acid (*loc. cit.*), can exert a condensing or catalytic action, phthalic anhydride, aluminium chloride, and benzene are allowed to react, the mass is cooled and treated with benzoyl chloride, and then is re-heated at 60—75°. The chief product is an additive compound,  $C_{20}H_{18}O_2 \cdot AlCl_3$ , of diphenylphthalide and aluminium chloride, the by-products, after the addition of water, being benzoic acid, benzophenone, and benzoylbenzoic acid. When ethyl bromide is used in place of the benzoyl chloride in the preceding experiment, no action occurs, and 99% of the theoretical yield of benzoylbenzoic acid is obtained.

When equal molecular quantities of phthalic anhydride, benzoyl chloride, benzene, and aluminium chloride are heated together, the reaction occurs preferentially with the phthalic anhydride rather than with the benzoyl chloride, 75·9% of the theoretical quantity of benzoylbenzoic acid being produced; the amount of benzophenone was not estimated.

[With ERICH GRÜNTAL.]—Anthracylbenzoic acid (*loc. cit.*) has been obtained in stout prisms, m. p. 242—243°; it yields anthraquinone by treatment with chromic and acetic acids, showing that the phthaloyl group is attached to a *meso*-carbon atom.

*α*-Chloro-naphthalene, phthalic anhydride, and aluminium chloride react to form ultimately *α*-4-chloronaphthoyl-*o*-benzoic acid,



m. p. 172—174°, the constitution of which is proved by the formation of 1-hydroxy-4-naphthoic acid (following abstract) by fusion with potassium hydroxide at 250—255°. When heated with concentrated sulphuric acid at 60—70°, the acid yields 1-chloro-3:4-naphthanthraquinone,  $C_6H_4 \begin{smallmatrix} CO \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} C_{10}H_5Cl$ , m. p. 180·5—181·5°, yellow needles.

*β*-3-Chloronaphthoyl-*o*-benzoic acid,  $C_{10}H_5Cl \cdot CO \cdot C_6H_4 \cdot CO_2H$ , m. p.

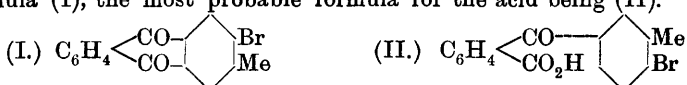
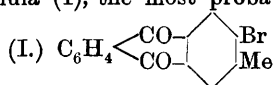
226—227°, prepared in a similar manner from  $\beta$ -chloronaphthalene, can be converted into 2-chloro-3:4-naphthanthraquinone, m. p. 233—234°, by sulphuric acid, and by oxidation by potassium permanganate yields a chlorinated acid by rupture of the naphthalene nucleus. C. S.

**$\alpha$ -Naphthol-4-carboxylic Acid.** GUSTAV HELLER [with HANS RUHTENBERG] (*Ber.*, 1912, 45, 674—679).— $\alpha$ -Naphthol-4-carboxylic acid,  $\text{OH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$ , m. p. 183—184°, is prepared by heating the corresponding aldehyde with potassium hydroxide and a little water at 250°. It crystallises in yellow needles, yields a chocolate precipitate with ferric chloride, and forms an *acetyl* derivative, m. p. 178—179°. It condenses with benzenediazonium chloride in alkaline solution to form benzeneazo- $\alpha$ -naphthol, yields nitroso- $\alpha$ -naphthol with nitrous acid, and by nitration in glacial acetic acid at 20° forms 2-nitro- $\alpha$ -naphthol-4-carboxylic acid, m. p. 258° (decomp.), yellow needles, which possesses dyeing properties and yields 2-amino- $\alpha$ -naphthol-4-carboxylic acid, m. p. 143° (decomp.), by reduction with alkaline sodium hyposulphite. The amino-acid gives a blood-red coloration with ferric chloride, and by treatment with 38% nitric acid (assisted by two drops of stronger acid) yields  $\beta$ -naphthaquinone-4-carboxylic acid,  $\text{C}_{11}\text{H}_6\text{O}_4$ , m. p. 164—165° (decomp.), yellowish-red crystals; the latter yields 1:2-dihydroxy-4-naphthoic acid, m. p. 195° (decomp.), by treatment with aqueous sodium hydrogen sulphite.

1-Hydroxy-4-naphthoic acid is converted by concentrated sulphuric acid at the ordinary temperature into 2-sulpho- $\alpha$ -naphthol-4-carboxylic acid,  $\text{C}_{11}\text{H}_8\text{O}_6\text{S}$ , m. p. 153° (decomp), the constitution of which is proved by the formation of benzeneazo- $\alpha$ -naphthol-2-sulphonic acid by condensation with benzenediazonium chloride. C. S.

**Abnormal Friedel-Crafts' Reactions.** GUSTAV HELLER [with ERICH GRÜNTAL and HANS RUHTENBERG] (*Ber.*, 1912, 45, 792—796).—*o*- and *p*-Chlorotoluenes combine with phthalic anhydride in presence of aluminium chloride to form the corresponding chlorotoluylbenzoic acids (*Abstr.*, 1908, i, 994).

The bromotoluenes behave differently: from *o*-, *p*-, or *m*-bromotoluene a mixture of several acids was obtained, from which only one bromotoluylbenzoic acid could be isolated, which was in each case the same and yielded the same bromomethylantraquinone having the formula (I), the most probable formula for the acid being (II). The



$\beta$ -position of the halogen in the anthraquinone is proved by the fact that no condensation product was obtained on heating with aniline or *p*-toluidine and sodium acetate. When heated with sodium in amyl alcohol and zinc dust, 3-methylantraquinone was formed.

*p*-Bromo-*m*-toluyl-*o*-benzoic acid crystallises in long, colourless needles, m. p. 183—184°.

2-Bromo-3-methylantraquinone separates in long, pale straw-yellow needles, m. p. 219—220°.

4-Anilino-1-methylantraquinone, obtained from 4-chloro-1-methyl-

anthraquinone on heating with aniline and sodium acetate, crystallises in reddish-black, bent needles, m. p. 144°. The corresponding 4-toluidino-1-methylantraquinone separates in deep red rods, m. p. 159—160°. 2-Anilino-1-methylantraquinone does not react with aniline or toluidine. E. F. A.

**Hydroxyphenyl-, Hydroxy-*p*-tolyl-, and Hydroxydiphenylhomocampholic Acids and Their Transformation into Benzylidene-, *p*-Tolylidene-, and Diphenylmethylenecamphors.** ALBIN HALLER (*Compt. rend.*, 1912, 154, 742—748. Compare Abstr., 1900, i, 452).—Hydroxyphenylhomocampholic acid, produced by the hydrolysis of benzylidenecamphor with hydrogen bromide, separates from methyl or ethyl alcohol below 50° in efflorescent crystals containing a molecule of alcohol, which is only lost at 130°; the product then has m. p. 205—207°. Hydroxy-*p*-tolylhomocampholic acid has m. p. 164° (not 217° as stated previously),  $[\alpha]_D + 71.45^\circ$ ; the sodium salt is readily hydrolysed by water. Hydroxydiphenylhomocampholic acid,  $\text{OH} \cdot \text{CPh}_2 \cdot \text{CH}_2 \cdot \text{C}_8\text{H}_{14} \cdot \text{CO}_2\text{H}$ , occurs in leaflets, m. p. 210°,  $[\alpha]_D + 111.06^\circ$ ; the sodium salt crystallises in pearly leaflets very sparingly soluble in water.

When heated with excess of acetyl chloride the foregoing acids lose  $2\text{H}_2\text{O}$ , and form the parent unsaturated compounds. Benzylidenecamphor and its homologues regenerated in this way show no loss in rotatory power. In the last instance, a yellow compound, m. p. 123°, formed simultaneously in small quantities, appears to be isomeric with diphenylmethylenecamphor. W. O. W.

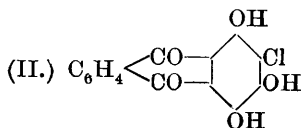
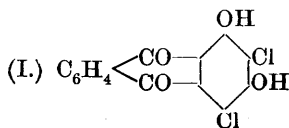
**Dichlorodihydroxybenzoylbenzoic Acid: its Conversion into Tetrachlorofluorescein and into Anthraquinone Derivatives.** CARL METTLER (*Ber.*, 1912, 45, 800—804).—It is possible to chlorinate dihydroxybenzoylbenzoic acid by means of sulphuryl chloride with the formation of 3:5-dichloro-2:4-dihydroxybenzoylbenzoic acid,  $\text{C}_6\text{HCl}_2(\text{OH})_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , which when heated above the melting point is converted into tetrachlorofluorescein. This dyes silk in practically the same manner as eosin, the colour being perhaps a shade more yellow.

When dichlorodihydroxybenzoylbenzoic acid is condensed with fuming sulphuric acid and boric acid, dichloroxanthopurpurin or chloropurpurin are produced according to the temperature.

3:5-Dichloro-2:4-dihydroxybenzoylbenzoic acid crystallises in cubes, m. p. 222° (decomp.).

Tetrachlorofluorescein is a red, crystalline powder, which softens at 295°, m. p. 305°.

Dichloroxanthopurpurin (I) is a yellow, crystalline powder, m. p.



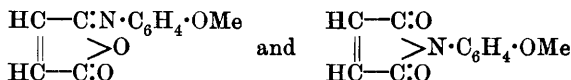
236—238°, the solution in sulphuric acid is yellow, and it dissolves in sodium carbonate with a reddish-orange coloration.

*Chloropurpurin* (II) crystallises in deep red needles, m. p. 270—273°. It dissolves in sodium carbonate with a brownish-red and in sulphuric acid with a purple-red coloration.

E. F. A.

**Chromoisomerides.** ARNALDO PIUTTI and E. DE' CONNO (*Mem. R. Accad. Lincei*, 1911, [v], 8, 793—810).—The authors have investigated the absorption spectra of solutions of a number of the pairs of isomeric compounds formerly described (compare Piutti, *Abstr.*, 1910, i, 672) with a view to determining in which cases the isomerism is physical, and in which chemical. The measurements were effected by Hartley's method, but the arc between iron electrodes (containing some manganese) was employed as the source of light. For each substance photographs were taken of the absorption spectra at ten different concentrations. The white and yellow forms of *p*-methoxyphenylphthalimide have the same absorption spectrum, and are therefore not chemical isomerides. [SCACCHI: the white isomeride crystallises in the rhombic system,  $a : b : c = 1.0096 : 1 : 1.0464$ .]

The two forms of *p*-methoxyphenylmaleinimide (m. p. 145—146° and 148.5° respectively) have different absorption spectra, and are therefore assigned the formulæ :



respectively. The two *p*-ethoxyphenylmaleinimides (m. p. 127° and 134—135° respectively) have also different absorption spectra, and are consequently assigned formulæ analogous to the above.

3-Nitroaceto-*p*-toluidide crystallises in two forms, which have the same absorption spectrum, and the same is true of the two forms of 2:4-dinitrophenyl-*o*-tolylamine.

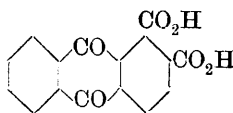
*p*-Hydroxy-, *p*-methoxy-, and *p*-ethoxy-phenylpyrocinchonimides each exist in two forms (white and yellow); the absorption spectra of all six are identical, so that the pairs are physical isomerides. The different substituting groups make no perceptible difference to the absorption spectrum.

*p*-Hydroxyphenylitaconamic acid exists in three forms: (1) m. p. 161—162° (white); (2) m. p. 118—119° (yellow); (3) m. p. 97—98° (white). *p*-Methoxyphenylitaconamic acid exists in three forms: (1) m. p. 166—167° (white); (2) m. p. 144—145° (yellow); (3) m. p. 135—136° (white). *p*-Ethoxyphenylitaconamic acid also exists in three forms: (1) m. p. 165—166°; (2) m. p. 148—149°; (3) m. p. 134—135°. Of these nine isomerides, the three numbered (1) and the three numbered (3) have identical absorption spectra, whilst the remaining three numbered (2) have a different absorption spectrum (which is identical in all three cases).

The two forms of *p*-methoxy- and *p*-ethoxy-phenylfumardiamides show different absorption spectra, and therefore these pairs are not physical isomerides.

R. V. S.

**Preparation of Anthraquinone-1:2-dicarboxylic Acids.**  
 ROLAND SCHOLL (D.R.-P. 241624).—*Anthraquinone-1:2-dicarboxylic acid* (annexed formula), a yellow, crystalline meal, is readily prepared



by oxidising naphthanthraquinone with either chromic acid, nitric acid, potassium permanganate, or potassium chlorate in the presence of sulphuric acid. The acid has m. p.  $270^{\circ}$  (approx.), at about which temperature it is converted into the *anhydride*, m. p.  $322-324^{\circ}$ , which can also be obtained by dissolving the acid in hot acetic anhydride. F. M. G. M.

**2:6-Dinitrobenzaldehyde.** SIEGMUND REICH [and J. PINCZEWSKI] (*Ber.*, 1912, 45, 804—809).—2:6-Dinitrobenzaldehyde has been prepared by the following series of reactions. 2:6-Dinitrotoluene, when heated with bromine in sealed tubes at  $150^{\circ}$ , forms 2:6-dinitrobenzyl bromide; this is condensed with aniline to 2:6-dinitrobenzylaniline, and the product oxidised with permanganate to 2:6-dinitrobenzylideneaniline, which on warming with dilute acids is hydrolysed to 2:6-dinitrobenzaldehyde and aniline.

Steric hindrance was not observed with 2:6-dinitrobenzaldehyde, which condenses with phenylhydrazine, hydroxylamine, and aniline or with acetic acid to 2:6-dinitrocinnamic acid. The 2:6-dinitrobenzonitrile could not be hydrolysed by boiling with concentrated hydrochloric acid. 2:6-Dinitrocinnamic acid does not form an additive product with bromine.

2:6-Dinitrobenzyl bromide separates in somewhat brown, well-formed crystals, m. p.  $81^{\circ}$ . 2:6-Dinitrobenzylaniline forms yellowish-red needles, m. p.  $108^{\circ}$ ; it is decomposed by sunlight, rapidly becoming dark red. The *platinichloride* crystallises in yellow needles.

Dinitrobenzyl bromide also condenses with *p*-anisidine,  $\alpha$ -naphthylamine, and anthranilic acid, forming respectively the compounds:  $C_6H_3(NO_2)_2 \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot OMe$ , bright red, slender needles grouped in bunches, m. p.  $119^{\circ}$ ;  $C_6H_3(NO_2)_2 \cdot CH_2 \cdot NH \cdot C_{10}H_7$ , red needles, m. p.  $154^{\circ}$ ; and  $C_6H_3(NO_2)_2 \cdot CH_2 \cdot NH \cdot C_6H_4 \cdot CO_2H$ , yellow needles, m. p.  $199^{\circ}$ .

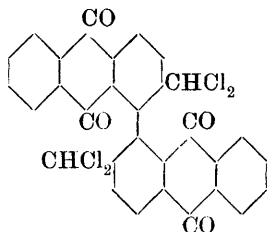
2:6-Dinitrobenzylideneaniline crystallises in very slender, pale yellow needles, m. p.  $131^{\circ}$ .

2:6-Dinitrobenzaldehyde crystallises in slender, colourless platelets, m. p.  $123^{\circ}$ . The *phenylhydrazone* crystallises in dark red needles, m. p.  $159^{\circ}$ ; the *oxime* separates in colourless needles, m. p.  $115^{\circ}$ . 2:6-Dinitrobenzonitrile forms faint brown-coloured needles, m. p.  $145^{\circ}$ .

2:6-Dinitrocinnamic acid crystallises in colourless needles, m. p.  $181^{\circ}$ ; the *ethyl ester* separates in slender needles, m. p.  $82^{\circ}$ . E. F. A.

**Preparation of Aldehydes in the Anthraquinone Series.**  
 BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 240834. Compare Abstr., 1907, i, 327, 539, 942).—When the halogenated dimethyldianthra-

quinonyl (annexed formula) or its derivatives are heated with concentrated sulphuric acid either with or without the addition of sulphur trioxide or boric acid, they yield the corresponding dianthraquinonyldialdehydes.



The following compounds have been prepared: 4:4'-Dichloro-1:1'-dianthraquinonyl-2:2'-dialdehyde, golden-yellow leaflets from  $\omega\omega\omega$ -4:4'-hexachloro-2:2'-dimethyl-1:1'-dianthraquinonyl, m. p. above  $320^\circ$ , which was obtained by chlorinating 4:4'-dichloro-2:2'-dimethyl-1:1'-dianthraquinonyl in the side-chain.

$\omega\omega\omega$ -6:6'-Hexachloro-2:2'-dimethyl-1:1'-dianthraquinonyl, m. p. 188— $191^\circ$ .

$\omega$ -Tetrabromo-2:2'-dimethyl-1:1'-dianthraquinonyl, decomp.  $330^\circ$  (about).

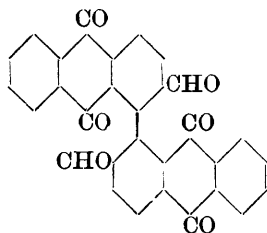
$\omega$ -Tetrachloro-2:2'-dimethyl-1:1'-dianthraquinonyl, m. p. 302— $305^\circ$ .

The tinctorial properties of these substances are tabulated in the original.

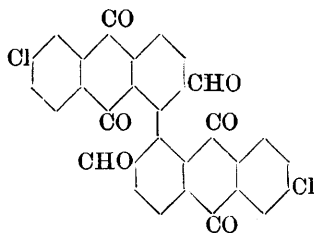
F. M. G. M.

**Preparation of Condensation Products in the Anthraquinone Series.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 241472. Compare preceding abstract).—When 1-chloroanthraquinonyl-2-aldehyde (or its substituted derivatives) is heated with halogen eliminating agents (such as copper) in nitrobenzene or naphthalene solution, condensation occurs, yielding 1:1'-dianthraquinonyl-2:2'-dialdehyde (formula I), which can be crystallised from *o*-dichlorobenzene.

The preparation of 6:6'-dichloro-1:1'-dianthraquinonyl-2:2'-di-



(I.)



(II.)

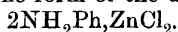
aldehyde (formula II) and other analogous compounds is described in the original.

F. M. G. M.

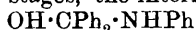
**Reversible Transformation of Many Carboxylic Acids into Keten-Hydrates.** ERNST MOHR (*J. pr. Chem.*, 1912, [ii], 85, 334—336).—The author refers to the researches of Fischer and Dilthey (Abstr., 1902, i, 269) on the formation of amides from esters of alkylmalonic acids, and to the investigations of Kelber (Abstr., 1910, i, 390) on phenyl  $\beta\beta$ -dithiolvinyl ketone in support of the view recently developed by Aschan (this vol., i, 198) that in

certain circumstances carboxylic acids may undergo a reversible transformation into keten-hydrates,  $>\text{CH}\cdot\text{CO}_2\text{H} \rightleftharpoons >\text{C}:\text{C}(\text{OH})_2$ , and gives an explanation of the interconversion of the stereoisomeric  $\beta$ -nitro- $\alpha$ -methoxy- $\alpha\beta$ -diphenylethanes (Heim, Abstr., 1911, i, 717) similar to that adopted by Aschan to account for the transformation of geometric isomerides. F. B.

**Zinc Chloride as Condensing Agent.** GUSTAV REDDELIEN (*Annalen*, 1912, 388, 165—199).—Benzophenone, fluorenone, benzoin, or benzil does not react with aniline at  $160^\circ$ . After the addition of a little zinc chloride (1/40 mol.), however, a violent evolution of steam is observed, and a good yield of the anil is obtained, the zinc chloride being recovered in the form of the double compound,

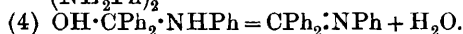
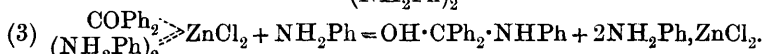
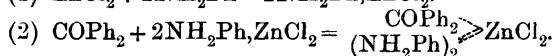
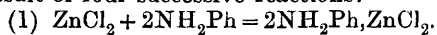


Similar phenomena are observed with the toluidines, xylydines, phenylenediamines, anisidine, and phenetidine, all of which form double compounds,  $2\text{NH}_2\text{Ar}\cdot\text{ZnCl}_2$ , but not with the nitroanilines, aminophenols, or benzidine, which do not form double compounds with zinc chloride. It is clear, therefore, that the condensation is due to the catalytic influence of the double compound. It is unlikely that the double compound is the direct cause of the elimination of water, because these compounds are stable and are not hygroscopic. Now Dimroth and Zoeppritz have shown that the formation of benzophenoneanil occurs in two stages, the intermediate product,



(which can be isolated in the form of the hydrochloride), being very unstable and easily losing water. At  $160^\circ$ , this decomposition will proceed extremely rapidly. The increased rate of formation of the anil in the presence of zinc chloride, therefore, must be due to an acceleration of the first stage of the reaction:  $\text{COPh}_2 + \text{NH}_2\text{Ph} = \text{OH}\cdot\text{CPh}_2\cdot\text{NHPh}$ . It can be shown experimentally that the double compound,  $2\text{NH}_2\text{Ar}\cdot\text{ZnCl}_2$ , loses a portion of its amine at  $160^\circ$ , even in the presence of an excess of the amine. Moreover, zinc chloride can combine, not only with amines, but also with ketones, to form well-characterised additive compounds. These additive compounds react with aniline at  $160^\circ$  to form the anil and steam. Equivalent quantities of the free ketone and the zinc chloride-aniline compound do not yield the anil at  $160^\circ$ ; the presence of an excess of aniline is necessary. This excess is required for the formation of the compound

$\text{Ph}_2\text{CO} \rightleftharpoons (\text{PhNH}_2)_2 \rightleftharpoons \text{ZnCl}_2$ . Consequently the formation of the anil is the result of four successive reactions:



Reactions (1) and (4) occur instantly, (2) and (3) require several minutes.

The formation of the anil is never complete, even after heating

benzophenone, aniline, and zinc chloride at  $160^\circ$  for one hour, some unchanged ketone and amine are recovered. Probably the system  $\text{COPh}_2 + \text{NH}_2\text{Ph} \rightleftharpoons \text{CPh}_2\text{:NPh} + \text{H}_2\text{O}$  attains a state of equilibrium. Since the zinc chloride (or zinc chloride-aniline) accelerates the formation of the anil, it must also accelerate its decomposition. This is found to be the case. Benzophenoneanil is decomposed very slowly by water at  $180$ — $200^\circ$ , but at about  $165^\circ$  in the presence of a little zinc chloride-aniline the hydrolysis is complete in thirty minutes.

Acetophenone and aniline do not yield acetophenoneanil even in the presence of the usual condensing agents. With zinc chloride, the ketone condenses with itself, and yields dypnone and *s*-triphenylbenzene. An explanation of this is found in the facts that acetophenone and aniline at  $160^\circ$  yield acetophenoneanil in thirty minutes in the presence of zinc chloride-aniline, but give 60% of *s*-triphenylbenzene in three to four minutes in the presence of aniline hydrochloride (or hydrobromide, hydriodide, sulphate, nitrate, phosphate, or thiocyanate). When zinc chloride is employed as the condensing agent, therefore, a little hydrochloric acid, present in the zinc chloride or produced by a by-reaction, forms aniline hydrochloride, and this catalyst stimulates the second rapid condensation more than does the zinc chloride-aniline the first, slower reaction.

In the formation of the anil, acetophenone probably reacts in the keto-form, because benzophenone and fluorenone yield anils under the same conditions. In the formation of *s*-triphenylbenzene, acetophenone reacts apparently in the enolic form,  $\text{CH}_2\text{:CPh}\cdot\text{OH}$ , because, under similar conditions, only ketones which are capable of enolising react to form *s*-trisubstituted benzenes; benzophenone and aniline do not react at  $160^\circ$  in the presence of aniline hydrochloride. The following anils have been prepared by heating the ketone and the amine at  $160$ — $180^\circ$  with a little zinc chloride-amine,  $\text{ZnCl}_2, 2\text{NH}_2\text{Ar}$ : *acetophenone-p-tolil*, b. p.  $181$ — $183^\circ/16$  mm. (*s*-triphenylbenzene and *dypnone-p-tolil* (?), m. p.  $110^\circ$ , are obtained as by-products); *acetophenone-m-tolil*, b. p.  $181$ — $182^\circ/13$  mm.; *acetophenone-p-anisidil*,  $\text{CPhMe}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , m. p.  $86^\circ$ ; *benzophenone-p-anisidil*, m. p.  $70^\circ$ .

*Fluorenone zinc chloride*,  $\text{C}_6\text{H}_4\text{>CO, ZnCl}_2$ , blackish-red needles, m. p.  $333$ — $334^\circ$  (decomp), and *benzophenone zinc chloride*,  $\text{Ph}_2\text{CO, ZnCl}_2$ ,

yellowish-brown oil, are obtained by adding the ketone to a suspension of zinc chloride in benzene. Each is converted into aniline-zinc chloride by aniline at the ordinary temperature. At  $163^\circ$ , benzophenone-zinc chloride and aniline yield benzophenoneanil, whilst aniline-zinc chloride and benzophenone do not visibly react.

Zinc chloride and phenylhydrazine form an additive compound,  $2\text{NHPh}\cdot\text{NH}_2, \text{ZnCl}_2$ ,

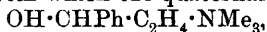
which catalytically accelerates the reaction between ketones and phenylhydrazine; thus benzophenonephenylhydrazone is obtained from benzophenone and phenylhydrazine at  $125^\circ$  in 28% yield without, and in 73% yield with, the presence of a little of the additive compound. At  $175^\circ$  phenylhydrazine-zinc chloride is converted into

ammonia, aniline-zinc chloride, and benzene, produced by the oxidation of a portion of the phenylhydrazine. When a suitable substance is present, it can be oxidised in the course of the preceding decomposition; thus acetophenoneanil is converted smoothly into 2-phenylindole. In the light of these facts, an explanation is given of the course of Fischer's indole syntheses from hydrazones by means of zinc chloride at 180°.

The catalytic influence of metallic salts other than zinc chloride, on the condensation of benzophenone and aniline, has been studied. It is found that zinc chloride, bromide, and iodide are about equally effective, and cadmium iodide somewhat less so; that cadmium chloride, nickel chloride, and cupric chloride have very little influence; that zinc thiocyanate, cadmium bromide, manganese chloride, and cobalt chloride exert an influence intermediate between that of the two preceding classes; and that mercury chloride, calcium chloride, magnesium chloride, and aluminium chloride have no catalytic influence at all. C. S.

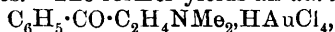
**Propiophenone Derivatives.** F. W. CALLIESS (*Arch. Pharm.*, 1912, 250, 141—154).—These products were obtained in the course of attempts to synthesise substances having the formula ascribed by Schmidt and Bümmling to ephedrine and  $\psi$ -ephedrine (*Abstr.*, 1909, i, 322). Comparison of the  $\alpha$ -aminopropiophenones prepared by Schmidt's method (*Abstr.*, 1890, 372) and by that of Behr-Bregowski (*Abstr.*, 1897, i, 458) shows that the two are identical.

The following derivatives of  $\alpha$ -aminopropiophenone were prepared: hydrochloride, slender needles, m. p. 179°; nitrate, columnar crystals, m. p. 139—140°; *aurichloride*, yellow needles, m. p. 151°; *mercurichlorides*,  $B, HCl, 2HgCl_2, H_2O$ , slender, colourless needles, m. p. 126°, and  $B, HCl, HgCl_2$ , colourless, dull needles, m. p. 165°; *stannichloride*,  $B_2H_2SnCl_6$ , m. p. 219—220°. On reduction with sodium amalgam in acid solution the amino-ketone yields *phenylaminoethylcarbinol*,  $OH \cdot CHPh \cdot CHMe \cdot NH_2$ , m. p. 101°, which separates from ether in yellow crystals, and gives a *hydrochloride*, m. p. 191°, colourless needles, a *platinichloride*,  $B_2, H_2PtCl_6, 2H_2O$ , m. p. 187—188°, yellowish-red needles, and an *aurichloride*,  $B, HAuCl_4$ , m. p. 130°, silky, yellow needles. On methylation the amino-alcohol gives a mixture of methylated products, from which the quaternary base,



was isolated in the form of its *aurichloride*,  $BCl, AuCl_3$ , m. p. 171—172°, yellow leaflets, and of its *platinichloride*, m. p. 245—247° (decomp.), slender needles, the latter being probably identical with the salts prepared in another manner by Göhring (*Abstr.*, 1909, i, 322).

$\alpha$ -Aminopropiophenone on methylation yields a mixture of tertiary and quaternary bases. The former yields an *aurichloride*,



m. p. 152°, small leaflets. The quaternary base has been prepared already by Göhring (*loc. cit.*). T. A. H.

**4'-Nitro-2:5-dimethoxybenzophenone.** HUGO KAUFFMANN and ALBRECHT DE PAY (*Ber.*, 1912, 45, 776—780).—4'-Nitro-2:5-dimethoxybenzophenone, m. p. 126°, obtained from *p*-nitrobenzoyl chloride,

quinol dimethyl ether, and aluminium chloride in carbon disulphide, forms yellow crystals, and is therefore an example of a constitutively unchangeable nitro-compound which exhibits colour. By oximation in alcoholic solution in the presence of sodium acetate, it yields two *oximes*; the more soluble one has m. p.  $145^{\circ}$ , forms a *benzoate*, m. p.  $158^{\circ}$ , white leaflets, and is also produced by prolonged heating in toluene of the less soluble *oxime*, m. p.  $195^{\circ}$  (*benzoate*, m. p.  $150^{\circ}$ , yellow crystals). 4'-Nitro-2:5-dimethoxybenzophenonephenylhydrazine exists in three modifications, having m. p.  $165^{\circ}$ ,  $145^{\circ}$ , and  $81^{\circ}$  respectively. The first two are obtained from the ketone and phenylhydrazine in glacial acetic acid, and are converted at their m. p.'s into the third modification. This modification changes into the first by prolonged heating on the water-bath, and into the second by crystallisation from alcohol. It is probable that two of these modifications are stereoisomerides, the remaining one being a polymorphous form of one of the others; which is which, it is impossible to say. C. S.

**Dissociation of Quinhydrone in Aqueous Solution.** ROBERT LUTHER and A. LEUBNER (*J. pr. Chem.*, 1912, [ii], 85, 314—321).—The dissociation of quinhydrone has been studied by determining its solubility in water, and also in aqueous solutions of quinone and quinol. At  $25^{\circ}$  in a saturated solution, quinhydrone is dissociated to the extent of 93%; the solubility of the undissociated quinhydrone is  $1.3 \times 10^{-3}$  gram-mol. per litre.

The dissociation constant,  $K = \text{quinhydrone} \times \text{quinol} / \text{quinhydrone}$  at  $25^{\circ} = 0.23$ . F. B.

**Action of Copper on Chloroanthraquinones.** FRITZ ULLMANN and WASSILY MINAJEFF (*Ber.*, 1912, 45, 687—690).—Some chlorinated anthraquinones lose their halogen, and are converted into anthraquinones by treatment with copper powder and potassium acetate; thus 1-chloro-4-methylantraquinone, potassium acetate, and a little copper powder react in boiling nitrobenzene to form 1-methylantraquinone and a very little 4:4'-dimethyl-1:1'-dianthraquinonyl,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_2\text{Me} \cdot \text{C}_6\text{H}_2\text{Me} \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_4$ , m. p.  $385\text{--}386^{\circ}$ , yellow plates. The latter becomes the chief product when 1-chloro-4-methylantraquinone is heated in nitrobenzene with copper powder (1 atom) alone. Scholl and Mansfeld's 1:1'-dianthraquinonyl is obtained in 75% yield by heating 1-chloroanthraquinone with copper powder in nitrobenzene; a 77% yield can be obtained by heating the two substances at  $290\text{--}300^{\circ}$  without nitrobenzene.

Chloroanthraquinones, which contain the halogen in position 2, are unattacked by copper powder. C. S.

**Constituents of Essential Oils. A New Primary Alcohol of the Sesquiterpene Series, Cedrenol,  $\text{C}_{15}\text{H}_{24}\text{O}$ .** FRIEDRICH W. SEMMLER and ERWIN W. MAYER (*Ber.*, 1912, 45, 786—791).—Cedar wood oil contains in addition to solid cedrol,  $\text{C}_{15}\text{H}_{26}\text{O}$ , m. p.  $85^{\circ}$ , a primary alcohol, cedrenol,  $\text{C}_{15}\text{H}_{24}\text{O}$ , which is tricyclic and contains one unsaturated linking. Cedrenol constitutes about 3% of the oil; it

has b. p. 161—167°/10 mm.,  $D^{20}_D$  1·0098,  $[\alpha]^{20}_D + 1^\circ$ ,  $n^{20}_D$  1·523. The *acetate* is a colourless, odourless liquid, b. p. 165—169°/9 mm.,  $D^{20}_D$  1·0168,  $n^{20}_D$  1·5021,  $[\alpha]^{20}_D - 2^\circ$ ; the pure cedrenol obtained from it on hydrolysis is optically inactive.

*Cedrenyl chloride*,  $C_{15}H_{23}Cl$ , is a colourless liquid, b. p. 150—165°/10 mm.,  $D^{20}_D$  1·001.

*Cedrene*,  $C_{13}H_{20}$   $\begin{smallmatrix} \text{CMe} \\ | \\ \text{CH} \end{smallmatrix}$ , the corresponding hydrocarbon, obtained by reduction of the chloride with sodium and alcohol, has b. p. 117—130°/7 mm.,  $D^{20}_D$  0·931,  $n_D$  1·5080,  $[\alpha]^{20}_D - 3^\circ$  to  $+13^\circ$ , according to the method of preparation. On decomposition of cedrene ozonide, cedrene ketonic acid was obtained, identical with that described by Semmler and Risse (this vol., i, 201), and this, on further oxidation, yielded cedrenedicarboxylic acid (Semmler and Risse, *loc. cit.*).

Cedrenol contains a  $CH_2 \cdot OH$  group in the same position as the  $CH_3$  group is situated in cedrene and cedrol.

E. F. A.

**Production of Formic and Acetic Acid by the Atmospheric Oxidation of Turpentine.** CHARLES T. KINGZETT and REGINALD C. WOODCOCK (*J. Soc. Chem. Ind.*, 1912, 31, 265—267).—It is shown that turpentine, pinene, and sylvestrene yield formic and acetic acids and hydrogen peroxide when submitted to atmospheric oxidation. It has not yet been ascertained definitely whether the hydrogen peroxide, the acetic acid, and the formic acid severally depend for their production on the interaction of water on one organic peroxide only, or more than one, but the authors favour the view that one organic peroxide alone is formed, and at the same time formaldehyde and acetaldehyde, the two latter substances being converted into their corresponding acids when the organic peroxide yields hydrogen peroxide on being placed in contact with water.

W. P. S.

**The Oxidation of Camphene.** OSSIAN ASCHAN (*Chem. Zentr.*, 1912, i, 415—416; from *Öfver. Finska Vet. Soc. Förhandl.*, 1911, 53, Afd. A, 1—18).—When terecamphene vapour mixed with air is passed over heated spongy platinum, an oily liquid is obtained, in which the presence of benzene and *m*-xylene can be established. The gaseous products contain much carbon dioxide.

By oxidation of terecamphene dissolved in glacial acetic acid by means of solid potassium permanganate, a mixture of neutral and acid compounds is obtained. Among the former are *camphenilone*, b. p. 80—84°/14 mm. (which yields a *semicarbazone*, m. p. 222—223°), a small quantity of a *substance*,  $C_9H_{14}O$ , b. p. 87—90°/14 mm., which gives the aldehyde reaction with ammoniacal silver nitrate, does not yield a semicarbazone, does not solidify at  $-15^\circ$ , and when exposed to air in the presence of water forms a monobasic acid,  $C_9H_{14}O_3$ , m. p. 136—137°, and finally a *substance*, b. p. 143—150°/14 mm., which when freshly distilled has no acid reaction, but when preserved during several days deposits needles or leaflets of an unsaturated monobasic acid,  $C_7H_{11} \cdot CO_2H$ , m. p. 141°.

From the acidic products, an oil, b. p. 148—150°/10 mm., 153°/14 mm., was isolated, which gradually partly solidified. After removal

of unsaturated substance by oxidation with potassium permanganate in alkaline solution, two isomeric acids,  $C_{10}H_{16}O_2$ , were obtained. The first, *camphenanic acid*, m. p.  $87-91^\circ$ , is monobasic, and forms a calcium salt,  $(C_{10}H_{15}O_2)_2Ca \cdot 5H_2O$ . The second, *isocamphenanic acid*, has m. p.  $75-76^\circ$ . Neither acid appears to be identical with Bredt's camphenilanic acids, nor to be the racemic form of these acids.

H. W.

**Sesquiterpenes.** V. ERNST DEUSSEN (*Annalen*, 1912, 388, 136—165. Compare Abstr., 1910, i, 575).—[With BENNO EGER.]—By passing nitrous fumes into an ethereal solution of caryophyllene, a voluminous precipitate is obtained of a substance,  $C_{12}H_{19}O_6N_3$ , m. p.  $159.5^\circ$ ,  $[\alpha]_D - 133.50'$ , which is identical with one of the two substances obtained by the decomposition of  $\beta$ -caryophyllene nitrosite by heat (Abstr., 1907, i, 945). So voluminous is the precipitate and so slight its solubility in most solvents, that the reaction furnishes an excellent method for the detection of  $\beta$ -caryophyllene. Two fractions, b. p.  $127-128.5^\circ/14$  mm. and  $118.5-122^\circ/11.5$  mm., respectively, of caryophyllene from oil of cloves were found to contain 25—27% of  $\beta$ -caryophyllene by this method. Oils of Para- and of Maracaibocopaiva balsams contain 5.15 and 2.0% respectively of  $\beta$ -caryophyllene. The sesquiterpenes obtained by the distillation with steam of oil of African copaiva balsam can be separated into two fractions, one, b. p.  $145.5-148^\circ/19.5$  mm., consists largely of *d*-cadinene, and the other, b. p.  $128-129.5^\circ/15$  mm., contains 13.2% of  $\beta$ -caryophyllene. Oil of West Indian sandal-wood contains 30—40% of sesquiterpenes, in which *d*-cadinene and  $\beta$ -caryophyllene have been detected.

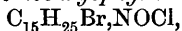
[With MAX ZIEM.]—According to Chapman (Trans., 1895, 67, 61, 780; 1903, 83, 505), oil of hop blossoms contains a terpene (subsequently identified as myrcene) and a sesquiterpene called humulene. The latter consists essentially of *i*- $\alpha$ -caryophyllene, but is shown to contain about 4% of  $\beta$ -caryophyllene by the nitrous fumes method.

[With KURT MEYER.]—The sesquiterpene regenerated from  $\beta$ -caryophyllene dihydrochloride by means of methyl-alcoholic potassium hydroxide is not *isocaryophyllene*, but is probably a mixture, because it gives only a 25% yield of  $\beta$ -caryophyllene dihydrochloride and forms an amorphous nitrosochloride, from which a *nitrolbenzylamine*, m. p.  $162^\circ$ , not identical with  $\beta$ -caryophyllenenitrolbenzylamine, m. p.  $166-167^\circ$ , is obtained. *isocaryophyllene*, obtained by boiling an alcoholic solution of  $\beta$ -caryophyllene nitrosite, gives a 100% yield of  $\alpha$ - and  $\beta$ -nitrosochlorides, and a 73% yield of  $\beta$ -caryophyllene dihydrochloride. It is probable that the constitutions of  $\beta$ -caryophyllene and of *isocaryophyllene* differ only in that the former contains the group  $>C:CMe_2$ , whereas the latter contains the group

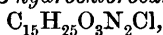


[With C. VIELITZ.]—The following experiments were undertaken to show the presence of two double linkings in  $\alpha$ - and  $\beta$ -caryophyllenes. A purified sample, b. p.  $130-131^\circ/16.5$  mm.,  $\alpha - 7.40'$  (consisting chiefly of  $\beta$ -caryophyllene, together with a little  $\alpha$ -caryophyllene), diluted with 2 vols. of methyl alcohol, is treated with colloidal palladium and saturated with hydrogen. The product is a *dihydro*-

*caryophyllene*,  $C_{15}H_{26}$ , b. p. 129—130°/14 mm.,  $\alpha - 25^\circ$ ,  $D^{19}_D$  0.8898,  $n^{20}_D$  1.49032. Since the following experiments prove that two double linkings are present in caryophyllene, it follows that they are functionally different, only one of them being saturated by hydrogen. A solution of  $\alpha$ -caryophyllene nitrosochloride in cold chloroform absorbs 2 atoms of bromine, yielding probably an unstable dibromide, which changes to a *hydrobromocaryophyllene nitrosochloride*,



m. p. 144—145° (decomp.), colourless needles. A suspension of  $\beta$ -caryophyllene nitrosite in methyl alcohol is treated with colloidal palladium and saturated with hydrogen in darkness, whereby a *substance*,  $C_{15}H_{26}O_3N_2$  or  $C_{15}H_{28}O_3N_2$ , m. p. 99—100°, is obtained, which readily decolorises bromine; consequently the addition of the hydrogen has occurred at the NO or the O·NO group. By saturating an ethereal solution of  $\beta$ -caryophyllene nitrosite with hydrogen chloride at  $-20^\circ$  to  $-15^\circ$ ,  *$\beta$ -hydrochlorocaryophyllene nitrosite*,



m. p. 137° (decomp.),  $[\alpha]_D + 930.4^\circ$  in benzene, is obtained in dark blue needles. The formation of this compound, not only proves the presence of the two double linkings in  $\beta$ -caryophyllene, but is also a strong support of Baeyer's theory that the blue colour of nitrosochlorides, nitrosites, and nitrosates is due to the union of the NO group with a tertiary carbon atom.

By treating  $\beta$ -caryophyllene nitrosite,  $\beta$ -caryophyllene nitrosochloride, or *isocaryophyllene* nitrosochloride with alcoholic potassium hydroxide, a dextrorotatory, crystalline *substance*,  $C_{17}H_{29}O_2N$ , m. p. 163°, containing an ethoxy-group is obtained. C. S.

**Essential Oils.** SCHIMMEL & Co. (*Bericht*, April 1912, pp. 22—133).—*Acronychia laurifolia* leaves furnish an oil having the following constants:  $D^{26}_D$  0.915,  $[\alpha]_D + 1^\circ 52'$ , saponification number 11, acetyl ester number 50.9, and free from aldehydes.

*Inula helenium* roots yield a semi-solid oil,  $D^{30}_D$  1.0374,  $[\alpha]_D + 123^\circ 45'$ ,  $n^{20}_D$  1.52208, acid number 6.4, ester number 180, and after acetylation 199, consisting of colourless needles in a brown, viscous liquid, and having an odour recalling that of *ladanum*.

*Artemisia frigida* herb grown in South Dakota yields, according to Rabak, 0.26% of oil,  $D^{24}_D$  0.940,  $[\alpha]_D - 24.2^\circ$ ,  $n^{24}_D$  1.4716, acid number 2.5, ester number 25, after acetylation 139, containing *l*-borneol, cineole, *l*-fenchone, probably heptic and octoic acids, valeric acid, and traces of formic and undecic acids. The total borneol amounts to 43%, of which 35.6% is in the free state.

Camphor leaves, distilled in Jamaica, yielded 2.35% of crude camphor, consisting of camphor 1.32%, camphor oil 0.54%, and moisture 0.49%. Camphor twigs gave 0.58% of camphor and 0.26% of camphor oil, whilst the wood yielded 0.61% of camphor. The oil contained, in addition to camphor, cineole, safrole, pinene, phellandrene, and dipentene.

"Cape" leaves from the Ivory Coast, according to Roure-Bertrand Fils, furnish 0.28% of a greenish-yellow oil,  $D^{15}_D$  0.977,  $[\alpha]_D + 39^\circ 38'$ ,

acid number 0.7, saponification number 109.2, soluble in its own volume of 80% alcohol, and having a patchouli odour.

*Cedrela odorata* wood, according to Rabak, gives 0.3% of a golden-yellow oil,  $D^{25}_D$  0.947,  $n^{25}_D$  1.5038, acid number 3.9, ester number 41.5, after acetylation 51, which is soluble in six volumes of 80% alcohol.

Ceylon citronella oil has been shown previously to contain citronellal, camphene, dipentene, methylheptenone, borneol, geraniol, methyl-eugenol, *l*-limonene, together with acetic and valeric acids as esters. A dextrorotatory sesquiterpene and possibly linalool have also been found. It is now shown that the following constituents are also present: *d*-citronellol in the form of its acetic and *n*-butyric esters, geranyl acetate, thujyl alcohol, nerol, an *alcohol* closely related to linalool, a *hydrocarbon*,  $C_{10}H_{16}$ ,  $D^{15}$  0.8323 to 0.8360,  $[\alpha]_D - 23^\circ 24'$  to  $-32^\circ 41'$ ,  $n^{20}_D$  1.48044, b. p. 40—41°C/4 mm., having a tarragon-like odour, and a levorotatory sesquiterpene. Linalool and valeric acid could not be found.

*Cymbopogon intermedius*, distilled in Buitenzorg, gave 0.03% of oil,  $D^{26}$  0.919,  $[\alpha]_D - 15^\circ 30'$ , and *C. odoratus* from the same source furnished 0.35% of oil,  $D^{26}$  0.914,  $[\alpha]_D - 31^\circ 10'$ .

American spearmint, grown in Michigan, according to Nelson, gave an oil,  $D^{25}_D$  0.9290,  $[\alpha]^{25}_D - 52^\circ 16'$ ,  $n^{25}_D$  1.4866, ester number 12.4, which contained 66% of carvone, together with phellandrene, *l*-limonene, and the acetic ester of dihydrocarveol. The oil also contains hexoic or octoic acid, butyric acid (?), with 0.1% of a solid acid, m. p. 182—184° (compare Elze, Abstr., 1910, i, 865).

Linaloe wood from Cayenne furnished, in addition to the oil, distillation water containing furfuraldehyde, *isovaleraldehyde* (?), linalool, methylheptenol, cineole, dipentene, and an aliphatic terpene, myrcene (?), which on hydration with acetic and sulphuric acids gave an ester, that on hydrolysis yielded an alcohol having an odour of linalool and terpineol.

*Magnolia glauca* leaves, according to Rabak, yield 0.05% of a yellow oil,  $D^{25}$  0.9240,  $[\alpha]_D + 3.96^\circ$ ,  $n^{25}_D$  1.4992, acid number 1.8, ester number 13, and after acetylation 28, which is insoluble in 80% alcohol.

*Melaleuca trichostachya* leaves furnish 1.25 to 2.58% of oil,  $D^{15}$  0.9144 to 0.9153,  $[\alpha]_D + 2.3^\circ$  to  $3.1^\circ$ ,  $n^{20}_D$  1.4636 to 1.4655, saponification number 2.1 to 2.8, acetyl ester number 13.9, soluble in 1.3 volumes of 70% alcohol, and containing cineole 80%, terpineol, terpinyl acetate, pinene (?), sesquiterpene (?), with traces of phenols and a low-boiling aldehyde. *M. bracteata* leaves and twigs gave 0.643 to 0.964% of an oil,  $D^{18}$  1.032 to  $D^{19}$  1.0358,  $[\alpha]_D - 1.4^\circ$  to  $3.1^\circ$ ,  $n^{20}_D$  1.5325 to 1.535, acid number 0.7 to 1.26, saponification number 5.3 to 20.8, soluble in 0.7 to 0.8 volumes of 70% alcohol, and containing eugenol, free and combined cinnamic acid, cinnamaldehyde, methyleugenol, 70%, cinnamyl cinnamate (?), and *l*-phellandrene (Baker and Smith, *J. Roy. Soc. New South Wales*, 1911, 44, 592).

*Micromeria japonica* herb, according to Muragama, yields 0.7% of a yellow, peppermint-like oil containing *l*-menthone and menthol (?).

*Nepeta nepetella* herb furnishes 0.059% of a viscid, yellow oil,  $D^{20}$  1.03984,  $[\alpha]_D + 15^\circ 12'$ , acid number 45.5, ester number 245.7, after

acetylation 314.5, soluble in two volumes of 70% alcohol, which deposits a solid substance with an odour of menthol, and on hydrolysis furnishes octoic and valeric acids.

*Persea pubescens* leaves, according to Rabak, yield 0.2% of oil,  $D_{25}^{25}$  0.9272,  $[\alpha]_D + 22.4^\circ$ ,  $n_D^{25}$  1.4695, acid number 2.8, ester number 14.5, after acetylation 64, soluble in 0.3 volume of 80% alcohol, containing free butyric acid with butyric, valeric, and heptonic acids as esters, together with *d*-camphor, cineole, and small quantities of borneol and formaldehyde.

Japanese peppermint oil yielded a fraction, b. p. 175—181°, containing *d*-ethyl-*n*-amylcarbinol,  $C_8H_{11} \cdot CH_2 \cdot OH$ .

*Pluchea foetida* herb, according to Rabak, yields 0.025% of a golden-yellow oil,  $D_{25}^{25}$  0.9329,  $[\alpha]_D - 5.4^\circ$  (50 mm. tube),  $n_D^{25}$  1.4845, acid number 4.1, ester number 44, after acetylation 104, soluble in one volume of 80% alcohol and containing cineole.

*Ramona stachyoides* herb yields, according to Rabak, 0.75% of a colourless oil,  $D_{24}^{24}$  0.9144,  $[\alpha]_D + 30.2^\circ$ ,  $n_D^{24}$  1.4682, acid number 2, ester number 2.5, after acetylation 27.1, soluble in 1.5 volumes of 70% alcohol, which deposits *d*-camphor when kept at  $-15^\circ$ , and contains cineole, and probably borneol, tanacetone, and pinene with acetic acid and traces of formic acid.

*Satureja montana* oil, distilled in Southern France, had  $D_{15}^{15}$  0.908 to 0.9194,  $[\alpha]_D - 1^\circ 42'$  to  $4^\circ 48'$ , and contained 27 to 32% of carvacrol (compare Pickles, Proc., 1911, 27, 285).

*Aframomum angustifolium* seeds from German East Africa gave 4.5% of a colourless oil,  $D_{15}^{15}$  0.9017,  $[\alpha]_D - 16^\circ 50'$ ,  $n_D^{20}$  1.46911, acid number 0.4, ester number 4.2, soluble in 6 or more volumes of 80% alcohol and containing much cineole. T. A. H.

The Essential Oil from Rhizoma Imperatoriae. FRITZ LANGE (*Chem. Zentr.*, 1912, i, 654; from *Arb. Pharm. Inst. Univ. Berlin*, 1911, 8, 98—120).—The oil obtained by distillation with steam is a greenish-yellow liquid,  $D_{15}^{15}$  0.8659,  $[\alpha]_D^{15} + 69.75^\circ$ , acid number 0.8, saponification number 17.9, ester number after acetylation 28.34. It consists of a mixture of free acids, alcohols, esters, terpenes, and sesquiterpene, terpenes constituting about 95% of the oil. Palmitic acid is contained among the free acids; acetic, formic, isobutyric, isovaleric, and  $\beta\beta$ -dimethylacrylic acids are present in the form of esters. The terpenes present include pinene, dipentene, *d*-limonene, *d*-phellandrene, chiefly the latter. The sesquiterpene yields a crystalline *dihydrochloride*, m. p. 157—157.5°. The oil also contains an alcohol, the formula of which is probably  $C_{13}H_{19} \cdot OH$ , which yields a *phenylurethane*, m. p. 145—146°. H. W.

The Essential Oil of the Catkins of Wild Myrtle (*Myrica Gale*). C. J. ENKLAAR (*Chem. Weekblad*, 1912, 9, 219—222. Compare Pickles, Trans., 1911, 99, 1764).—The oil obtained from the catkins of wild myrtle is a viscid, yellow liquid, and with a characteristic odour. It has  $D_{15}^{15}$  0.899, and  $[\alpha]_D - 5^\circ 36'$ . About 80% of it consists of terpenes, of which a pinene and a sesquiterpene,  $C_{15}H_{24}$ , constitute about 40%. It also contains cineole, phellandrene, and a small proportion of a substance not identified, which crystallises in long needles

and has a myrtle-like odour. The sesquiterpene probably contains caryophyllene. It has b. p. 150—152°/17 mm. or 263—265°/760 mm., and  $[\alpha]_D + 4^\circ 30'$ . A. J. W.

**Minjak Lagam.** LEOPOLD VAN ITALLIE and MAX KERBOSCH (*Pharm. Weekblad*, 1912, 49, 274—279).—The volatile oil obtained from the liquid variety of Minjak lagam is caryophyllene. The semi-solid form yields the same substance. A. J. W.

**Oleo-resin of Abies cephalonica.** EMMANUEL J. EMMANUEL (*Arch. Pharm.*, 1912, 250, 104—110).—The crude oleo-resin had acid number, direct 113·54, indirect 128·31; saponification number 137·06 (cold), 157·54 (hot), and was soluble in alcohol, ether, or chloroform.

From the ether solution 1% ammonium carbonate solution extracted *elatic acid*,  $C_8H_{12}O_2$ , m. p. 124—126°, and then 3% sodium carbonate solution removed a mixture of two acids, *elatinic acid*,  $C_{12}H_{18}O_2$ , m. p. 78—80°, which gives a lead salt insoluble in alcohol, and *elatic acid*,  $C_9H_{16}O_2$ , m. p. 118—120°, the lead salt of which is soluble in alcohol. These products are amorphous, and the two latter together form 70% of the oleo-resin.

The residue, after the removal of the ether, was steam distilled, and yielded 17·4% of essential oil,  $D^{15}_D$  0·9279,  $n_D$  - 68° in 200 mm. tube,  $n_D^{13.5}$  1·4745, which was colourless and on distillation yielded three fractions, b. p. 89—150°, 150—155°, 155—175°, of which the first two had a terpene-like odour.

The residual matter in the flask was amorphous *resen*, m. p. 92—96°, with water containing a bitter substance. The acids and the *resen* gave phytosterol reactions. T. A. H.

**Cretan Ladanum.** EMMANUEL J. EMMANUEL (*Arch. Pharm.*, 1912, 250, 111—117).—Ladanum is a resinous exudation of *Cistus*, spp., that examined being from *Cistus creticus*. It was dark brown in colour, softened readily when worked in the fingers, and had a peculiar, pleasant odour with a balsamic, bitter pungent taste. It dissolved to the following amounts in the solvents named: ether 61%, chloroform 69%, alcohol 57%, and was practically insoluble in water or light petroleum. It contained 12·0% of ash.

The portion soluble in ether on extraction with sodium carbonate solution yielded a viscid, brown resin acid. The portion insoluble in ether, but soluble in alcohol, was a viscid, bright brown resin. An essential oil,  $D$  0·928, b. p. 225°,  $n_D^{13.5}$  1·5118, was obtained by steam distilling the residue of the ethereal extract after treatment with sodium carbonate solution. After the removal of the essential oil, a solid, crystalline substance, *ladaniol*,  $C_{17}H_{30}O$ , m. p. 89°, colourless prisms, began to distil over. This resembled champacol and guaiol (Wallach and Tuttle, *Abstr.*, 1894, i, 538). The portion of ladanum insoluble in ether and alcohol contained (1) a bassorin-like gum, which gave mucic acid on oxidation with nitric acid; (2) a greyish-white, pulverulent *resen*, and (3) a bitter substance. T. A. H.

**The Cerebrosides of the Brain.** II. HERMANN LOENING and HANS THIERFELDER (*Zeitsch. physiol. Chem.*, 1912, 77, 202—217. Compare *Abstr.*, 1911, i, 898).—The author's method of separating

cerebrosides from "protagon" depends on their resistance to barium hydroxide, and their solubility in hot acetone. After boiling cerebrone with baryta water for an hour, 90.4% was subsequently recovered in crystalline form; the loss may be due to the destruction of the cerebrone, or to its decomposition by alkali. In the present research, "protagon" was employed, and some evidence that barium compounds are formed is adduced; the loss on boiling with barium hydroxide is small, and was determined by estimating the yield of galactose after hydrolysis. Judged by this standard, from 93 to 97% of the cerebroside was recovered. A similar resistance to boiling with a 2.8% solution of potassium hydroxide containing methyl alcohol was also noted. The actual quantity of galactose obtained from the various preparations of protagon used varied from 6 to 13%. Thudichum's sphingosine was not obtained from cerebrone. The quantity of cerebroside obtained from protagon, taking into account the amount separated out from the acetone, as well as that which remained in solution, was about 39%. From dried brain powder, 2.13 grams of galactose were obtained; 73.2% of this passed into the alcoholic extract, and the remainder, which is an unexpectedly high amount, into the ethereal extract.

W. D. H.

**Cerebrone.** V. OTTO RIESSER and HANS THIERFELDER (*Zeitsch. physiol. Chem.*, 1912, 77, 508—510).—On treatment of cerebrone with methyl alcoholic sulphuric acid, dimethylsphingosine,  $C_{19}H_{39}O_2N$ , was obtained (Kitagawa and Thierfelder, *Abstr.*, 1907, i, 168). It is now shown that when ethyl alcohol is substituted, the corresponding *diethylsphingosine*,  $C_{21}H_{43}O_2N$ , is obtained. It forms a matted mass of lustrous platelets, m. p. 113—115°. The alkylsphingosines are accordingly not present in the cerebrone molecule, but are formed at the moment of hydrolysis; sphingosine, therefore, contains two hydroxyl groups.

E. F. A.

**Cerebrone.** VI. KARL THOMAS and HANS THIERFELDER (*Zeitsch. physiol. Chem.*, 1912, 77, 511—515).—On acetylation of sphingosine either with acetyl chloride or acetic anhydride and sodium acetate, a *triacetate*,  $C_{17}H_{32}O_2NAC_3$ , is obtained; it crystallises in thin needles pointed at both ends, which soften at 98°, m. p. 99—100°. This characterises sphingosine as an unsaturated bivalent amino-alcohol.

The sparingly soluble sulphate of a base previously obtained (Kitagawa and Thierfelder, *Abstr.*, 1907, i, 168) by the action of methyl-alcoholic sulphuric acid on cerebrone is now shown to be sphingosine contaminated with the dimethyl compound.

E. F. A.

**Glucosides of Digitalis purpurea Leaves.** FRIEDRICH KRAFT (*Arch. Pharm.*, 1912, 250, 118—141).—Schmiedeberg and, more recently, Kiliani in their investigation of digitalis constituents have used as a raw material "digitalinum germanicum," a mixture of substances prepared from digitalis seeds by extraction with alcohol and precipitation with tannin. From this material the following products have been obtained: Schmiedeberg's amorphous inactive digitonin, Kiliani's crystalline digitonin, Kiliani's digitalin, digitoxin, and

digitalein. As digitalis leaves are chiefly used in medicine, the author has examined them to ascertain whether they contain the constituents present in the seeds, and has obtained two new glucosides, gitalin and gitin, together with digitoxin. Schmiedeberg's amorphous digitonin is shown to be a mixture of saponins, which is also present in the leaves. In Keller's method for the valuation of digitalis leaves the product obtained is chiefly gitalin, with a little digitoxin (compare Burmann, this vol., ii, 379).

The leaves were extracted first with water and then with 50% alcohol, and the two extracts examined separately. The aqueous extract was defecated in the usual way with lead acetate, followed by sodium phosphate, and the glucosides precipitated by tannin solution and recovered from the precipitate by mixing this with zinc oxide and extraction with methyl alcohol. The residue left on distilling off the solvent was dissolved in water and shaken repeatedly with chloroform, which extracted an active glucoside, gitalin, and left in solution a mixture of saponins. *Gitalin*,  $C_{28}H_{48}O_{10}$ , m. p. 150—155°, is a colourless, amorphous, neutral substance, soluble in most organic solvents, except light petroleum, and in 600 parts of water. When dissolved in 1.5 parts of alcohol to which 0.75 part of water is added, it separates as a crystalline *hydrate*,  $C_{28}H_{48}O_{10} \cdot 4H_2O$ , m. p. 75°, soluble in 3000 parts of water, which is re-converted into the anhydrous form by drying over sulphuric acid. Solutions of gitalin are very unstable, and when kept deposit mixtures of gitalin with *anhydrogitalin*,  $C_{28}H_{46}O_9$ , m. p. 255°, which crystallises from diluted alcohol, is nearly insoluble in chloroform, and soluble in 800 parts of boiling alcohol. On hydrolysis by acids, all three substances yield (1) digitoxose, identical with the sugar obtained from digitoxin by Kiliani, and (2) *anhydrogitaligenin*,  $C_{22}H_{34}O_5$ , m. p. 216—219°, which crystallises from boiling alcohol in colourless plates.

The *digitosaponins*, obtained as described above, were freed from colouring matter by extraction with acetone, and then fractionated into  $\alpha$ -,  $\beta$ -, and  $\gamma$ -saponins by extraction in turn with alcohol and methyl alcohol,  $\gamma$ -saponin being nearly insoluble in both these solvents. They are colourless, amorphous substances, which on hydrolysis by 5% sulphuric acid yield digitosapogenin and a pentose giving a phenyl-azone, m. p. 156—158°. The most soluble  $\alpha$ -saponin passes into the less soluble  $\beta$ - and  $\gamma$ -forms when boiled in alcohol. They appear to be identical with Schmiedeberg's digitonin.

The alcoholic extract, after treatment with lead acetate, was evaporated to a small bulk with calcium carbonate, cooled, filtered, and shaken out with ether, which removed lateolin. Digitoxin was then extracted with chloroform, and from the residue gitin was extracted by boiling alcohol. The digitoxin thus obtained contained gitalin, from which it was freed by repeated evaporation of an alcoholic solution, whereby the impurity was gradually converted into sparingly soluble anhydrogitalin. The purified digitoxin formed tabular crystals from boiling alcohol, melted sharply at 245°, and on hydrolysis yielded digitoxenin and digitoxose, but Kiliani's digitoxin hydrate could not be obtained by crystallisation from aqueous alcohol.

*Gitin*, m. p. 265° (decomp.), crystallises from alcohol in long, colour-

less needles, is soluble in 250 parts of boiling methyl alcohol or 120 parts of boiling alcohol, but is insoluble in water or chloroform. It is isomeric with Kiliani's digitonin, which it resembles in yielding digitogenin on hydrolysis, but differs from it in containing a galactose in place of a dextrose residue. It is physiologically inactive. Full experimental details are given in the original of the complicated processes used in isolating these substances, and their colour reactions with Keller's and Kiliani's reagents are recorded. T. A. H.

**Constituents of Digitalis Leaves.** RUDOLPH TAMBACH (*Pharm. Zentr.-h.*, 1912, 53, 392—393).—From the precipitate obtained by the addition of tannin to a cold aqueous extract of digitalis leaves the author has isolated a substance called *digin*, m. p. 271—273°, colourless needles, which has little, if any, physiological activity, does not react with Kiliani's or Keller's reagent, and contains C 73·68% and H 10·33%. It presents points of similarity to Kraft's gitin (preceding abstract), but differs in its m. p., in its solubility in chloroform, and in its composition. The examination of the substance is being continued. C. S.

**A Second Crystalline Compound of Phenolic Character from Fresh or Preserved Cola-nut.** A. GORIS (*Chem. Zentr.*, 1912, i, 266; from *Bull. Sci. pharmacol.*, 18, 138 142. Compare *Abstr.*, 1907, i, 631).—This compound, *collatein*, is insoluble in ether, chloroform, and light petroleum, but soluble in hot water, alcohol, and acetone. From water it separates with water of crystallisation in the form of needles, which effloresce over sulphuric acid; from anhydrous acetone and chloroform it separates in prisms, m. p. 257—258°. It is precipitated by lead acetate, gives a green coloration with ferric chloride, which turns blue on addition of ammonia, and does not set free carbon dioxide from carbonates. It has a bitter taste.

S. B. S.

**"Peristaltin."** ALEXANDER TSCHIRCH and L. MONIKOWSKI (*Arch. Pharm.*, 1912, 250, 92—103).—"Peristaltin" is a patent preparation, used as a purgative, and obtained from the bark of *Rhamnus purshiana* (*Cascara sagrada*). It is a yellow, bulky powder, soluble in water or alcohol, partly in acetone, but insoluble in ether or light petroleum, and contains 4·2% water and 0·5% ash. It contains a reducing sugar, giving a phenylosazone, m. p. 208°. The substance appears to be a mixture of glucosides, and on hydrolysis by steam yields rhamnose, chrysophanic acid (chrysophanol), emodin methyl ether, and *cascarol*, together with a minute amount of a yellow colouring matter. When boiled with hydrochloric acid, peristaltin yields furfuraldehyde, and 2·06% of pentoses were found by Flint and Tollens' method. The product contains no nitrogenous substance.

*Cascarol*,  $C_{15}H_{10}O_5$ , m. p. 218°, forms yellow needles from pyridine or alcohol, is soluble in acetone or alcohol, insoluble in water, chloroform, ether, or cold sodium hydroxide solution, and yields a crystalline *acetyl* derivative, m. p. 204—205°.

The yellow colouring matter crystallises from hot water, melts at

203—204°, is soluble in alkalis, and gives a fluorescent solution in sulphuric acid.

T. A. H.

**$\alpha$ -Phyllohæmin and the Formula of  $\alpha$ -Phylloporphyrin.** LEON MARCHLEWSKI and J. ROBEL (*Ber.*, 1912, 45, 816—821. Compare this vol., i, 288).— $\alpha$ -Phyllohæmin, obtained by the action of Mohr's salt on  $\alpha$ -phylloporphyrin, can be purified by treatment with chloroform and quinine, and pouring the solution into glacial acetic acid saturated with common salt and heated nearly to boiling. After a time well-formed, brown, glistening, rhombic crystals are obtained, having a composition corresponding with either  $C_{31}H_{34}O_2N_4FeCl$  or  $C_{32}H_{34}O_2N_4FeCl$ . The analytical figures obtained for phylloporphyrin itself make the formula  $C_{32}H_{36}O_2N_4$  the most probable for this substance.

$\alpha$ -Phyllohæmin dissolves in organic solvents more easily than hæmin. In chloroform solution it has four absorption bands, which in comparison with those of hæmin are displaced somewhat towards the violet. In presence of quinine only two bands are visible.

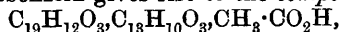
$\alpha$ -Phyllohæmochromogen, obtained on reduction with Stokes' reagent, is very similar to hæmochromogen from hæmin.

E. F. A.

**Resorcinolbenzein and Fluorescein.** HANS VON LIEBIG (*J. pr. Chem.*, 1912, [ii], 35, 97—136, 241—284).—I. *Resorcinolbenzein*.—In continuation of previous work (Abstr., 1905, i, 781; 1906, i, 445; 1908, i, 98) the author has made a detailed examination of resorcinolbenzein obtained by the methods of Doebner (Abstr., 1883, 861) and Cohn (Abstr., 1893, i, 719; 1894, i, 120), and finds that it exists in four different forms.

The simplest form,  $\alpha$ -resorcinolbenzein, has the composition  $C_{19}H_{12}O_3$ , and is identical with the resorcinolbenzein of Kehrmann and Dengler (Abstr., 1908, i, 1002; 1909, i, 249), whilst the  $\beta$ -,  $\gamma$ -, and  $\delta$ -compounds are respectively ter-, quadri-, and multi-molecular modifications.

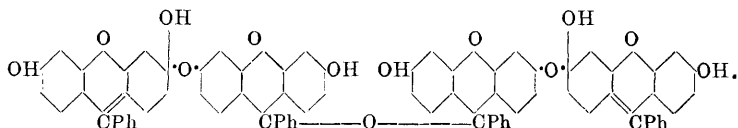
The product obtained by fusing benzoic acid or benzoic anhydride with resorcinol and zinc chloride at 180—210°, when treated with hot water and then with cold alcohol, yields a residue consisting of a compound of 2:4-dihydroxybenzophenone and  $\gamma$ -resorcinolbenzein,  $2C_{19}H_{12}O_3 \cdot C_{13}H_{10}O_3 \cdot H_2O$ , which forms light brown leaflets, m. p. 243—244°. On crystallisation from hot alcohol this yields a substance, m. p. 320—330°, having the same percentage composition, but crystallising in brownish-red, rhombic leaflets of a bluish lustre. Addition of acetic acid to an alcoholic solution of dihydroxybenzophenone- $\gamma$ -resorcinolbenzein gives rise to the compound,



which crystallises in brown leaflets of a silvery lustre, and is identical with the resorcinolbenzein of Cohn and Doebner.

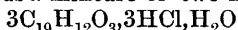
$\gamma$ -*Resorcinolbenzein* is obtained in brownish-red leaflets of the composition  $4C_{19}H_{12}O_3 \cdot 2H_2O \cdot EtOH$ , by dissolving the above-mentioned additive compound in alcoholic ammonia, and removing the excess of ammonia on the water-bath; it has also been prepared (1) by the oxidation of 3:6-dihydroxyphenylxanthen in alcoholic solution with lead dioxide in the presence of aqueous ammonia, and (2) by the action

of hydrogen peroxide on an ammoniacal solution of  $\alpha$ - and  $\beta$ -resorcinolbenzein. It loses  $1\text{H}_2\text{O}$  at  $100^\circ$  and, when dried at  $140^\circ$ , has the composition  $4\text{C}_{19}\text{H}_{12}\text{O}_3, \text{H}_2\text{O}$ ; the remaining water is removed at  $240^\circ$ . It is considered by the author to be a quinhydrone of the following formula :



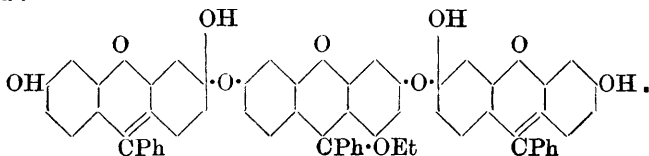
When treated with warm alcoholic hydrogen chloride and the resulting hydrochloride decomposed by ammonia,  $\gamma$ -resorcinolbenzein is converted into the  $\alpha$ -compound. The main product obtained by heating benzo-trichloride with resorcinol consists of a mixture of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -resorcinolbenzein; it is accompanied by small amounts of the following substances: (1) 2:4-Dihydroxybenzophenone. (2) The compound,  $\text{C}_{19}\text{H}_{12}\text{O}_3, \text{H}_2\text{O}, \text{C}_{13}\text{H}_{10}\text{O}_3$ , which forms a greenish-black powder, is resolved by boiling with alkalis and strong acids into dihydroxybenzophenone, and does not form salts. (3)  $\delta$ -Resorcinolbenzein,  $(\text{C}_{19}\text{H}_{14}\text{O}_4)_x$ , a brownish-red, crystalline substance, insoluble in the common solvents with the exception of aniline and nitrobenzene; it is best prepared by fusing benzoic acid and resorcinol with zinc chloride at  $250$ — $260^\circ$ .

The above-mentioned mixture of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -resorcinolbenzeins is sparingly soluble in alcohol, and is therefore readily separated from the remaining products of the reaction. On treatment with alcohol and hydrochloric acid, it yields a mixture of two hydrochlorides,



and  $\text{C}_{19}\text{H}_{12}\text{O}_3, \text{HCl}$  (compare Kehrman and Dengler, *loc. cit.*), from which the corresponding bases are liberated by aqueous ammonia and separated by extraction with a mixture of alcohol and benzene.

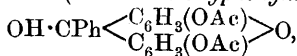
$\alpha$ -Resorcinolbenzein, the more readily soluble base, crystallises in light red leaflets or needles of the composition  $\text{C}_{19}\text{H}_{12}\text{O}_3, \text{EtOH}$ ; these lose their alcohol at  $140$ — $150^\circ$ , and have m. p.  $333^\circ$ . The residue from the extraction consists of  $\beta$ -resorcinolbenzein, which separates from alcohol in red needles or leaflets of the composition  $3\text{C}_{19}\text{H}_{12}\text{O}_3, 3\text{EtOH}$ ; at  $140^\circ$  it loses two molecules of alcohol. The author considers that the third molecule of alcohol is combined in the form of an ether, and assigns to  $\beta$ -resorcinolbenzein the following formula :



When dissolved in alcoholic ammonia and the excess of the latter removed by boiling, the  $\beta$ -compound yields red leaflets of the composition  $3\text{C}_{19}\text{H}_{12}\text{O}_3, \text{H}_2\text{O}, 2\text{EtOH}$ ; at  $140^\circ$  these lose water and one molecule of alcohol, the second being removed at  $240^\circ$ .

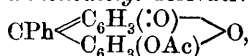
The condensation of 2:4-dihydroxybenzophenone and resorcinol yields mainly  $\beta$ -resorcinolbenzein. The  $\alpha$ -,  $\beta$ -, and  $\gamma$ -compounds when dissolved in aqueous ammonia and the solutions acidified with acetic acid yield crystalline *hydrates* of the same composition,  $C_{19}H_{12}O_3 \cdot H_2O$ .

*Diacetylresorcinolbenzein* (3 : 6-diacetoxyphenylxanthanol),



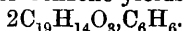
crystallises in white leaflets, m. p.  $171^\circ$ , containing one molecule of ether which is lost at  $140^\circ$ . It dissolves in methyl alcohol, yielding the *methyl ether*,  $OMe \cdot CPh \left\langle \begin{array}{c} C_6H_3(OAc) \\ C_6H_3(OAc) \end{array} \right\rangle O$ , white leaflets, m. p.  $122^\circ$ ; the *ethyl ether* forms colourless prisms, m. p.  $147^\circ$ .

On treatment with acetic acid, acetic anhydride, and sulphuric acid, resorcinolbenzein yields a *monoacetyl* derivative,



which crystallises in small, yellowish-red prisms, m. p.  $197^\circ$ , or in yellow needles containing benzene; in one instance an *acetyl* derivative of a dimolecular form,  $C_{40}H_{28}O_8$ , crystallising in colourless leaflets, m. p.  $198^\circ$ , was obtained. When methylated by means of methyl sulphate and aqueous sodium hydroxide, it forms the resorcinolbenzein monomethyl ether of Kehrman and Dengler, together with an *anhydride* of *resorcinolbenzein dimethyl ether*, which crystallises from ether in colourless prisms, m. p.  $152$ — $153^\circ$ , containing one molecule of the solvent,  $(C_{21}H_{17}O_3)_2O \cdot C_4H_{10}O$ ; the latter compound is converted by hot ethyl alcohol into the ethyl ether, m. p.  $157^\circ$ , described by Kehrman; the corresponding methyl ether has m. p.  $112^\circ$ .

3 : 6-Dihydroxyphenylxanthen (Abstr., 1909, i, 98) separates from benzene in crystals of the composition  $C_{19}H_{14}O_3 \cdot C_6H_6$ ; its ethereal solution on evaporation over benzene yields the *compound*,

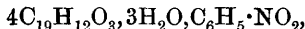


The compound,  $C_{38}H_{30}O_9$ , previously obtained (*loc. cit.*) by boiling resorcinol with aqueous potassium hydroxide is now found to consist of 2 : 4-dihydroxybenzophenone.

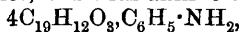
3 : 6-Diacetoxyphenylxanthen has m. p.  $183$ — $184^\circ$ , and often separates from ethyl acetate in crystals, m. p.  $179^\circ$ , of the composition  $4C_{19}H_{12}(OAc)_2 \cdot H_2O \cdot CH_3 \cdot CO_2Et$ ; crystallised from benzene, it has the composition  $4C_{19}H_{12}(OAc)_2 \cdot C_6H_6$ .

3 : 6-Diacetoxyphenylxanthenesulphonic acid,  $C_{23}H_{18}O_5 \cdot SO_3H$ , prepared by dissolving the preceding diacetoxy-compound in cold concentrated sulphuric acid, crystallises in white needles, and forms a *barium* salt.

Resorcinolbenzein forms with nitrobenzene the *compound*,



crystallising in red needles, and with aniline the *compound*,



dark red needles of a bluish lustre; the *compound* with phenol,



forms lustrous, light red needles.

The blue dye (resorcinol-blue) obtained by atmospheric oxidation of an ammoniacal resorcinol solution is more readily prepared by oxidising

the solution with hydrogen peroxide. It has the composition



and m. p. above  $360^\circ$ ; the filtrate on acidification with sulphuric acid yields a blue compound,  $\text{C}_{18}\text{H}_{15}\text{O}_8\text{N}$ . The successive addition of acetic acid and ammonium sulphate to an aqueous solution of resorcinol-blue gives rise to a mixture of the compounds,  $\text{C}_{18}\text{H}_{15}\text{O}_8\text{N}, (\text{NH}_4)_2\text{SO}_4, \text{H}_2\text{O}$  and  $\text{C}_{18}\text{H}_{15}\text{O}_8\text{N}, (\text{NH}_4)_2\text{SO}_4, \text{NH}_3$ .

When oxidised with aqueous hydrogen peroxide, resorcinol yields a brown dye (*resorcinol-brown*),  $\text{C}_{18}\text{H}_{14}\text{O}_8$ .

II. *Fluorescein*.—In addition to the ordinary red variety, fluorescein exists in five different yellow modifications, distinguished by the author as  $\alpha$ ,  $\beta$  I,  $\beta$  II,  $\gamma$  and  $\delta$ -fluorescein. The existence of these yellow modifications, all of which are unimolecular in acetone solution, is explained on the assumption that the three phenyl groups of triphenyl-methane are not always freely moveable about the central atom, but, in certain circumstances, may take up different, fixed positions to one another. From molecular weight determinations in phenol solution, Kehrman has drawn the conclusion that the red variety of fluorescein is also unimolecular. The author points out, however, that determinations in phenol solution give the molecular weight, not of the red form, but of the yellow modification, since on allowing the solution to solidify and removing the phenol with benzene or ether, yellow leaflets of a compound of fluorescein with phenol,



are obtained. It is suggested that the red form is a multimolecular quinhydrone of fluorescein.

$\alpha$ -*Fluorescein*,  $\text{C}_{20}\text{H}_{12}\text{O}_5$ , is obtained as a pale yellow powder, m. p.  $347^\circ$ , by acidifying an alkaline solution of ordinary fluorescein with sulphuric acid, extracting with ether, and shaking the ethereal solution with aqueous potassium hydroxide in insufficient amount for complete solution. It crystallises unchanged from benzene, amyl alcohol, and formic acid, but is converted by ethyl alcohol, acetone, ethyl acetate, and ether into the red form. From a mixture of methyl alcohol and ether, it separates in yellow crystals containing one molecule of methyl alcohol.

$\beta$ -*Fluorescein* I is obtained by acidifying an aqueous solution of the disodium salt of fluorescein with sulphuric acid. It separates from ether in transparent, light yellow crystals, often in the form of hexagonal platelets, of the composition  $4\text{C}_{20}\text{H}_{12}\text{O}_5, \text{H}_2\text{O}, 4\text{C}_4\text{H}_{10}\text{O}$ . It sinters and becomes brown at  $140$ – $150^\circ$ , loss of ether taking place simultaneously; at  $200^\circ$  it loses water and becomes red. When dry, it is very stable, but in the moist condition and on exposure to light it is transformed into the red variety. It differs from the preceding modification in being stable in ethereal solution.

$\beta$ -*Fluorescein* II, prepared by shaking an aqueous solution of the disodium salt of fluorescein with methyl sulphate, crystallises with ether in hexagonal platelets of the composition  $\text{C}_{20}\text{H}_{12}\text{O}_5, \text{C}_4\text{H}_{10}\text{O}$ ; the ether is lost at  $150$ – $154^\circ$ . It has about the same solubility as the  $\beta$  I modification, but differs from the latter in separating from acetone in yellow crystals containing one molecule of the solvent; it also crystallises with  $1\text{MeOH}$ .

When heated at 220—240°, 2:4-dihydroxybenzoylbenzoic acid (m. p. 210—211°) yields two forms of fluorescein: (1) a red modification, which crystallises in lustrous, hexagonal leaflets, separates from methyl alcohol in yellow crystals of the composition  $C_{20}H_{12}O_5$ , MeOH, and differs in some respects from the ordinary red variety; (2)  $\gamma$ -fluorescein, which forms a pale yellow, crystalline powder of the composition  $4C_{20}H_{12}O_5 \cdot H_2O$ , has approximately the same solubility as  $\alpha$ -fluorescein, but differs from the latter in that it may be repeatedly crystallised from cold alcohol without undergoing change.

$\delta$ -Fluorescein is obtained together with a brown substance,  $C_{40}H_{80}O_5$  (?), m. p. above 350°, by acidifying an aqueous solution of the mono- or di-sodium and potassium salts of fluorescein, which have been previously heated to 300—350°. It crystallises with one molecule of ether in crusts of transparent, yellow needles. From cold alcohol it separates in slender, chamois-coloured needles, which have the composition  $C_{20}H_{12}O_5$ , darken at 280—290°, and have m. p. 340°.

All the yellow forms of fluorescein give the same diacetyl derivative, m. p. 205—206° (Baeyer gives 200°); the *monoacetyl* derivative has m. p. 215°.

2:4-Dihydroxybenzoylbenzoic acid crystallises from water in leaflets of the composition  $2C_{14}H_{10}O_5 \cdot 3H_2O$ ; the *diacetyl* derivative forms rhombohedra, m. p. 136°.

Fluorescein, prepared by reducing fluorescein with zinc dust and acetic acid in the presence of alcohol and aqueous ammonia, crystallises with  $2H_2O$  in colourless or yellow leaflets, m. p. 253—254° (compare Herzig, Abstr., 1892, 1319). It crystallises with ether in needles, and with benzene (2 mols.) in leaflets; the *diacetyl* derivative has m. p. 213—214°, and forms crystals containing alcohol, m. p. 113—114°.

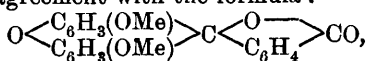
III. *Alkali Salts of the Fluorescein Series.*—This section contains an account of the preparation of the sodium and potassium salts of fluorescein, and of some allied compounds, together with a discussion of their constitution.

The *monopotassium* salt of fluorescein,  $C_{20}H_{11}O_5K$ , prepared from fluorescein or its diacetyl derivative and alcoholic potassium hydroxide, crystallises with alcohol (1 mol.) in orange or light red needles, and is almost instantly decomposed by water with the separation of fluorescein; the *ammonium* salt,  $C_{20}H_{15}O_5N \cdot EtOH$ , forms lustrous, red leaflets. The *dipotassium* salt,  $C_{20}H_{10}O_5K_2 \cdot 3H_2O$ , obtained as a greenish-black mass of a bluish lustre, gives light red solutions which become dark red on the addition of a trace of alkali; this change is referred by the author to the rupture of the oxygen bridge of the central ring; the *disodium* salt is similar in character.

The *potassium* salt of fluoran,  $C_{20}H_{13}O_4K \cdot EtOH$ , forms long, colourless needles. When methylated by means of methyl sulphate and aqueous potassium hydroxide, quinolphthalein yields a *dimethyl ether*,  $2C_{20}H_{10}O_8(OMe)_2 \cdot H_2O$ , which crystallises in bluish leaflets, m. p. 198°, and yields a colourless *potassium* salt,  $C_{44}H_{17}O_4(OMe)_4K_3$ . The *sodium* and *potassium* salts of resorcinolbenzein,  $C_{19}H_{11}O_8Na$  (or K), crystallise in light, red needles or leaflets; the *dipotassium* salt of quinolphthalein,  $C_{20}H_{10}O_5K_2 \cdot 3H_2O$ , is bluish-black.

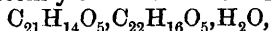
IV. *The Methyl Ethers of Fluorescein.*—The author discusses the

constitution of the methyl ethers of fluorescein, and gives an account of the products obtained by methylating fluorescein under different conditions. The monomethyl ether described by Fischer (Abstr., 1895, i, 291) has m. p.  $266^{\circ}$ ; it is pale yellow in colour, and has the constitution  $\text{O} \langle \text{C}_6\text{H}_3(\text{OMe}) \rangle \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ . The interaction of methyl sulphate and the disodium salt of fluorescein yields, in addition to the above compound, the previously-described dimethyl ethers of m. p.  $198^{\circ}$  and  $208^{\circ}$ , together with a new *dimethyl ether*, which crystallises in small, colourless prisms, m. p.  $255^{\circ}$ ; the properties of the latter compound are in agreement with the formula :



which, however, has already been assigned to the dimethyl ether of m. p.  $198^{\circ}$ .

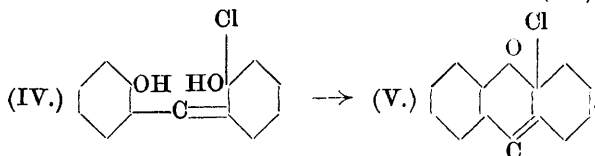
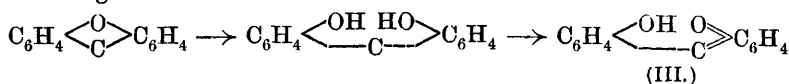
On treatment with methyl iodide in methyl-alcoholic solution, the disodium salt of fluorescein yields a bimolecular *methyl ether*,



crystallising in slender, orange-yellow needles, m. p.  $164\text{--}165^{\circ}$  (decomp.).

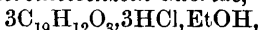
When fluorescein is methylated according to Fischer's method (Abstr., 1895, i, 291) and the product of the action extracted with ether, a *hydrate* of the dimethyl ether, m. p.  $208^{\circ}$ , is obtained; this crystallises in orange-yellow needles, sintering at  $173\text{--}174^{\circ}$ , and has the composition  $3\text{C}_{22}\text{H}_{16}\text{O}_5, 2\text{H}_2\text{O}$ . Extraction with cold methyl alcohol yields a *hydrate*,  $2\text{C}_{22}\text{H}_{16}\text{O}_5, \text{H}_2\text{O}$ , light yellow needles, m. p.  $190^{\circ}$ , whilst the hot methyl-alcoholic extract furnishes a *hydrate*,  $3\text{C}_{22}\text{H}_{16}\text{O}_5, \text{H}_2\text{O}$ , crystallising in orange-yellow needles, which often pass spontaneously into dark red prisms, m. p.  $194^{\circ}$ . All three hydrates when heated at  $140^{\circ}$ , or repeatedly crystallised from ethyl acetate, yield the anhydrous dimethyl ether, m. p.  $208^{\circ}$ .

V. *Quinhydrone and Oxonium Salts*.—In this section the author advances arguments in favour of the view that the compounds of resorcinolbenzein and fluorescein with dihydroxybenzophenone and alcohol described in sections I and II, and also the oxonium salts of the xanthen series have a quinhydrone structure. The formation of oxonium salts is due to the rupture of the oxygen bridge and intermediate formation of an *o*-quinonoid compound (III), as shown in the following scheme :



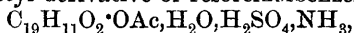
In the solid condition the salts are represented by formula (V) and in solution by (IV).

*α-Resorcinolbenzein chloride*,  $C_{19}H_{12}O_8, HCl$ , prepared by the action of alcoholic hydrogen chloride on *α-resorcinolbenzein*, forms light yellow needles or leaflets. *β-Resorcinolbenzein chloride*,



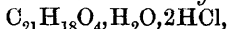
crystallises in brownish-yellow needles or leaflets. *γ-Resorcinolbenzein* and alcoholic hydrogen chloride yield either the above *α-chloride* or *γ-resorcinolbenzein chloride*,  $4C_{19}H_{12}O_8, 4HCl, H_2O$ , which forms steel-blue, rhombic, broad leaflets.

On treatment with a mixture of sulphuric and acetic acids, *resorcinolbenzein* forms a *sulphate*,  $(C_{19}H_{12}O_8)_2SO_4$ , crystallising in yellow needles of a violet lustre. When boiled with 25% sulphuric acid, it forms a *sulphate*,  $C_{19}H_{12}O_8, H_2SO_4$ ; this crystallises in yellow leaflets, which are transformed by water into lustrous, red needles of the composition  $4C_{19}H_{12}O_8, 2H_2SO_4, 2H_2O$ . When treated successively with acetic anhydride and sulphuric acid, and the resulting product dissolved in aqueous ammonia, *resorcinolbenzein* yields an *ammonium* salt of the monoacetyl derivative of *resorcinolbenzein sulphate*,



which forms glistening, red needles.

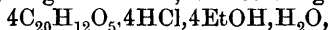
The *chloride* of *resorcinolbenzein dimethyl ether*,



crystallises in long, slender, yellow needles, the *sulphate* in yellow leaflets.

When boiled with glacial acetic acid, the ordinary red fluorescein yields a red *acetate*,  $4C_{20}H_{12}O_5, CH_3 \cdot CO_2H$ ; the yellow varieties of fluorescein yield a golden-yellow *acetate*,  $C_{20}H_{12}O_5, CH_3 \cdot CO_2H$ , which crystallises in leaflets of a green lustre.

With alcoholic hydrogen chloride, fluorescein gives a *chloride*,



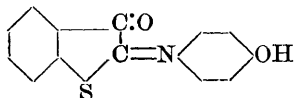
crystallising in yellow, hexagonal leaflets of a green lustre (decomp.  $270^\circ$ ); the *sulphate*,  $2C_{20}H_{12}O_5, H_2SO_4$ , is also described.

The dimethyl ether of fluorescein of m. p.  $198^\circ$  forms a yellow *chloride* of the composition  $3C_{22}H_{16}O_5, 2HCl$ .

When boiled with 2% hydrochloric acid the dimethyl ether of m. p.  $208^\circ$  yields a termolecular *chloride*,  $3C_{22}H_{16}O_5, 2HCl, 4H_2O$ , crystallising in red needles (decomp.  $120^\circ$ ); with alcoholic hydrogen chloride it forms a unimolecular *chloride*,  $C_{22}H_{16}O_5, HCl, 2H_2O$ , which crystallises in large, dark red prisms of a blue lustre (decomp.  $120^\circ$ ). F. B.

**Preparation of *p*-Hydroxyaryl Derivatives of 2-Imino-3-ketodihydro-(1)-thionaphthens.** KALLE & Co. (D.R.-P. 241623).

—When *α*-(2)-derivatives of 2:3-diketodihydro-(1)-thionaphthens are oxidised in the presence of hydroxyarylamines in alkaline solution, condensation products are produced.



The compound (annexed formula), yellow needles, was obtained by the action of potassium ferricyanide on a mixture of *p*-aminophenol and 3-keto-(1)-thionaphthen-2-carboxylic acid in aqueous alkaline solution. The *sodium* salt is soluble in water with violet

coloration, and when boiled with 20% sulphuric acid furnishes 2:3-diketodihydro-(1)-thionaphthen. F. M. G. M.

*apoHarminecarboxylic Acid, apoHarmine, and Some Derivatives of this Base.* VICTOR HASENFRATZ (*Compt. rend.*, 1912, 154, 704—706. Compare this vol., i, 209).—*apoHarminecarboxylic acid* may be obtained directly from harmic acid by heating it at 250—280° in a vacuum. A second molecule of carbon dioxide is lost at 330°, and *apoharmine* is formed; harmic acid, therefore, appears to be *apo-harmine-2:3-dicarboxylic acid*.

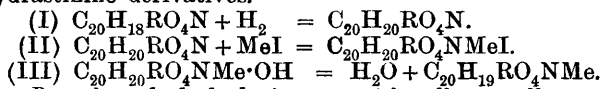
*Iodoapoharmine*,  $C_8H_7N_2I$ , prepared by the action of iodine on *apoharmine* in presence of potassium hydroxide, occurs in long needles, m. p. 158°; the *platinichloride* and *nitrate* were prepared, the latter crystallises with  $1H_2O$ . By the action of methyl iodide, *iodomethyl-apoharmine hydriodide* is obtained; the *base*,  $C_8H_6MeN_2I$ , crystallises in needles, m. p. 155—156°.

*apoHarminesulphonic acid*,  $C_8H_7N_2 \cdot SO_3H$ , crystallising in colourless prisms, is formed when *apoharmine* dissolves in sulphuric acid. Harmaline likewise yields *harmalinesulphonic acid*,  $C_{13}H_{13}ON_2 \cdot SO_3H$ , in the form of long, golden-yellow needles, which give an intensely fluorescent, blue solution in water. W. O. W.

**Resolution of Racemic Histidine into the Optically Active Components.** EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1912, 77, 435—453).—Natural *l*-histidine has been racemised by heating under pressure, and this resolved into *d*- and *l*-histidines by means of *d*-tartaric acid (compare Pyman, *Trans.*, 1911, 99, 1386).

Formyl-*l*-histidine has  $[\alpha]_D^{20} + 56.73^\circ$ . Formyl-*dl*-histidine could not be resolved by means of brucine. *dl*-Histidine is partly resolved by yeast, *d*-histidine remaining unattacked. Pure *d*-histidine was obtained from the urine of rabbits fed with *dl*-histidine. E. F. A.

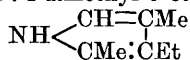
**Preparation of Hydrastinine and Analogous Bases from Berberine.** MARTIN FREUND (D.R.-P. 241136).—A general method for the preparation of hydrastinine bases consists of the following procedure. The  $\alpha$ -alkyl-,  $\alpha$ -alkaryl-, or  $\alpha$ -aryl-dihydroberberines are reduced to the tetrahydro-condition (I), converted into the quaternary compound (II), and finally into the ammonium base (III) and the pseudo-base, for which several formulæ may be given; further elimination of water may take place, yielding a complicated series of compounds, or the base may be converted by oxidation into hydrastinine derivatives.



*$\alpha$ -Benzyltetrahydroberberine*, greenish-yellow needles, m. p. 163—165°, is prepared by reducing benzyl-dihydroberberine with tin and alcoholic hydrochloric acid; the *stannichloride* which crystallises out is decomposed with ammonium sulphide, and the free base extracted with chloroform. *Tetrahydroberberine methiodide* is obtained by heating the foregoing base with methyl iodide at 225° during four or five hours;

this when digested with silver hydroxide in 50% alcoholic solution furnishes a crystalline *base*, m. p. 121—122°, which when oxidised with sodium dichromate in 50% acetic acid solution furnishes a 65—78% yield of hydrastinine. F. M. G. M.

**Action of Sodium Ethoxide on Pyrrole Derivatives. I.** HANS FISCHER and ERICH BARTHOLOMÄUS (*Zeitsch. physiol. Chem.*, 1912, 77, 185—201).—By reduction of the hydrazone of 3-acetyl-2:4-dimethylpyrrole with sodium ethoxide, Knorr and Hess (Abstr., 1911, i, 1019) obtained 2:4-dimethyl-3-ethylpyrrole,



On repetition of this operation, a ketazine is obtained instead of the hydrazone, which, when reduced at 220°, affords an oil differing greatly in properties from that obtained by Knorr and Hess. The new oil does not immediately form a picrate with picric acid or yield methylethylmaleinimide when treated with lead peroxide. It is characterised by the formation of a crystalline azo-dye with diazobenzenesulphonic acid. An azo-dye of similar properties is obtained from Piloty's phonopyrrole.

On immediate addition of picric acid to the ethereal solution of the freshly distilled oil, a *picrate*, m. p. 89—90°, was obtained, corresponding with a dimethyldiethylpyrrole. The free pyrrole was not obtained crystalline; it does not couple with diazobenzenesulphonic acid.

2:4-Dimethyl-5-ethylpyrrole,  $\text{NH} \begin{array}{c} \text{CEt}=\text{CMe} \\ \diagdown \quad | \\ \text{CMe}:\text{CH} \end{array}$ , was obtained synthetically from ethyl acetoacetate and methyl propyl ketoxime. By means of the azo-dye compound it is shown to be identical with the above oil obtained from the ketazine. By the action of sodium ethoxide at 220°, 2:4-dimethyl-3:5-diethylpyrrole,  $\text{NH} \begin{array}{c} \text{CEt}=\text{CMe} \\ \diagdown \quad | \\ \text{CMe}:\text{CEt} \end{array}$ , identical with that derived from the picrate, is obtained.

3-Acetyl-2:4:5-trimethylpyrrole,  $\text{NH} \begin{array}{c} \text{CMe}:\text{CMe} \\ \diagdown \quad | \\ \text{CMe}:\text{C}:\text{COMe} \end{array}$ , from methyl ethyl ketoxime and acetylacetone, has m. p. 209°; it does not couple with diazobenzenesulphonic acid. By the action of hydrazine-hydrate, a mixture of ketazine and hydrazone, m. p. 235—236°, is obtained; when this is heated with sodium ethoxide at 220°, 2:4:5-trimethyl-3-ethylpyrrole is obtained, m. p. 65—67°, which forms a picrate, m. p. 104—105°, identical with phyllopyrrole picrate.

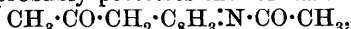
E. F. A.

**Electrolytic Reduction of Chelidamic Acid to 4-Hydroxypiperidine-2:6-dicarboxylic Acid.** BRUNO EMMERT and AUGUST HERTERICH (*Ber.*, 1912, 45, 661—665).—The cathodic and the anodic compartments of Tafel's apparatus contain respectively chelidamic acid in *N*-sodium hydroxide and 10% sodium carbonate. The reduction is effected at 25—30° at a lead cathode, the current density being 11

amperes per sq. decimetre. 4-Hydroxypiperidine-2:6-icarboxylic acid,  $C_7H_{11}O_5N$ , decomp. above  $240^\circ$ , crystallises in short prisms, rapidly absorbs moisture from the air, and forms a hydrochloride decomp.  $230^\circ$ . It can be esterified only with difficulty. The ethyl ester has b. p.  $206-208^\circ/15$  mm. (hydrochloride, decomp.  $195^\circ$ ); the methyl ester has b. p.  $185-187^\circ/15$  mm.; the diamide has m. p.  $245^\circ$  (decomp.). C. S.

**Action of Acetic Anhydride on  $\alpha$ -Picoline.** MAX SCHOLTZ (*Ber.*, 1912, 45, 734-747).—When  $\alpha$ -picoline is treated with acetic anhydride at  $200-220^\circ$ , interaction occurs according to the equation:  $C_8H_7N + 2(CH_3 \cdot CO)_2O = C_{12}H_{11}O_2N + CH_3 \cdot CO_2H + 2H_2O$ .

The compound,  $C_{12}H_{11}O_2N$ , possessed no basic properties, and hence probably does not contain the pyridine ring. This is confirmed by the fact that no pyridinecarboxylic acid could be obtained by oxidising it. With hydroxylamine, phenylhydrazine, and semicarbazide it forms crystalline condensation products. It readily condenses with two molecules of aromatic aldehydes, whilst, in some cases, monoaldehyde compounds can also be isolated. It therefore contains the group  $\cdot CH_2 \cdot CO \cdot CH_2 \cdot$  or, more probably,  $\cdot CH_2 \cdot CO \cdot CH_2 \cdot$ . It combines with two or four atoms of bromine, yielding very unstable products. When boiled with moderately concentrated sulphuric or hydrochloric acid, it yields a base,  $C_8H_7N$ , isomeric with indole. For the substance,  $C_{12}H_{11}O_2N$ , which probably possesses the formula



the name *picolide* is proposed.

The compound,  $C_8H_7N$ , is a very weak base, from which crystalline salts could not be obtained. It does not react with methyl iodide at  $100^\circ$ . It is very readily oxidised. It gives the pyrrole reaction with isatin and with a pine shaving, whilst with oxalic acid it gives the indole reaction. When reduced, it yields a compound,  $C_8H_9N$ , which is not basic, but behaves as a pyrrole derivative. For these two compounds the formulæ:



are proposed, and the former is named *pyrrocoline*. Both it and its dihydro-derivative form crystalline compounds with aldehydes, in which two molecules of the pyrrole derivative unite with one molecule of aldehyde.

2:4-Lutidine, when treated with acetic anhydride, yields methylpicolide,  $C_{13}H_{15}O_2N$ .

*Picolide*,  $C_{12}H_{11}O_2N$ , is best obtained by heating  $\alpha$ -picoline at  $200-220^\circ$  with a large excess of acetic anhydride and boiling the product with much water. On cooling, picolide separates in long needles, m. p.  $176^\circ$ . Its formation can be used to detect the presence

of 2-picoline in commercial pyridine. It yields an *oxime*, m. p. 244°, a *phenylhydrazone*, m. p. 168°, and a *semicarbazone*, m. p. 233°. By treating its alcoholic solution with aromatic aldehydes, the following condensation products were obtained: *dibenzylidenepicolide*, m. p. 208°; *di-p-methylbenzylidenepicolide*, m. p. 202°; *mono-p-methylbenzylidenepicolide*, m. p. 152°; *difurfurylidenepicolide*, m. p. 210°; *dicinnamylidenepicolide*, m. p. 217°; *di-p-isopropylbenzylidenepicolide*, m. p. 214°; *dipiperonylidenepicolide*, m. p. 141°, and *piperonylidenepicolide*, m. p. 152°. These aldehyde condensation products give characteristic colorations on treatment with concentrated sulphuric acid.

*Pyrrocoline*,  $C_8H_7N$ , obtained by boiling picolide during an hour with 25% hydrochloric acid and purified by distillation with steam, has m. p. 74°, b. p. 205°. When dissolved in very dilute sulphuric acid and treated with potassium iodate, it gives an intensely blue solution. When condensed with aldehydes, it yields the following compounds, which are somewhat sensitive to the action of air: *benzylidenedipyrrocoline*, m. p. 210—212°; *p-methylbenzylidenedipyrrocoline*, m. p. 92°; *cinnamylidenedipyrrocoline*, darkening above 200°; *furfurylidenedipyrrocoline*, m. p. 148—149°; *piperonylidenedipyrrocoline*, m. p. 145—150°; *chloralpyrrocoline*,  $CCl_3 \cdot CH(OH) \cdot C_8H_6N$ , m. p. 92°.

*Dihydropyrrocoline* (2-butadienylpyrrole),  $C_8H_9N$ , obtained by reducing pyrrocoline by sodium and alcohol, is a colourless oil, b. p. 198—199°/754 mm. When dissolved in alcohol and treated with an alcoholic solution of mercuric chloride, it yields a compound,  $C_8H_9NCl_4Hg_2$ , decomposing above 90°. When warmed with the respective aldehydes, dihydropyrrocoline yields *benzylidene-bis-dihydropyrrocolene*, m. p. 118—120°, and *furfurylidene-bis-dihydropyrrocolene*, m. p. 132°.

*Methylpicolide*, m. p. 180°, is obtained in small yield by heating 2 : 4-lutidine with acetic anhydride. H. W.

**New Metallo-quinolides.** Metallo-quinolides of Silver Nitrate. I. UMBERTO POMILIO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iii], 17, 326—341).—When quinoline and silver nitrate are brought together in aqueous solution or in the solid state, the compound,  $AgNO_3(C_9H_7N)_2$ , is produced (compare Lachowicz, *Abstr.*, 1890, 444). When a solution of silver nitrate in excess of quinoline is heated for some hours at 30—35°, the crystalline compound,  $AgNO_3(C_9C_7N)_4$  is obtained on cooling. This substance readily loses quinoline when treated with solvents, the diquinolide being formed.

R. V. S.

**New Metallo-quinolides.** Metallo-quinolides of Nickel Chloride. II. UMBERTO POMILIO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iii], 17, 342—352).—Quinoline and well-dried, anhydrous nickel chloride were left in contact for some weeks, then heated at 100° for a few days, and finally kept at 200° for some hours. The liquid, after being filtered while warm, deposited a dark blue, crystalline compound,  $NiCl_2(C_9H_7N)_2$ . When the reaction mixture was cooled rapidly, a

yellow *compound* of the same composition was obtained mixed with the blue substance. A mixture of the two substances kept in a sealed tube was entirely converted into the yellow compound in a few hours, and the two substances are therefore to be regarded as isomerides or polymerides. When the blue compound is heated at 140—150°, and finally at 160—170°, or when the yellow salt is heated at 120—130° and subsequently at 150—170°, the red *compound*,  $\text{NiCl}_2 \cdot \text{C}_9\text{H}_7\text{N}$ , is produced. All three substances are readily decomposed by solvents (especially alcohol), and this may explain the failure to obtain such compounds previously (compare Lachowicz, *Abstr.*, 1889, 569).

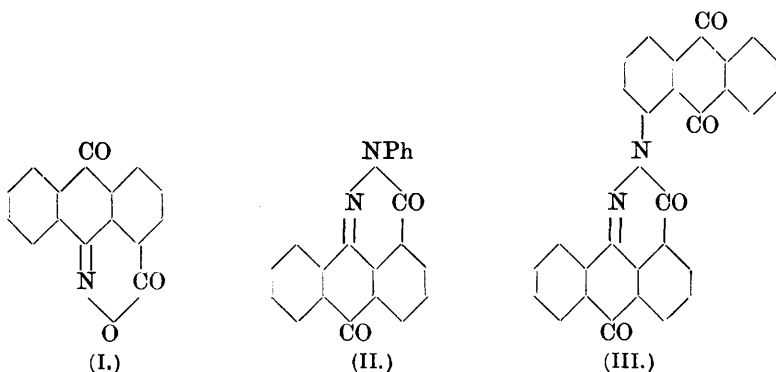
Anhydrous nickel sulphate and quinoline, kept at 100° for some days, yield a stable *compound*, which forms a violet, crystalline crust, m. p. 98—99°. R. V. S.

**Anthraquinone Series. VII. Anthraquinone-1-carboxylic Acid.** FRITZ ULLMANN and WILLEM VAN DER SCHALK (*Annalen*, 1912, 388, 199—216).—Anthraquinone-1-carboxylic acid is easily obtained in 70% yield by the following series of reactions. Anthraquinone is nitrated at 50° by nitric (D 1·4) and sulphuric acids. The 1-nitroanthraquinone (separated from the little dinitroanthraquinone produced by solution in toluene) is reduced by sodium sulphide and boiling water to 1-aminoanthraquinone. This is diazotised and the separated diazonium sulphate is treated in the usual manner with cuprous cyanide at 70°, and the resulting nitrile is hydrolysed by boiling dilute sulphuric acid (3:1 by volume). The acid is purified by solution in aqueous ammonia and precipitation by dilute nitric acid.

In a similar manner 2-bromo-1-aminoanthraquinone is converted into 2-bromo-1-cyanoanthraquinone, m. p. 308° (corr.), and 2-bromoanthraquinone-1-carboxylic acid, m. p. 292° (corr.), yellow octahedra. 5-Nitroanthraquinone-1-carboxylic acid, decomp. above 330°, yellow plates, is obtained by the nitration of the acid or by converting 5-nitro-1-aminoanthraquinone into the *nitrile*, m. p. 390°, and subsequent hydrolysis. By reduction with boiling aqueous sodium sulphide, it yields 5-aminoanthraquinone-1-carboxylic acid, m. p. 277° (decomp.), dark red leaflets.

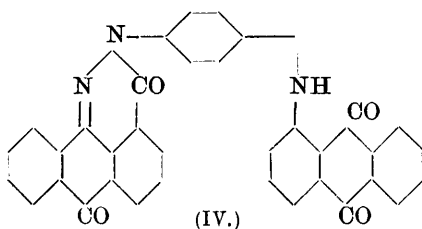
*Oxazonanthrone* (anhydro-anthraquinone-9-oxime-1-carboxylic acid), m. p. 247° (corr.), almost colourless needles, is obtained from anthraquinone-1-carboxylic acid and hydroxylamine in boiling aqueous solution, and receives the formula (1). It is soluble in boiling alkalis, and is reprecipitated by acids. The analogously constituted *pyridazonanthrone*,  $\text{C}_{15}\text{H}_8\text{O}_2\text{N}_2$ , m. p. 430°, almost colourless needles, is obtained by the slow addition of aqueous hydrazine hydrate to a pyridine solution of ethyl anthraquinone-1-carboxylate or to a benzene solution of the acid chloride. Anthraquinone-1-carboxylic acid and potassium acetate react with phenylhydrazine in boiling 50% acetic acid to form *phenylpyridazonanthrone* (formula II), m. p. 292° (corr.), yellow needles, by the sulphonation of which *phenylpyridazonanthrone-p-sulphonic acid*, yellow needles, is produced. This acid, which is also

obtained from anthraquinone-1-carboxylic acid and phenylhydrazine-*p*-sulphonic acid, forms a *sodium* salt,  $C_{21}H_{11}O_5N_2SNa$ , yellow, felted needles, which dyes wool in yellow shades fast to light and washing. 5-Aminoanthraquinone-1-carboxylic acid and phenylhydrazine in 50% acetic acid containing potassium acetate yield 5-amino-*N*-phenylpyridazonanthrone,  $C_{21}H_{13}O_2N_3$ , m. p.  $320^\circ$ , carmine-red leaflets, which develops a violet coloration in warm, concentrated sulphuric acid. *N*- $\alpha$ -Anthraquinonylpyridazonanthrone, m. p.  $339^\circ$ , yellow needles



(formula III), is prepared by boiling pyridazonanthrone,  $\alpha$ -chloroanthraquinone, copper powder, and potassium and copper acetates in nitrobenzene for ten hours. It is reduced by alkaline sodium

hyposulphite to a brownish-red vat, which has only a slight affinity for cotton. When treated in a similar manner, *p*-bromophenylpyridazonanthrone,  $C_{21}H_{11}O_2N_2Br$ , m. p.  $308^\circ$  (corr.), yellow needles (prepared from anthraquinone-1-carboxylic acid and *p*-bromophenylhydrazine), and 1-amino-



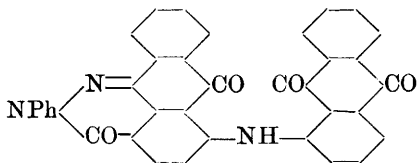
anthraquinone yield  $\alpha$ -anthraquinonyl-*p*-aminophenylpyridazonanthrone (formula IV), brownish-red needles, which reduces to a red vat dyeing cotton in weak red shades.

C. S.

**Anthraquinone Series. VIII. 4-Chloroanthraquinone-1-carboxylic Acid.** FRITZ ULLMANN and WASSILY MINAJEFF (*Annalen*, 1912, 388, 217—221).—4-Chloroanthraquinone-1-carboxylic acid, obtained by the oxidation of 4-chloro-1-methylanthraquinone by 100% sulphuric acid at  $120^\circ$ , is converted by hydrazine hydrate (compare preceding abstract) into 4-chloropyridazonanthrone,  $C_{15}H_7O_2N_2Cl$ , m. p.  $319^\circ$  (corr.), yellow needles, which reacts with boiling *p*-toluidine and potassium and copper acetates to form 4-*p*-toluidinopyridazonanthrone,  $C_{22}H_{15}O_2N_3$ , m. p.  $352^\circ$  (corr.), orange-red needles. 4-Chloro-*N*-phenylpyridazonanthrone,  $C_{21}H_{11}O_2N_2Cl$ , m. p.  $285^\circ$  (corr.), yellow needles, prepared from 4-chloroanthraquinone-1-carboxylic acid and phenyl-

hydrazine (*loc. cit.*), reacts readily with *p*-toluenesulphonamide and potassium and copper acetates in boiling nitrobenzene to form 4-*p*-toluenesulphonamino-*N*-phenylpyridazonanthrone, which is converted by concentrated sulphuric acid on the water-bath into 4-amino-*N*-phenylpyridazonanthrone, m. p. 340° (corr.), yellow needles.

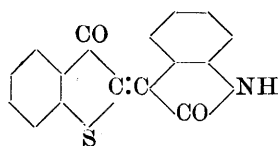
4- $\alpha$ -Anthraquinonylamino-*N*-phenylpyridazonanthrone (annexed formula), m. p. 405°, red needles, is prepared from 4-chloro-*N*-phenylpyridazonanthrone, 1-aminoanthraquinone, and potassium and copper acetates in boiling nitrobenzene.



4- $\beta$ -Anthraquinonylamino-*N*-phenylpyridazonanthrone, m. p. 430°, brown needles, is prepared in a similar manner from 2-aminoanthraquinone; unlike the  $\alpha$ -isomeride, it yields a vat with sodium hyposulphite, and produces yellowish-brown shades on cotton.

C. S.

[Preparation of Oxindole Derivatives of 2:3-Diketodihydro-1-thionaphthen.] KALLE & Co. (D.R.-P. 241327).—



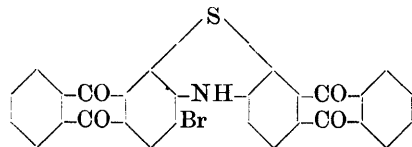
The compound (annexed formula), a brown, crystalline powder, was obtained by boiling oxindole and 2:3-diketodihydro-(1)-thionaphthen together in acetic acid solution in the presence of zinc chloride until the formation of colour was complete. The 2:3-diketodihydro-(1)-thionaphthen can be re-

placed by its derivatives substituted in the ring.

F. M. G. M.

Thiodiphenylamines of the Anthraquinone Group. IRMA ULLMANN and FRITZ ULLMANN (*Ber.*, 1912, 45, 832—834. Compare *Abstr.*, 1911, i, 466, 489, 739, 1010).—In extension of the earlier investigations it was desired to prepare compounds in which the

carbonyl group of the anthraquinoneacridones is replaced by a sulphur atom.



Bromodianthraquinonylthiodiphenylamine (annexed formula) was obtained by interaction of 1:3-dibromo-2-aminoanthra-

quinone with anthraquinone-1-thiol in hot nitrobenzene solution in the presence of potassium hydroxide; it forms violet needle crystals, which sublime without melting (decomp.) above 400°. Its solutions in organic solvents are violet, and it can be reduced to a brownish-red vat which dyes cotton violet-blue.

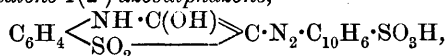
D. F. T.

Sulphazone Dyes. MAX CLAASS (*Ber.*, 1912, 45, 747—756).—*o*-Nitrophenylthiolacetic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 163—164°, yellowish-brown, slender needles, obtained from *o*-nitrophenyl mercaptan and chloroacetic acid in warm alkaline solution, is converted into *o*-nitrophenylthionylacetic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , decomp.,

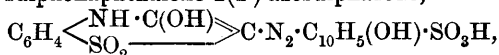
185—186°, by 3% hydrogen peroxide, and into *o*-nitrophenylsulphone-acetic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 173—174°, colourless prisms, by 40% hydrogen peroxide. The latter is reduced by zinc

dust and hot 50% acetic acid to *sulphazone*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NH} \cdot \text{CO} \\ \text{SO}_2 \cdot \text{CH}_2 \end{smallmatrix}$ , m. p.

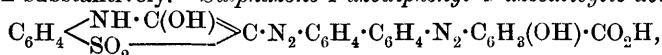
207—208°, brown leaflets, which is insoluble in sodium carbonate, dissolves in sodium hydroxide, and does not give a coloration with ferric chloride. The hydrogen atoms in the group  $\cdot \text{SO}_2 \cdot \text{CH}_2 \cdot \text{CO}$  are very reactive. The present paper deals with the sulphazone dyes obtained by condensing sulphazone with diazonium salts in alkaline solution. Thus diazotised,  $\alpha$ -naphthylamine-5-sulphonic acid yields *5-sulphonaphthalene-1(2')-azosulphazone*,



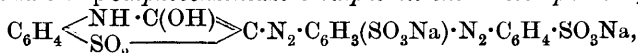
in the form of its *sodium* salt, a dark brown powder, which dyes wool yellow or brownish-yellow, and silk golden-yellow. Diazotised 8-hydroxy- $\beta$ -naphthylamine-6-sulphonic acid yields the *sodium* salt of 8-hydroxy- $\beta$ -sulphonaphthalene-2(2')-azosulphazone,



a brown powder, which dyes wool yellowish-brown, and cotton violet-brown substantively. *Sulphazone-1-azodiphenyl-4'-azosalicylic acid*,



obtained by condensing tetrazotised benzidine with sulphazone and salicylic acid in alkaline solution, is a dark brown, substantive dye, which produces a brilliant golden-orange shade on cotton. The *sodium* salt of *p*-sulphobenzeneazo-3-sulphobenzene-4-azosulphazone,



obtained by condensing diazotised sulphanilic acid with sodium *o*-aminobenzenesulphonate, diazotising the product, and condensing it with sulphazone, is a reddish-brown powder, which dyes wool and silk a fine reddish-orange.

By reactions similar to the preceding, 2:4-dinitrophenyl mercaptan has been converted successively into 2:4-dinitrophenylthiolacetic acid,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 160°, yellowish-brown needles, and 2:4-dinitrophenylsulphoneacetic acid,  $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{SO}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , which has not been obtained pure, but forms a *lead* salt, yellow needles, and readily loses carbon dioxide, yielding 2:4-dinitrophenylmethylsulphone, m. p. 185°. The reduction of the lead salt by tin and hydrochloric acid

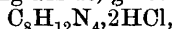
yields 6-aminosulphazone,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{NH} \cdot \text{C} \cdot \text{OH} \\ \text{SO}_2 \cdot \text{CH} \end{smallmatrix}$ , decomp. 280° (*hydrochloride*, brown prisms), which can be easily diazotised and subsequently condensed with amines or phenols, yielding dyes of very varying colour.

C. S.

**Hydantoins. IX. Action of Potassium Thiocyanate on Alanine.** TREAT B. JOHNSON (*J. Biol. Chem.*, 1912, 11, 97—101. Compare Johnson and Nicolet, this vol., i, 53; Komatsu, *Abstr.*, 1911, i, 683).—Alanine reacts smoothly with potassium thiocyanate in

the presence of acetic anhydride, forming *2-thiol-3-acetyl-4-methylhydantoin*,  $\text{CS} \begin{smallmatrix} \text{NH}-\text{CO} \\ \text{NAc} \cdot \text{CHMe} \end{smallmatrix}$ ; no evidence of the formation of a thiohydantoic acid as described by Komatsu (*loc. cit.*) was obtained. The same acetylthiolhydantoin was formed from acetylalanine; on digestion with hydrochloric acid it is converted quantitatively into *2-thiol-4-methylhydantoin* (Wheeler, Nicolet, and Johnson, *Abstr.*, 1911, i, 1031). Like the thiopolypeptides, the new thiolhydantoin contains the thioamide group,  $-\text{CS} \cdot \text{NH}-$ , which is probably active in the natural synthesis of sulphur proteins from simpler substances. *2-Thiol-3-acetyl-4-methylhydantoin* crystallises in stout prisms, m. p.  $166^\circ$ .  
E. F. A.

**Derivatives of Piperazine.** ANTOINE P. N. FRANCHIMONT and E. KRAMER (*Rev. trav. chim.*, 1912, 31, 40—75. Compare *Abstr.*, 1907, i, 395; 1909, i, 327; 1910, i, 139).—An amplification of a previous paper (compare *Abstr.*, 1910, i, 139). Piperazinediacetonitrile, like the corresponding amide, gives a compound,



with hydrochloric acid, which decomposes above  $200^\circ$ . Methyl piperazinediacetate monomethiodide, when shaken with silver hydroxide in methyl alcohol, gives a betaine compound, m. p.  $235^\circ$ , to which the formula  $\text{CO} \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix} \text{NMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{N} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$  has been assigned.

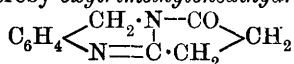
Contrary to the statement in the previous paper (*loc. cit.*), the authors now find that piperazinediformonitrile is not reduced to piperazinedimethylenediamine, and consequently they have not, as yet, succeeded in isolating the latter compound. The only products of reduction were piperazine and ammonia. By warming a mixture of the formonitrile and aniline hydrochloride to  $230\text{--}250^\circ$ , *piperazinediphenylamidine*,  $\text{NPh} \cdot \text{C}(\text{NH}_2) \cdot \text{N} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{N} \cdot \text{C}(\text{NH}_2) \cdot \text{NPh}$ , is obtained in glistening plates, m. p.  $221\text{--}222^\circ$ . It yields a crystalline *hydrochloride*, a *platinichloride*, a *mercurichloride*,  $\text{C}_{18}\text{H}_{22}\text{N}_6 \cdot \text{HgCl}_2 \cdot 2\text{HCl}$ , and a *picrate*, m. p.  $235^\circ$ . Reduction of the amidine only gives piperazine, aniline, and ammonia.  
W. G.

**Buchner's Pyrazolinecarboxylic Acid.** AUGUST DARAPSKY (*Ber.*, 1912, 45, 797—799).—Polemical (compare Bülow, this vol., i, 134, 316; Buchner, this vol., i, 213). Bülow's azine formula is not accepted, and Buchner's original view that the condensation products of aliphatic diazo-compounds with ethylene compounds are to be formulated as pyrazolinecarboxylic acids is upheld.  
E. F. A.

**Reduction of Acyl Derivatives of *o*-Nitrobenzylamine.** SIEGMUND GABRIEL (*Ber.*, 1912, 45, 713—725).—The reduction of formylated derivatives of *o*-nitrobenzylamine or of *o*-nitrobenzylalkyl (aryl) amines leads to the formation of dihydroquinazolines instead of the corresponding amino-derivatives (Paal and Busch, *Abstr.*, 1890, 71; Paal and Krecke, *Abstr.*, 1890, 1443; 1892, 80; Gabriel and Jansen,

1890, 1442; 1892, 217). If, however, the formyl group is replaced by the acetyl or benzoyl group, the corresponding amino-derivative is formed, and may then undergo further transformation; thus, Widman (Abstr., 1893, i, 438) has shown that *o*-nitrobenzylacetanilide on reduction yields *o*-aminobenzylaniline, *o*-acetylaminobenzylaniline, and phenylmethyldihydroquinazoline. The present investigation deals with the reduction of derivatives of *o*-nitrobenzylamine, in which both the aminohydrogen atoms are replaced by a bivalent acyl group. They are found in this respect to resemble the formyl compounds.

*o*-Nitrobenzylsuccinimide was reduced by stannous chloride and hydrochloric acid, whereby *oxytrimethylenedihydroquinazoline*,



(m. p. 183—184°), was obtained. This can be distilled under diminished pressure, dissolves readily in acid, and is precipitated as a *hydrochloride* by excess of hydrochloric acid. It yields a crystalline *aurichloride*, *platinichloride*, and *chromate*. Its *stannichloride* and *hydriodide* were analysed.

When warmed with barium hydroxide, the base yields *barium dihydroquinazolinepropionate*,  $(\text{C}_{11}\text{H}_{11}\text{N}_2\text{O}_2)_2\text{Ba} + \text{H}_2\text{O}$ . From this salt *dihydroquinazolinepropionic acid* was obtained, which becomes discoloured at 205°, and has m. p. 221—223° (decomp.). When distilled in a vacuum it re-forms the base,  $\text{C}_{11}\text{H}_{10}\text{ON}_2$ . The *hydrochloride* of the acid softens at 200—202°, and becomes black at 240°. When an alkaline solution of the acid is oxidised with potassium ferricyanide, *quinazolinepropionic acid*, m. p. 215—217° (decomp.), after becoming discoloured at 200°, is obtained.

*o*-Benzoylenedihydroquinazoline,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \cdot \text{N} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{N} = \text{C} \cdot \text{C}_6\text{H}_4 \end{array}$ , was obtained by the reduction of *o*-nitrobenzylphthalimide dissolved in glacial acetic acid with stannous chloride and hydrochloric acid. It has m. p. 182—183°, dissolves in dilute acid, and gives a precipitate of the *hydrochloride* when treated with concentrated hydrochloric acid. Its *stannichloride* was analysed. After treatment of the base with alkali (compare above), the *hydrochloride*,  $\text{C}_{15}\text{H}_{12}\text{O}_2\text{N}_2 \cdot \text{HCl}$ , decomposing from 220° onwards, and the *barium salt* ( $+ 2\text{H}_2\text{O}$ ) of dihydroquinazolinebenzoic acid were obtained. The free acid could not be isolated, owing to the ease with which it loses water and forms *o*-benzoylenedihydroquinazoline. On oxidation of its alkaline solution by means of potassium ferricyanide, *quinazolinebenzoic acid*, m. p. 208—209°, was obtained.

*o*-Benzylenedihydroquinazoline,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{CH}_2 \cdot \text{N} \cdot \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{N} = \text{C} \cdot \text{C}_6\text{H}_4 \end{array}$ , was obtained by reducing *o*-nitrobenzylphthalimide dissolved in glacial acetic acid with tin and hydrochloric acid at the temperature of the boiling water-bath. Its m. p. depends somewhat on the rate of heating. It becomes red at 130°, softens at 155°, and melts at 162—164°. Its *hydrochloride* and *platinichloride* were analysed.

Reduction of dihydroquinazolinebenzoic acid in alkaline solution by means of sodium amalgam yields *tetrahydroquinazolinebenzoic acid*,

$\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{NH} \\ \text{NH} \cdot \text{CH} \end{smallmatrix} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H} + \text{H}_2\text{O}$ , which softens at  $137-140^\circ$ , and has m. p.  $205-206^\circ$ . When heated at  $100^\circ$ , the acid slowly loses

$2\text{H}_2\text{O}$ , yielding *benzoylenetetrahydroquinazoline*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{N} \cdot \text{CO} \\ \text{NH} \cdot \text{CH} \end{smallmatrix} \cdot \text{C}_6\text{H}_4$ .

The same substance, m. p.  $216-218^\circ$ , is obtained when the tetrahydro-acid is distilled in a vacuum. Further reduction of this substance takes place when it is boiled with hydriodic acid, whereby a new base,  $\text{C}_{15}\text{H}_{14}\text{ON}_2$ , m. p.  $153-154^\circ$ , is obtained. Its *hydrochloride*, *hydriodide*, and *platinichloride* ( $+3\text{H}_2\text{O}$ ) were examined. The base is regarded

as *o*-aminobenzylphthalimidine,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{N} \cdot \text{CH}_2 \\ \text{NH}_2 \cdot \text{CO} \end{smallmatrix} \cdot \text{C}_6\text{H}_4$ , and this view is

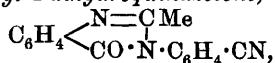
confirmed by its conversion, by heating with hydriodic acid or fuming hydrochloric acid at  $165-170^\circ$ , into benzylenedihydroquinazoline. The presence of the amino-group was established by its conversion into *o*-phthaliminobenzylphthalimidine, m. p.  $204-205^\circ$ . By the action of nitrous acid, the amino-group was replaced by hydroxyl with the formation of *o*-hydroxybenzylphthalimidine. For comparison the latter substance was prepared by the reduction of *salicylphthalimide* (m. p.  $175-176^\circ$ , obtained by heating *o*-hydroxybenzylamine with phthalic anhydride). The synthetic product softened at  $155^\circ$ , had m. p.  $159-160^\circ$ , and when mixed with the above product showed no change in m. p.

H. W.

**Dihydroquinazolines. XXIX. Further Study of the Stilbazoles, Hydrazones, and Schiff Bases of the 4-Dihydroquinazolone Group.** MARSTON T. BOGERT and GEORGE DENTON BEAL (*J. Amer. Chem. Soc.*, 1912, 34, 516-524. Compare Bogert, Beal, and Amend, *Abstr.*, 1911, i, 162).—In the condensation of quinazolones with aldehydes, the alkines are either not produced under the conditions of the experiments, or are so unstable as to lose water immediately with formation of the stilbazole. The stilbazoles derived from 4-quinazolones differ from many other stilbazoles in not being easily reduced. 2-Styryl-4-dihydroquinazolone appears to be reduced to some extent by hydriodic acid and amorphous phosphorus, but a pure hydro-compound could not be isolated. Bromine reacts with the same quinazolone with formation of bromo-derivatives instead of an additive compound.

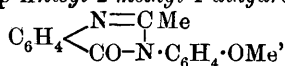
The styrylquinazolones are generally pale yellow or nearly colourless, and crystallise in fluffy masses of short, silky needles.

The following dihydroquinazolones have been prepared. 3-*p*-Cyanophenyl-2-methyl-4-dihydroquinazolone,



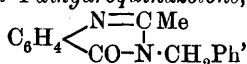
m. p.  $240^\circ$  (corr.), from *p*-aminobenzonitrile and acetylanthranil, forms faintly pink prisms, and when hydrolysed with potassium hydroxide is converted into the corresponding acid, m. p.  $259^\circ$  (uncorr.), which crystallises in short, yellow needles; the *ethyl* ester has m. p.

172—173° (corr.). 3-*p*-Anisyl-2-methyl-4-dihydroquinazoline,



m. p. 170° (corr.), from *p*-anisidine and acetylanthranil, forms colourless, hexagonal prisms. 3-*p*-Phenetyl-2-methyl-4-dihydroquinazoline,

m. p. 148° (corr.), yields a *sulphonic acid*, not melting below 300°, the *sodium salt* of which forms a grey powder, and does not melt below 300°. 3-Benzyl-2-methyl-4-dihydroquinazoline,

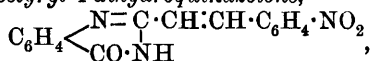


m. p. 123° (corr.), from benzylamine and acetylanthranil, crystallises in colourless flakes.

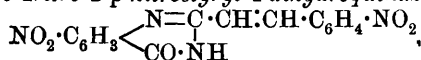
By condensing the respective aldehydes with 2-methyl-4-dihydroquinazolones, which do not contain a primary amino-group, the following simple styryldihydroquinazolones have been obtained. The *hydrochloride* of 2-styryl-4-dihydroquinazoline (*loc. cit.*) has m. p. 310° (decomp.).

6-Nitro-2-styryl-4-dihydroquinazoline,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{array}{l} \text{N}=\text{C} \cdot \text{CH} : \text{CH} \text{ Ph} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{NH} \end{array}$ ,

m. p. 323.5° (uncorr.), obtained either by nitrating 2-styryl-4-dihydroquinazoline with fuming nitric acid, or by condensing benzaldehyde with 6-nitro-2-methyl-4-dihydroquinazoline, forms short, yellow needles. 2-*o*-Nitrostyryl-4-dihydroquinazoline,



has m. p. 300° (uncorr.), and 2-*p*-nitrostyryl-4-dihydroquinazoline, m. p. 350° (uncorr.). 6-Nitro-2-*p*-nitrostyryl-4-dihydroquinazoline,

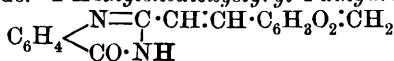


m. p. 335° (uncorr.), was obtained as an orange-yellow solid by the action of a mixture of fuming nitric acid and sulphuric acid on 2-styryl-4-dihydroquinazoline. *Bromo-2-styryl-4-dihydroquinazoline* decomposes at about 345°, and the *dibromo-derivative* does not melt below 300°. 2-Styryl-3-methyl-4-dihydroquinazoline (*loc. cit.*) can be prepared by the action of methyl iodide on 2-styryl-4-dihydroquinazoline in presence of potassium hydroxide. 2-Styryl-3-ethyl-4-dihydroquinazoline, from 2-methyl-3-ethyl-4-dihydroquinazoline and benzaldehyde, has m. p. 125° (corr.). 3-Phenyl-2-styryl-4-dihydroquinazoline, from 3-phenyl-2-methyl-4-dihydroquinazoline and benzaldehyde, has m. p. 201° (corr.). The following compounds were obtained in a similar manner. 3-*p*-Tolyl-2-styryl-4-dihydroquinazoline, m. p. 197° (corr.), and the corresponding 3-benzyl derivative, m. p. 142° (corr.), 3-*p*-anisyl derivative, m. p. 223° (corr.), 3-*p*-phenetyl derivative, m. p. 204° (corr.), 3- $\alpha$ -naphthyl derivative, m. p. 187° (uncorr.), 3- $\beta$ -naphthyl derivative, m. p. 240° (uncorr.), and 3-anilino-derivative, m. p. 217° (uncorr.). 3-Phenyl-2-*o*-hydroxy-

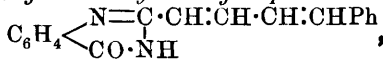
styryl-4-dihydroquinazoline,  $\text{C}_6\text{H}_4 \begin{array}{l} \text{N}=\text{C} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH} \\ \diagup \quad \diagdown \\ \text{CO} \cdot \text{NPh} \end{array}$ , m. p.

270° (uncorr.), was obtained from 3-phenyl-2-methyl-4-dihydroquinazoline

and salicylaldehyde. 2-Methylenedioxystryryl-4-dihydroquinazolone,



m. p. 305° (uncorr.), from 2-methyl-4-dihydroquinazolone and piperonaldehyde, and 2-phenylbutadienyl-4-dihydroquinazolone,



m. p. 257—258° (uncorr.), from cinnamaldehyde and 2-methyl-4-dihydroquinazolone, are also described.

The following compounds were prepared by the condensation of aldehydes with amino-2-methyl-4-dihydroquinazolones. 3-Acetylamino-2-stryryl-4-dihydroquinazolone, m. p. 259° (uncorr.), was obtained both by the action of acetic anhydride on 3-amino-2-stryryl-4-dihydroquinazolone and by the condensation of 3-acetylamino-2-methyl-4-dihydroquinazolone with benzaldehyde. Attempts to effect the condensation of 3-amino-2-methyl-4-dihydroquinazolone with citral, furfuraldehyde, and glyoxal were not successful. On boiling an alcoholic solution of 3-amino-2-methyl-4-quinazolone and benzil, a

substance, probably  $\text{C}_6\text{H}_4 \begin{array}{c} \text{N}=\text{C} \cdot \text{CH} : \text{CPh} \\ | \\ \text{CO} \cdot \text{N} - \text{N} : \text{CPh} \end{array}$ , m. p. about 292° (decomp.), separates as a yellow, granular solid. When 2-amino-4-dihydroquinazolone is heated with benzaldehyde at 180°, condensation does not take place.

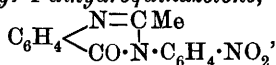
An attempt to effect the condensation of 2-methyl-4-dihydroquinazolone with ethyl oxalate in presence of sodium ethoxide did not meet with success.

E. G.

Dihydroquinazolines. XXX. Study of the Bromination and Nitration of 4-Dihydroquinazolones, the Corresponding Aminoquinazolones, and Certain Other New 4-Dihydroquinazolones. MARSTON T. BOGERT and GEORGE AUGUSTUS GEIGER (*J. Amer. Chem. Soc.*, 1912, 34, 524—534).—The 4-dihydroquinazolones are not easily brominated, but bromo-derivatives of 4-dihydroquinazolone and 2-methyl-4-dihydroquinazolone have been obtained by the Juvalta process (D.R.-P. 50177). Nitration is also difficult to effect, but by using a mixture of fuming nitric acid and concentrated sulphuric acid at a high temperature, one nitro-group can be introduced into the 4-quinazolone nucleus.

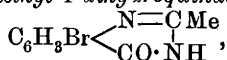
3-Methyl-4-dihydroquinazolone was first prepared by Knape (Abstr., 1891, 909), who assigned to it the m. p. 71°. It has now been found that this m. p. is that of the form containing 1H<sub>2</sub>O, but that the anhydrous compound has m. p. 105° (corr.). 2:3-Dimethyl-4-dihydroquinazolone also crystallises with 1H<sub>2</sub>O; the m. p.'s of the anhydrous and hydrated forms are 107—109° and 70° respectively. 3-Ethyl-4-

dihydroquinazolone,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{N}=\text{CH} \\ | \\ \text{CO} \cdot \text{NEt} \end{array}$ , m. p. 102° (corr.), b. p. 182°/15 mm., prepared by the action of ethyl iodide on 4-quinazolone in presence of alcohol and potassium hydroxide, crystallises in colourless needles. 2-Benzyl-4-dihydroquinazolone has m. p. 116° (corr.).

3-*p*-Nitrophenyl-2-methyl-4-dihydroquinazolone,

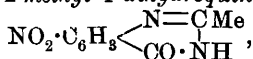
m. p. 193° (corr.), from acetylanthranil and *p*-nitroaniline, forms pale yellow, lustrous scales. 3-*p*-Tolyl-2-methyl-4-dihydroquinazolone has m. p. 151° (corr.), and the corresponding 3- $\alpha$ -naphthyl and 3- $\beta$ -naphthyl compounds melt at 136° (corr.) and 175° (corr.) respectively.

Bromo-4-dihydroquinazolone,  $\text{C}_6\text{H}_3\text{Br} \begin{array}{l} \text{N}=\text{CH} \\ \diagup \\ \text{CO} \cdot \text{NH} \end{array}$ , has m. p. 258° (uncorr.), and bromo-2-methyl-4-dihydroquinazolone,



m. p. 277° (uncorr.).

Nitro-4-dihydroquinazolone,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{array}{l} \text{N}=\text{CH} \\ \diagup \\ \text{CO} \cdot \text{NH} \end{array}$ , m. p. 284° (decomp.), forms silky, yellow plates; the nitro-group is probably in the 6-position. 6-Nitro-2-methyl-4-dihydroquinazolone,



m. p. 299° (decomp.), obtained by the nitration of 2-methyl-4-quinazolone, crystallises in pale yellow needles. Nitro-3-methyl-4-

dihydroquinazolone,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{array}{l} \text{N}=\text{CH} \\ \diagup \\ \text{CO} \cdot \text{N Me} \end{array}$ , m. p. 196° (corr.), can be

prepared either by the methylation of nitro-4-dihydroquinazolone or by the nitration of 3-methyl-4-dihydroquinazolone. The corresponding 3-ethyl compound has m. p. 165° (corr.). By the nitration of 2-methyl-3-ethyl-4-dihydroquinazolone, the 6-nitro-derivative was obtained of the same m. p. as that prepared by Bogert and Cook (Abstr., 1906, i, 988) by the action of ethylamine on 5-nitroacetylanthranil. Dinitro-3-phenyl-2-methyl-4-dihydroquinazolone, m. p. 267° (uncorr.), obtained by the nitration of 3-phenyl-2-methyl-4-dihydroquinazolone, is probably the 6-nitro-3-*o*-nitrophenyl compound. Nitro-3-*p*-nitrophenyl-2-methyl-4-dihydroquinazolone has m. p. 264° (decomp.). Dinitro-3-*p*-tolyl-2-methyl-4-dihydroquinazolone has m. p. 275° (decomp.).

The following amino-compounds were obtained by reducing the corresponding nitro-compounds with stannous chloride and hydrochloric acid. Amino-4-dihydroquinazolone,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{array}{l} \text{N}=\text{CH} \\ \diagup \\ \text{CO} \cdot \text{NH} \end{array}$ , m. p. 318° (corr.), which yields an acetyl derivative, m. p. 335° (corr.). 6-Amino-2-methyl-4-dihydroquinazolone, m. p. 314–315° (corr.), identical with the compound prepared from 2:5-diacetylaminobenzoic acid (Bogert, Amend, and Chambers, Abstr., 1910, i, 895). Amino-3-

methyl-4-dihydroquinazolone,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \begin{array}{l} \text{N}=\text{CH} \\ \diagup \\ \text{CO} \cdot \text{N Me} \end{array}$ , m. p. 209° (uncorr.), which yields an acetyl derivative, m. p. 269° (uncorr.). 6-Amino-2:3-dimethyl-4-dihydroquinazolone, m. p. 244° (uncorr.). 6-Amino-2-methyl-3-ethyl-4-dihydroquinazolone, m. p. 185° (corr.).

2-Methyl-4-dihydroquinazolone is not appreciably affected when heated for six hours with concentrated hydrochloric acid at 155°,

slight decomposition occurs at  $190^{\circ}$ , and at  $250^{\circ}$  it is completely decomposed into aniline, ammonia, and carbon dioxide. An attempt to prepare 4-chloro-2-methylquinazoline by the action of benzoyl chloride on 2-methyl-4-dihydroquinazolone (2-methyl-4-hydroxyquinazoline) was not successful.

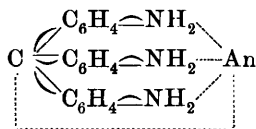
E. G.

**Indigotindisulphonic Acid, Atmospheric Oxygen and Hydroxyl Ions.** M. TSCHILIKIN and W. MILANOWSKY (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 359—373).—According to Friedländer's investigations on the action of alkali on indigotin, the principal products of the reaction are indoxyl-2-aldehyde and anthranilic acid, the chrysanic acid formed being the result of a secondary condensation of these two products; these results were confirmed by similar experiments on "thioindigo" (*Ber.*, 1877, 10, 1971).

The authors have investigated the action of alkali hydroxide on indigotindisulphonic acid, in which the blue colour of the latter is destroyed. They find that the action of the alkali is mainly a catalytic effect of the hydroxyl ions, and that the reaction depends also on the presence of atmospheric oxygen and is of an order varying with the number of molecules of oxygen available. When the concentration of atmospheric oxygen dissolved in the solution is kept constant, the reaction is unimolecular. These results are not in agreement with the scheme of the reaction given by Friedländer.

T. H. P.

**Constitution of Triphenylmethane Dyes.** HUGO KAUFFMANN (*Ber.*, 1912, 45, 781—786).—The author points out objections to the quinonoid representation of the constitution of the triphenylmethane-



dyes, and emphasises the advantages of his formulæ, which are based on the auxochromic theory and the theory of the divisibility of the valency bond. Pararosaniline, for example, is represented by the annexed formula, in which An denotes a univalent anion and the dotted lines denote the divisions of the valency bond of the univalent anion. The total affinity represented by the dotted lines corresponds with one valency unit.

C. S.

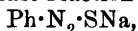
**Precipitate Produced by Mercuric Acetate from Molasses. Isolation of Adenine.** STOLTZENBERG (*Zeitsch. Ver. deut. Zuckerind.*, 1912, 318—322).—After clarifying molasses with lead acetate the precipitate produced by mercuric acetate does not contain any substance of high optical rotatory power in neutral solution. Lævorotatory substances could not be detected; some constituents of the precipitate were dextrorotatory in solution in hydrochloric acid. The precipitate contains at least two acids and two bases, but aspartic acid is not present. The chief product is adenine.

E. F. A.

**The Action of Arsenites and Cyanide-Sulphides on Diazo-compounds.** AUGUST GUTMANN (*Ber.*, 1912, 45, 821—832. Compare *Abstr.*, 1898, ii, 570; 1907, i, 671; 1908, i, 497, 597, 972; 1909, i, 128, 144, 895).—From his earlier results on the addition of oxygen

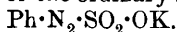
or sulphur to an alkali arsenite or to a mixture of alkali cyanide and sulphide, from thiosulphates, thiosulphonates, alkyl nitrates, etc., the author is of opinion that the reactive oxygen, sulphur, or chlorine atom is present in a special form of a higher valency than the usual. Similar active atoms are found in some of the diazo-compounds.

Sodium arsenite solution is oxidised to arsenate by both benzene-diazonium chloride solution and sodium benzene-*n*-diazoxide solution, whilst the latter also oxidises a mixture of potassium cyanide and sodium sulphide to thiocyanate; benzene and nitrogen are also formed in each reaction, but in the last reaction a thiodiazo-compound,

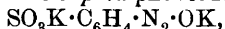


is probably an intermediate product (compare Hantzsch and Freese, Abstr., 1905, i, 24). Solutions of *p*-nitrobenzenediazonium chloride and of potassium *p*-nitrobenzene-*n*-diazoxide likewise reacted with sodium arsenite, but the reaction was far from quantitative. Potassium benzene *isodiazoxide*, potassium *p*-nitrobenzene *isodiazoxide*, azoxybenzene, *p*-hydroxyazobenzene, diazoaminobenzene, azobenzene, nitrosodimethylaniline, nitrosophenol, and phenylnitrosoamine were stable towards sodium arsenite.

A suspension of the labile potassium benzenediazosulphonate (Bamberger, Abstr., 1905, i, 25) reacted with sodium arsenite and with the cyanide-sulphide mixture, whereas the stable isomeride did not react either in acid or alkaline solution. Sodium benzene-*n*-diazoxide was unaffected by sodium sulphite solution, but benzenediazonium chloride solution treated with barium chloride and sulphur dioxide caused precipitation of barium sulphate. It is suggested that the labile diazosulphonate may be formulated  $\text{Ph}\cdot\text{N}_2\cdot\text{O}\cdot\text{SO}_2\text{K}$ , whilst the stable isomeride may be of the ordinary sulphonate structure



The di-potassium derivative of *p*-sulphobenzenediazohydroxide,



oxidises arsenite to arsenate and the cyanide-sulphide reagent to thiocyanate. The final products of reaction are nitrogen and a salt of benzenesulphonic acid, but in the reaction with cyanide-sulphides, a salt of *p*-sulphobenzenediazonium hydrosulphide,  $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{SH}$ , is probably an intermediate step (compare Klason, Abstr., 1887, 478).

Diazobenzene perbromide and diazobenzeneimide oxidise both the above reagents, the main organic products being bromobenzene and aniline respectively. Hydrazoic acid does not show similar oxidising power.

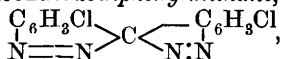
Nitrosoacetanilide and benzoylphenylnitrosoamine both act as oxidising agents towards the two reagents used, and it is therefore suggested that their structure is similar to that of the labile diazo-oxides and should be written  $\text{R}\cdot\text{N}:\text{N}\cdot\text{OAc}$ .

D. F. T.

**endo-Azo-compounds.** HENRI DUVAL (*Compt. rend.*, 1912, 154, 780—781. Compare Abstr., 1907, i, 663; 1908, i, 706).—The only *oo*-diamino-derivatives of diphenylmethane hitherto known to form *endo*-azo-compounds are those with a carbon-containing group in the para-position. It is now found that other electronegative radicles

confer the power of forming these substances, and that the presence of one amino-group is sufficient to admit of their formation.

4 : 4-Dichloro-2 : 2-bisendoazodiphenylmethane,



prepared by diazotising dichlorodiaminodiphenylmethane and heating to  $80^\circ$ , separates from pyridine in orange crystals, decomposing at about  $300^\circ$ .

When *o*-acetylaminodiphenylmethane is treated at  $5^\circ$  with sulphuric and fuming nitric acids, two nitro-derivatives are formed and may be separated by alcohol. *Dinitro-o*-acetylaminodiphenylmethane has m. p.  $265^\circ$ , whilst the *trinitro*-derivative has m. p.  $213^\circ$ . Hydrolysis followed by diazotisation converts these substances into *dinitro-o*-endoazodiphenylmethane,  $(\text{NO}_2)_2\text{C}_{12}\text{H}_7\text{N}=\text{N} > \text{CH}$ , m. p.  $324^\circ$ , and *trinitro-o*-endoazodiphenylmethane, m. p.  $248^\circ$ .

W. O. W.

**Azo-dyes of Substituted Pyrroles.** LEON MARCHLEWSKI (*Zeitsch. physiol. Chem.*, 1912, 77, 247—248).—A reply to Fischer and Bartholomäus (this vol., i, 323). It was shown (Abstr., 1908, i, 710) beyond question that the azo-dye from hæmopyrrole was a diazo-compound. Hæmopyrrole also forms a monoazo-dye with benzene-diazonium chloride crystallising in orange-yellow needles, which in presence of excess of the diazonium salt pass over into the reddish-brown needles of the diazo-compound.

E. F. A.

**Investigations by means of the Dilatometer on the Heat Coagulation and Solution of Albumin.** TULLIO GAYDA (*Biochem. Zeitsch.*, 1912, 39, 400—409).—The thermal expansion of pure albumin is greater than that of water. The volume changes taking place when the temperature is very slowly raised during coagulation are very small. Below the coagulation temperature, the rate of increase of volume change is greater below the clotting temperature, and remains so whilst the clot is forming, giving rise to a slower rate of increase as the albumin reaches the stage of complete coagulation. During the solution of albumin a contraction of volume takes place. This is possibly due to a true solution of the water in the substance of the colloidal particles.

S. B. S.

**Proteins of Liebig's Extract of Meat.** KARL MAYS (*Zeitsch. physiol. Chem.*, 1912, 78, 37—52).—Liebig's extract of meat contains a non-coagulable protein, which closely resembles gluten in its reactions, and has many reactions in common with the albumoses. It yields glycine and proline, but not glutamic acid on hydrolysis. The protein is formed during the cooking of the meat with water at  $80$ — $94^\circ$  in the commercial preparation of the extract.

E. F. A.

**The Action of Various Conditions on Carboxyhæmoglobin.** H. HARTRIDGE (*J. Physiol.*, 1912, 44, 22—33).—Dilution, carbon dioxide, and certain salts have no influence on

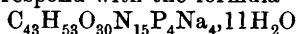
the final saturation of hæmoglobin with carbon monoxide. Light, especially ultra-violet rays, lessens the stability of carboxy-hæmoglobin, and temperature has a marked influence, the change in saturation being about 0.5% for every degree rise. Equilibrium is reached at different saturations by the blood of animals of different species.

W. D. H.

**Heat Coagulation of Hæmoglobin Compounds.** H. HARTRIDGE (*J. Physiol.*, 1912, 44, 34—42).—The results obtained with oxy-hæmoglobin confirm those of Chick and Martin, and apply also to carboxyhæmoglobin. The temperature-coefficient of the latter is 1.18, and so it is comparatively stable. Nitric oxide-hæmoglobin is unstable, and tends to change spontaneously at room temperature into alkaline methæmoglobin; alkaline methæmoglobin has a temperature-coefficient higher than that of oxy- or carboxy-hæmoglobin, being near to that of egg-albumin.

W. D. H.

**Formation of Nucleic Acids from the Thymus Gland.** HERMANN STEUDEL (*Zeitsch. physiol. Chem.*, 1912, 77, 497—507).—Sodium nucleate when dried over sulphuric acid and heated, continues to lose water until it decomposes. Preparations of constant composition containing water of crystallisation, dried by means of absolute alcohol and ether, have been analysed. Those prepared by different workers agree closely, and correspond with the formula



put forward in 1907 (Steuvel, *Abstr.*, 1907, i, 168, 1097), or still better with the formula  $\text{C}_{43}\text{H}_{53}\text{O}_{32}\text{N}_{15}\text{P}_4\text{Na}_4, 11\text{H}_2\text{O}$ , deduced from the products of the quantitative hydrolysis of nucleic acid.

Nucleic acid as a tetrabasic acid is derived from the annexed phosphoric acid skeleton, and the correct formula becomes  $\text{C}_{43}\text{H}_{61}\text{O}_{34}\text{N}_{15}\text{P}_4, 9\text{H}_2\text{O}$ . During drying more water than  $9\text{H}_2\text{O}$  will probably tend to be eliminated.

Thymus-nucleic acid behaves differently from yeast-nucleic acid as regards the formation of vernine (guanosine) on hydrolysis. From thymus-nucleic acid a quantity of guanine corresponding with the inorganic phosphorus liberated is produced. Apparently the hexose is much less firmly united to the alloxuric bases than is the pentose with the purine compounds in yeast-nucleic acid.

E. F. A.

**Tannage by means of Halogens.** L. MEUNIER and ALPHONSE SEYEWETZ (*Bull. Soc. chim.*, 1912, [iv], 11, 344—347).—Lumière and Seyewetz have shown already (*Abstr.*, 1908, i, 710) that gelatin is rendered “insoluble” (tanned) by halogens, and in the present paper the best conditions for accomplishing this are described (compare Cross, Bevan, and Briggs, *Abstr.*, 1908, i, 374).

Gelatin cannot be rendered insoluble with gaseous chlorine, as it undergoes decomposition under these conditions, and the same is true of chlorine water at atmospheric temperatures. Good results are

obtained by macerating gelatin (10 grams) at  $0^{\circ}$  in (1) 500 c.c. of chlorine water, containing 50 grams of sodium chloride, or (2) 100 c.c. of commercial sodium hypochlorite solution, diluted with 400 c.c. of water, and containing 2 c.c. of hydrochloric acid ( $21^{\circ}\text{B}$ ). Under these conditions the gelatin absorbs 9% of chlorine; this can be reduced to 0.3% by washing with 10% sodium hydrogen sulphite solution, and the gelatin remains insoluble after this treatment. Similar results are obtained by using (a) 100 c.c. of bromine water, diluted to 500 c.c. with water and containing 100 grams of sodium chloride, or (b) bromine 3 grams, sodium hydroxide 1.5 grams in 500 c.c. of water. Iodine and hypiodites have no action of this kind on gelatin. Skin may be rapidly tanned by the use of bromine water in presence of sodium chloride, the bromine being subsequently removed by washing with sodium hydrogen sulphite. The action probably consists in the formation of halogenated amino-groups in the protein molecule.

T. A. H.

**Condensation of Tryptophan with Certain Aldehydes.** ANNIE HOMER (*Proc. Camb. Phil. Soc.*, 1912, 16, 405—408).—When tryptophan is kept in contact with moist ether which has been locally heated with a glass rod, a crystalline compound,  $\text{C}_{24}\text{H}_{26}\text{O}_5\text{N}_4$ , of acidic nature, m. p.  $322^{\circ}$ , is obtained.

The compound,  $\text{C}_{12}\text{H}_{12}\text{O}_2\text{N}_2$ , from formaldehyde and tryptophan has m. p.  $235\text{--}240^{\circ}$ ; it is readily hydrolysed by water, dilute acids, and alkalis to form the ether oxidation product above.

Glyoxylic acid reacts with tryptophan to form a crystalline derivative,  $\text{C}_{13}\text{H}_{11}\text{O}_4\text{N}_2$ , m. p.  $322^{\circ}$ . When heated at  $205^{\circ}$ , carbon dioxide is evolved, and the ether oxidation product is obtained.

Formaldehyde is shown to play an important part in the colour reaction of tryptophan with concentrated sulphuric acid, and this rather than glyoxylic acid is the substance essential to the formation of the characteristic violet colour in the Adamkiewicz reaction.

E. F. A.

**Plasteins.** J. HERRMANN and A. CHAIN (*Zeitsch. physiol. Chem.*, 1912, 77, 289).—Plasteins injected into rabbits yield an antiserum which precipitates them. As only proteins act as antigens in the precipitin reaction, this is regarded as a proof of the protein nature of the plasteins. Various plasteins give precipitates with the same antiserum; this is a proof of a similarity in their structure.

W. D. H.

**Nitrosalmine.** E. WECHSLER (*Zeitsch. physiol. Chem.*, 1912, 78, 53—54. Compare Kossel and Kennaway, *Abstr.*, 1911, i, 667; Kossel and Cameron, this vol., i, 326).—Salmine forms a nitro-derivative which on hydrolysis with boiling sulphuric acid is converted into nitroarginine.

E. F. A.

**Activity of the Sucrase of "Aspergillus" in Presence of Different Acids.** GABRIEL BERTRAND, M. ROSENBLATT, and (Mme.) M. ROSENBLATT (*Compt. rend.*, 1912, 154, 837—839).—A tabular statement gives the concentration of different organic and inorganic acids, in the presence of which the sucrase of *Aspergillus niger* shows its maximum

diastatic activity. The conclusions drawn are precisely similar to those set forth in recent communications on the sucrase of yeast (this vol., i, 148, 327). The optimum concentrations of acids for the enzyme from the two sources are very different. W. O. W.

**Diastase.** T. CHRZASZCZ (*Woch. Brauerei*, 1911, 28, 510).—A preliminary note on work which the author has in progress on barley extracts, from which he assumes that diastase consists of two distinct substances that are differently acted on by starch. F. M. G. M.

**The Influence of Lecithin and Lipoids on Diastase.** D. MINAMI (*Biochem. Zeitsch.*, 1912, 39, 355—380).—Lecithin even in very small concentrations in aqueous suspension inhibits the action of diastase. In methyl-alcoholic solution lecithin inhibits the pancreatic and salivary diastase. In the case of serum diastase, the methyl-alcoholic solution was in one case without influence, and in another case it exerted an activating action. The amounts of methyl alcohol alone used in these experiments were without action. The serum alone has, however, an activating tendency, and it was found that a lecithin-serum mixture was less active than the serum alone. The phosphatides of the liver activate diastases; the substances exerting this action are soluble in ether, benzene, and light petroleum. Weak aqueous alcoholic suspensions of the acetone extract of liver inhibited diastatic action. The expressed juice of liver exerts an activating influence, which does not appear to be due to the phosphatides. The activating influence of serum on diastase is very slightly diminished by extracting it with ether. This is, however, due to the ether alone, which remains dissolved in the serum. The phosphatides of egg-yolk act as an activator. This activator is soluble in ether. The author is unable to agree with the statement of Bang that diastatic action depends on the action of lipoids. S. B. S.

**The Influence of Bile on Diastase (Amylase).** D. MINAMI (*Biochem. Zeitsch.*, 1912, 39, 339—354).—The bile by itself has only a small diastatic power, but it can activate amylase. The activator is soluble in water and alcohol, but not in ether; the ethereal extract, on the other hand, exerts an inhibiting influence, both alone and in presence of alcoholic and aqueous extracts. Sodium taurocholate and cholate are without action on diastase in weak solutions and inhibit the action in strong solutions. Sodium glycocholate in two instances exerted a slight activating action on salivary diastase, but acted like the other bile salts on pancreatic diastase. Cholesterol exerted an inhibitory action, especially in presence of lecithin. The action of the bile pigments was also inhibitory. S. B. S.

**Takadiastase.** JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1912, 39, 324—338).—The amylase of taka-diastase is not so sensitive to the action of acids as the amylase of saliva, in that it requires stronger concentrations of acid to produce a corresponding inhibition of its action. It is sensitive to alkalis also, but again this sensitiveness is less than in the case of the salivary amylase. The amylase action of taka-diastase

is accelerated by the presence of many salts in the concentration of  $N/10$ , smaller concentrations having little or no influence. Taka-diastase exerts a tryptic action which is stronger in weak alkaline or neutral solutions than in slightly acid solutions. Sera inhibit the action. It contains a milk-clotting enzyme of chymosin-like character. It contains no peptolytic ferment (action on glycytryptophan), whereas it has a strong ereptic power. This fact is regarded as a proof that the so-called peptolytic and ereptic ferments are not identical. Taka-diastase also contains a lipase, which can hydrolyse neutral fats, monobutyrim, and lecithin, but it is not present in large quantities. It also contains an adrenalase. One gram of the diastase contains as much trypsin as 100 c.c. of human pancreatic juice. S. B. S.

**Quantitative Measurement of Oxydases.** HERBERT H. BUNZEL (*Proc. Amer. Soc. Biol. Chem.*, 1911, xxvi; *J. Biol. Chem.*, 11).—Measurements were made of the oxidising power of potato juice towards a series of aromatic substances. If two or three oxidisable substances were used in the same experiment, the result is not a summation of the individual oxidations when the oxidation by the same juice is measured separately, but corresponds roughly with the result obtained in the case of the most rapidly oxidised substance.

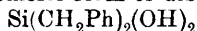
W. D. H.

**The Separation of Peroxydase and Catalase.** A. KASANSKI (*Biochem. Zeitsch.*, 1912, 39, 64—71).—Advantage is taken of the fact that the catalase becomes inactive when treated with pyrogallol. If, for example, the juice from hemp seedlings is treated with pyrogallol in sufficient quantity (2%), a precipitate is formed. Neither the precipitate nor the filtrate contain a catalase, although a peroxydase is present in the latter. Examples are given of the application of the pyrogallol method for the preparation of catalase-free peroxydase from various sources. S. B. S.

**The Mode of Action of Phosphatase.** II. HANS VON EULER and HJ. OHLSEN (*Zeitsch. physiol. Chem.* 1912, 76, 468—477. Compare *Abstr.*, 1911, i, 1051).—When a 20% solution of dextrose, dried yeast extract, and 5% disodium phosphate solution are mixed, no disappearance of the inorganic phosphate takes place as a rule. When, however, the dextrose solution is set to ferment for a few minutes with living yeast, then filtered and boiled before the addition of the dried yeast extract and phosphate, there is a rapid and complete disappearance of inorganic phosphate, which is converted into hexosephosphate. Yeast dried by Lebedeff's process slowly effects the same change without previous fermentation of the dextrose. Thymol acts adversely on the change, but toluene is without effect.

If the preliminary fermentation of the dextrose is prolonged, the rate of esterification becomes very much less. An excess of disodium phosphate also retards esterification. The addition of the sodium salt of the hexosephosphate very markedly accelerates the rate of esterification. It has a similar accelerating effect on the fermentation of dextrose by living yeast, being about ten times as effective as an addition of a like quantity of disodium phosphate. E. F. A.

**Dibenzyl- and Diphenyl-silicols and -silicones.** GEOFFREY MARTIN (*Ber.*, 1912, 45, 403—409. Compare Dilthey and Eduardoff, *Abstr.*, 1904, i, 464; Robison and Kipping, *Trans.*, 1908, 93, 439).—The more easily fusible isomeric form of dibenzyl-silicol,



(m. p. 74°), is convertible into the other (m. p. 101°) by the action of aqueous potassium hydroxide on the solution in methyl or ethyl alcohol, and subsequent precipitation by acetic acid.

If dibenzylsilicol (m. p. 101°) is treated with water in a closed vessel at 100°, or a solution in aqueous potassium hydroxide exposed to the air, a white, amorphous dibenzylsilicone,  $\text{SiO}(\text{CH}_2\text{Ph})_2$ , is obtained. A different form of this substance is obtained by exposing to the air the gummy mass obtained by the action of dilute ammonia on dibenzylsilicon chloride; the product is a white mass, m. p. approx. 200°.

Diphenylsilicol,  $\text{SiPh}_2(\text{OH})_2$ , obtained by the action of dilute ammonia solution on diphenylsilicon chloride, is a white, crystalline substance, m. p. varying in different specimens from 140° to 160°; a specimen of m. p. 160° dissolved in dilute potassium hydroxide solution and reprecipitated by acid gave a product m. p. approx. 144°, probably identical with that obtained by Dilthey (*loc. cit.*); when this is dissolved in a little methyl alcohol and warmed with a large excess of potassium hydroxide, the precipitate obtained on acidifying consists of the original form (m. p. 160°). Both these forms of diphenylsilicol when heated alone, or when left in contact with dilute hydrochloric acid, give a pasty, amorphous silicone; when heated with acetic anhydride, this is converted into a crystalline silicone, m. p. 188°, probably identical with that obtained by Dilthey. By dissolving either form of diphenylsilicol in glacial acetic acid and afterwards reprecipitating by water, an amorphous substance is produced, which, after purification, has m. p. 111°.

The author confirms Dilthey's statement as to the existence of two forms of termolecular diphenylsilicone, and in addition has obtained small quantities of two other crystalline substances, m. p. 125° and 186° respectively. Another form of diphenylsilicone (m. p. above 360°) was obtained: (a) by the prolonged action of methyl-alcoholic potash on diphenylsilicol, previously heated to 140°; (b) by warming diphenylsilicol with potassium hydroxide solution for several hours at 100°.

*Phenylbenzylsilicon chloride*,  $\text{SiPh}(\text{CH}_2\text{Ph})\text{Cl}_2$ , obtained by the action of magnesium phenyl bromide on benzylsilicon trichloride, is a colourless liquid, b. p. 240—250°/100 mm.; on treatment with dilute ammonia solution it gives a white solid, which, when placed in contact with potassium hydroxide solution, dissolves partly; the solution on acidifying precipitates *phenylbenzylsilicol*, m. p. 104°, after repeated recrystallisation.

D. F. T.

## Organic Chemistry.

**$\gamma$ -Ethylhexane.** LATHAM CLARKE and EMILE RAYMOND RIEGEL (*J. Amer. Chem. Soc.*, 1912, **34**, 674—679).—In continuation of a study of the paraffin hydrocarbons (this vol., i, 150, and earlier abstracts), the synthesis of  $\gamma$ -ethylhexane has been effected.

$\gamma$ -Ethylhexan- $\gamma$ -ol,  $\text{CH}_2\text{Me}\cdot\text{CEt}(\text{OH})\cdot\text{CH}_2\cdot\text{CH}_2\text{Me}$ , b. p. 155—159°/756 mm., prepared by the action of magnesium propyl iodide on diethyl ketone, has an odour resembling that of musty apples. On treating this compound with iodine and amorphous phosphorus,  $\gamma$ -iodo- $\gamma$ -ethylhexane,  $\text{CH}_2\text{Me}\cdot\text{CEtI}\cdot\text{CH}_2\cdot\text{CH}_2\text{Me}$ , is produced, which is converted by alcoholic potassium hydroxide into  $\gamma$ -ethyl- $\Delta^2$ -hexene,  $\text{CHMe}\cdot\text{CEt}\cdot\text{CH}_2\cdot\text{CH}_2\text{Me}$ , b. p. 119.6—120.5°/769 mm., a liquid with a strong odour. When the latter compound is passed over freshly reduced nickel at 160—180° in a current of hydrogen,  $\gamma$ -ethylhexane,  $\text{CH}_2\text{Me}\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{CH}_2\text{Me}$ , b. p. 118.8—119°/766 mm.,  $D_{15}^{25}$  0.7175,  $n_D^{25}$  1.3993, is obtained as a colourless, very mobile, almost odourless liquid.

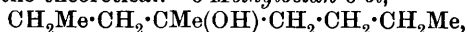
A second method was devised for the synthesis of the hydrocarbon which involved the preparation of ethyl ethylpropylacetoacetate and its hydrolysis with formation of  $\gamma$ -ethylhexan- $\beta$ -one, the reduction of the latter into  $\gamma$ -ethylhexan- $\beta$ -ol, and the conversion of this into the corresponding carbonyl iodide. The iodide on treatment with alcoholic potassium hydroxide should yield  $\gamma$ -ethyl- $\beta$ -hexene, which would then be reduced to  $\gamma$ -ethylhexane. The method was not carried out completely, however, owing to the difficulty of obtaining a sufficient quantity of  $\gamma$ -ethylhexan- $\beta$ -one.

$\gamma$ -Ethylhexan- $\beta$ -one,  $\text{CH}_3\cdot\text{CO}\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{CH}_2\text{Me}$ , b. p. 157.5—158.5°/761 mm., is a liquid with a peppermint-like odour, and on reduction is converted into  $\gamma$ -ethylhexan- $\beta$ -ol,  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CHEt}\cdot\text{CH}_2\cdot\text{CH}_2\text{Me}$ , b. p. 167.5—168.5°/760 mm., which has an odour resembling that of musty apples.

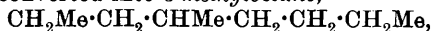
E. G.

**$\delta$ -Methyloctane.** LATHAM CLARKE (*J. Amer. Chem. Soc.*, 1912, **34**, 680—683).—In earlier papers (this vol., i, 150), the synthesis of two nonanes, namely,  $\beta\delta$ - and  $\beta\epsilon$ -dimethylheptanes, has been described. An account is now given of the synthesis of  $\delta$ -methyloctane.

When methyl butyl ketone is treated with magnesium propyl iodide,  $\delta$ -methyloctan- $\delta$ -ol and  $\delta$ -methyleneoctane are produced in proportions depending on the conditions of the experiment. A method is described by which the methyleneoctane can be obtained in a yield of about 80% of the theoretical.  $\delta$ -Methyloctan- $\delta$ -ol,



b. p. 178—183°, is a colourless, oily liquid, with a sweet aromatic odour.  $\delta$ -Methyleneoctane,  $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_2)\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\text{Me}$ , b. p. 142—144°/768 mm., is a liquid with a faint, sweet odour; when passed over freshly reduced nickel at 160—180° in a current of hydrogen, it is converted into  $\delta$ -methyloctane,



b. p. 141.7—141.9°/771 mm.,  $D_{15}^{25}$  0.7320,  $n_D^{25}$  1.4027, which is a colourless, almost odourless, very mobile liquid. E. G.

**Preparation of Isoprene.** CARL HARRIES (D.R.-P. 243075 and 243076).—Isoprene having a refractive index of  $52^{\circ}15'$ — $52^{\circ}50'$  and suitable for the preparation of caoutchouc is produced when the dihalogen or halogen-hydrin derivatives of isopentane are slowly dropped on to soda-lime (or other basic oxides) at a temperature of about 600°. The following substances may be employed for this reaction: amylene dichloride,  $\text{CMe}_2\text{Cl}\cdot\text{CHMeCl}$ , or the corresponding dibromide; amylene chlorohydrin,  $\text{OH}\cdot\text{CMe}_2\cdot\text{CHMeCl}$ ; the bromohydrin or other allied crude substances obtainable from amylene,  $\text{CMe}_2\cdot\text{CHMe}$ , by halogenation. The yield of isoprene from the bromides is 50—60%, that from the chlorides 30—40% of the theory.

The second patent states that  $\alpha\delta$ -dibromo- $\beta$ -methylbutane,  $\text{CH}_2\text{Br}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$ , and dichloroisopentane,  $\text{CH}_2\text{Cl}\cdot\text{CMeCl}\cdot\text{CH}_2\text{Me}$ , can also be employed in the above reaction, that their vapour can be drawn over the strongly heated oxide, and that this may be replaced by a carbonate or other halogen eliminating agent. F. M. G. M.

**The Function of the Sulphhydryl Group in the Decomposition of Iodoform in the Animal Organism.** TORSTEN THUNBERG (*Skand. Arch. Physiol.*, 1911, 25, 343—346).—When cysteine hydrochloride or thiolactic acid is heated at 37° with a suspension of iodoform in gum arabic solution, iodine is liberated and may be detected after a few hours. The action is attributed to the sulphhydryl (SH) group, and attention is drawn to the probability that this group takes part in the decomposition of iodoform in the animal body.

A new reaction for cysteine is given, namely, a red coloration with nitrous acid. This reaction is not specific for cysteine, but is also given by thiolactic acid and by other thio-compounds. W. J. Y.

**Catalytic Dehydration of Alcohols.** JEAN B. SENDERENS (*Ann. Chim. Phys.*, 1912, [viii], 25, 449—529).—In this paper the author considers in detail the dehydration of alcohols by metals and non-metals, oxides, and salts and the products formed in these reactions, and discusses the influence of temperature and the mode of action of the catalytic agents. The data utilised have been given in great part already in the following papers: Abstr., 1907, i, 577; 1907, ii, 248; 1908, i, 494, 495; 1908, ii, 166; 1909, i, 127, 286, and 1910, i, 649, but a number of new observations are also recorded, as well as results obtained by other chemists.

In their activity towards ethyl alcohol, the catalytic agents are divided into two groups, "good" and "medium." The former decompose ethyl alcohol at 250—270°, and at 340° furnish from 60 to 90 c.c. of ethylene per minute. Examples of these are aluminium silicate, "modelling clay," anhydrous aluminium sulphate, and alumina. The second group begins to decompose alcohol at 320°, and at 340° yields from 2 to 9 c.c. of ethylene per minute. Examples of these are

dicalcium and tricalcium phosphates, dimagnesium and aluminium phosphates. Intermediate between the two groups are precipitated silica and magnesium pyrophosphate.

T. A. H.

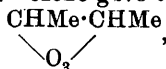
**Preparation of Alkyl Esters of Metaphosphoric Acid.** KURT LANGHELD (D.R.-P. 242613).—*Ethyl metaphosphate*,  $\text{PO}_2 \cdot \text{OEt}$ , can be readily prepared by boiling together equal parts of phosphoric oxide and ether (which has been dried over sodium) during three days; a clear syrup is formed which is separated, dissolved in chloroform, and precipitated therefrom with ether; this ester is readily hydrolysed by cold alkali hydroxides, and is of therapeutic value.

F. M. G. M.

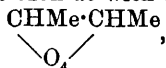
**The Constituents of Ozone.** CARL D. HARRIES (*Ber.*, 1912, 45, 936—944).—The presence of oxozone ( $\text{O}_4$ ) in ordinary ozone (compare this vol., ii, 343) is confirmed by a comparison of the effect produced on ethylenic substances by ordinary ozone and ozone previously washed with concentrated sulphuric acid and sodium hydroxide solution. It also provides an explanation of the frequently discordant descriptions of the ozonides obtained by various investigators.

The ozone used was, when first formed, of 11—14% strength, but treatment with sulphuric acid and sodium hydroxide reduced this, so that the “washed” ozone varied from 4.8 to 9.3%.

*s*-Butylene with “washed” ozone gave the normal *ozonide*,



a mobile oil distillable in a vacuum, together with a syrupy *dimeric* product,  $(\text{C}_4\text{H}_8\text{O}_3)_2$ , which was not distillable. “Unwashed” ozone gave a mixture of the above ozonide with a liquid *oxozonide*,



and a viscous *dimeric* oxozonide,  $(\text{C}_4\text{H}_8\text{O}_4)_2$ .

[With RICHARD SEITZ.]—“Washed” ozone forms with ethylenic substances normal ozonides instead of oxozonides or mixtures of the latter with ozonides; for example, *cyclohexene* in hexane solution (compare Harries and Neresheimer, *Abstr.*, 1906, i, 833) gives a white *ozonide* (m. p. 60—65°), which is probably  $(\text{C}_6\text{H}_{10}\text{O}_3)_2$ , together with the normal monomeric *cyclohexene* ozonide, which is a pungent oil (b. p. 59—60°/12 mm.).

*Pinene* (compare Harries and Neresheimer, *Abstr.*, 1908, i, 194) similarly gives a solid *ozonide*, probably  $(\text{C}_{10}\text{H}_{16}\text{O}_3)_2$ , together with an oily ozonide, probably the monomeric  $\text{C}_{10}\text{H}_{16}\text{O}_3$ .

*Terpineol* gives only a white solid *ozonide*,  $\text{C}_{10}\text{H}_{17}(\text{OH})\text{O}_3$ .

*Citronellol* (compare Harries and Himmelman, *Abstr.*, 1908, i, 662) gives a viscous ozonide,  $\text{C}_{10}\text{H}_{19}(\text{OH}) \cdot \text{O}_3$ ; the ozonides previously obtained from *terpineol* and *citronellol* ( $\text{C}_{10}\text{H}_{16}\text{O}_6$  and  $\text{C}_{10}\text{H}_{20}\text{O}_6$  respectively) must have been formed with an accompanying loss of a molecule of water.

*Cholesterol* (compare Dorée and Gardner, *Trans.*, 1908, 93, 1328; Diels, *Abstr.*, 1908, i, 728; Molinari and Fenaroli, *Abstr.*, 1908, i,

882) whether in carbon tetrachloride or hexane solution gave a microcrystalline ozonide,  $C_{27}H_{45}(OH) \cdot O_3$ .

[With FRITZ HAGEDOR.]—When caoutchouc is treated with "washed" ozone, the product is the earlier described syrupy unimolecular diozonide,  $C_{10}H_{16}O_6$ ; but with the unwashed 14% ozone, the chief product, although somewhat resembling the last, is less viscous and more easily soluble, and its analysis indicates the formula  $C_{10}H_{16}O_8$ , namely, a *dioxozonide*. The dioxozonide on treatment with water yields more lævulic acid than aldehyde, the reverse being the case with the diozonide (compare Abstr., 1904, i, 757; 1905, i, 364).  
D. F. T.

**Preparation of Formic Acid from Alkali Formates.** CHEMISCHE FABRIK GRÜNAU LANDSHOFF & MAYER, EMIL FRANKE AND WALTER KIRCHNER (D.R.-P. 243225).—When the Solvay process is applied to commercial sodium formate, the following reaction takes place:  $HCO_2Na + H_2O + NH_3 + CO_2 = NaHCO_3 + HCO_2 \cdot NH_4$ .

The ammonium formate is readily separated from traces of hydrogen sodium carbonate by evaporation or sublimation, and on decomposition furnishes formic acid in a pure condition.  
F. M. G. M.

**Preparation of Solutions of Aluminium and Chromium Formates.** ALBERT WOLFF (D.R.-P. 244320).—When dry sodium formate is added to moderately concentrated solutions of chromium (about 30%  $Cr_2O_3$ ) or aluminium sulphates, double decomposition occurs, and the sodium sulphate is quantitatively precipitated from the solution, which can be concentrated in a vacuum at temperatures not exceeding 40°, and to a density of 41° Bé in the case of chromium or to 32° Bé when aluminium is employed.  
F. M. G. M.

**Action of Acetic Anhydride on Nitrates.** ERNST SPÄTH (*Monatsh.*, 1912, 33, 235—251).—Metallic nitrates with water of crystallisation interact readily, either in the cold or on warming, with acetic anhydride, forming the corresponding anhydrous acetates (compare Vanino, Abstr., 1911, ii, 898). The reaction is accelerated catalytically by acids, and also apparently by water, as the same nitrates in the anhydrous state do not react so readily. Nitrates which do not form hydrates at the ordinary temperature do not react in the same way with acetic anhydride; the reaction appears to depend on the unsaturated character of the hydrated nitrates.

Anhydrous magnesium, cadmium, ferric, cobalt, manganic, cupric, and chromic acetates have been prepared for the first time.

*Cupric acetate* is blue, cuprous acetate colourless. *Cadmium acetate* forms colourless, slender plates, m. p. 254—256°. Anhydrous *magnesium acetate* is a colourless salt, m. p. 323°. *Cerium acetate* has m. p. 308°. *Manganic acetate* forms a brown, crystalline crust. *Ferric acetate* crystallises in lustrous plates of a sealing-wax red colour, and decomposes when heated. *Cobalt acetate* forms red crystals which sublime at 260—300°/15 mm. in a current of hydrogen. *Nickel acetate* has a whitish-green colour. *Chromic acetate* forms a green, crystalline powder.

Only small proportions of acetate were obtained by this method in the case of sodium, potassium, strontium, barium, thallium, lead, and silver nitrates.

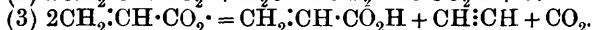
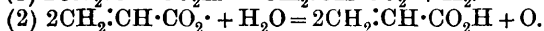
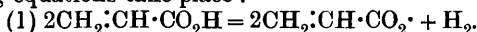
E. F. A.

**Hydrolysis of Fats by Sulphuric Acid.** ADOLF GRÜN and OCTAVIAN CORELLI (*Zeitsch. angew. Chem.*, 1912, 25, 665—670, 947).—Apart from Reimer and Will's observation that old Turkey-red oil contains diercin, it has not been observed previously that the hydrolysis of the triglycerides takes place through the  $\alpha\beta$ -diglycerides. The authors find that both tripalmitin and tristearin are hydrolysed by sulphuric acid with the production of the corresponding diglycerides and the free acids; probably the sulphuric acid ester of the diglyceride is first formed in each case, but this could not be isolated.

$\alpha\beta$ -Distearin sulphate was obtained as a soft, microcrystalline mass by treating  $\alpha\beta$ -distearin in ether with chlorosulphuric acid, special precautions being taken to avoid contact with water or rise in temperature. The *brucine* salt, obtained by adding brucine dissolved in dry alcohol to the acid ester, forms yellow needles, m. p.  $204^\circ$ ,  $[\alpha]_D -20.49^\circ$  in chloroform.

T. A. H.

**Electrolysis of the Sodium Salts of Organic Acids.** V. JULIUS PETERSEN (*Oversigt K. Danske Vidensk Selsk. Forh.*, 1912, No. 1, 25—47. Compare Abstr., 1900, ii, 522).—In the electrolysis of sodium acrylate in acid solution, the reactions represented by the following equations take place:



(1) and (2) are the chief reactions, (3) being only subsidiary. The formation of acetylene was observed whether the solution was acid, neutral, or alkaline. Carbon monoxide was also formed in small quantity, according to the equation:  $2\text{C}_2\text{H}_2 + 3\text{O}_2 = 4\text{CO} + 2\text{H}_2\text{O}$ . Experiments on a larger scale to test whether the reaction:  $2\text{CH}_2\text{:CH}\cdot\text{CO}_2\cdot = \text{CH}_2\text{:CH}\cdot\text{CH}\text{:CH}_2 + 2\text{CO}_2$  takes place, which reaction would be similar to that occurring in the electrolysis of salts of fatty acids, indicated that not divinyl, but a little ethylene was produced. This ethylene may have been formed by the reduction of acetylene, or from propionic acid formed by reduction of some of the acrylic acid. A little acetaldehyde was also formed, probably by the hydration of acetylene.

The reactions taking place on the electrolysis of solutions of potassium crotonate are similar to (1), (2), and (3) given above, the hydrocarbon produced being allylene. Some acetone is also formed by the addition of water to the allylene, and the solution contains an aldehyde, probably propaldehyde.

The chief reaction occurring in the electrolysis of solutions of potassium undecenoate is the formation of the diolefine,  $\text{C}_{10}\text{H}_{19}\cdot\text{C}_{10}\text{H}_{19}$ , according to the equation:  $2\text{C}_{10}\text{H}_{19}\cdot\text{COO}\cdot = \text{C}_{10}\text{H}_{19}\cdot\text{C}_{10}\text{H}_{19} + 2\text{CO}_2$ . This reaction is thus analogous to that occurring in the electrolysis of salts of the fatty acids. The acetylene hydrocarbon,  $\text{C}_{10}\text{H}_{18}$ , is also formed according to reaction (3), and this, by the addition of water,

gives rise to a mixture of the primary and secondary unsaturated alcohols,  $C_{10}H_{19}\cdot OH$ . The amount of oxygen evolved during the electrolysis is vanishingly small.

The electrolysis of solutions of potassium oleate gave results similar to those obtained with potassium undecenoate, the chief product being the diolefine,  $C_{17}H_{33}\cdot C_{17}H_{33}$ . The accompanying products were the acetylene hydrocarbon,  $C_{17}H_{32}$ , and a mixture of the unsaturated alcohols,  $C_{17}H_{33}\cdot OH$ . T. S. P.

**Acyclic Aldehydes. Succinic Semi-aldehyde [ $\beta$ -Aldehydopropionic Acid].** E. CARRIÈRE (*Compt. rend.*, 1912, 154, 1173—1175).—Harries and Alefeld (Abstr., 1909, i, 132, 133) prepared  $\beta$ -aldehydopropionic acid by decomposing allylacetic acid ozonide with water, but according to the present author the product was not pure. The substance is best prepared by hydrolysing ethyl monoformylsuccinate with oxalic acid in aqueous solution. As thus obtained, it is a liquid, b. p.  $142-153^\circ/15$  mm., which changes spontaneously into a polymeride, m. p.  $167^\circ$ ; molecular weight determinations show that this substance is termolecular and not bimolecular, as stated by Harries and Alefeld. On distillation in a vacuum, the solid furnishes  $\beta$ -aldehydopropionic acid, whilst the residue is a compound, m. p.  $146^\circ$ , resulting from the elimination of  $1H_2O$  from two molecules of the aldehyde.

Unimolecular  $\beta$ -aldehydopropionic acid gives a semicarbazone, m. p.  $194-195^\circ$  (decomp.), a *p*-nitrophenylhydrazone, m. p.  $180-181^\circ$ , an *oxime*, m. p.  $102-103^\circ$ , and a compound with pyruvic acid and  $\beta$ -naphthylamine, m. p. above  $250^\circ$ . The foregoing boiling and melting points are considerably higher than those given by Harries and Alefeld.

The possibility of the aldehyde having a lactonic structure appears to be excluded by the fact that on esterification with ethyl alcohol it yields an *ester*, b. p.  $84^\circ/12$  mm., and an *acetal*, b. p.  $105^\circ/12$  mm. The ester alone is obtained on esterifying the polymeride; it forms a crystalline *semicarbazone*, a *p*-nitrophenylhydrazone, and an *oxime*, b. p.  $139^\circ/14$  mm. Hydrazine hydrate gives a compound, m. p.  $37^\circ$ , b. p.  $145^\circ/19$  mm. W. O. W.

**Synthesis by means of Mixed Organo-metallic Zinc Derivatives. Aldehydes.** EDMOND É. BLAISE (*Compt. rend.*, 1912, 154, 1086—1088. Compare Abstr., 1911, i, 175, 260).—Hydrolysis of the *cycloacetals* described in a previous communication (this vol., i, 236) leads to the formation of aldehydes in accordance with the equation

$$CHR\langle\begin{smallmatrix} CO\cdot O \\ \diagdown \quad \diagup \\ O \end{smallmatrix}\rangle CHMe + H_2O = CH_3\cdot CH(OH)\cdot CO_2H + R\cdot CHO.$$

The yields are moderately good.

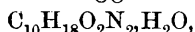
*$\alpha$ -Formoxypropionic acid* crystallises in needles, m. p.  $78^\circ$ , b. p.  $120-121^\circ/13$  mm.; the *chloride*, b. p.  $59^\circ/10$  mm., gives an *anilide*, m. p.  $82^\circ$ , and on treatment with zinc *n*-propyl iodide yields the normal *cycloacetal* of lactic acid, b. p.  $82^\circ/17$  mm., together with the *cycloacetal*,  $CHMe\langle\begin{smallmatrix} CO\cdot O \\ \diagdown \quad \diagup \\ O \end{smallmatrix}\rangle CHMe$ , the latter arising by elimination of  $3CO$  and  $2H_2O$  from 2 mols. of the acid chloride.

*Formoxyisobutyric acid* occurs in needles, m. p.  $64-65^\circ$ , b. p.

125—126°/15 mm.; the *chloride* has b. p. 53·5—54°/14 mm., and the *anilide*, m. p. 100—101°. Treatment of the acid chloride with zinc *n*-propyl iodide gives the corresponding *cycloacetal*, b. p. 84—85°/20 mm. On boiling with aqueous oxalic acid an 80% yield of butaldehyde is obtained. W. O. W.

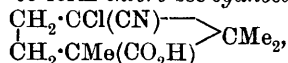
*cis-trans*-Camphoramide, Chlorocyanocamphoric Acid, and Camphoronitrile. JULIUS BREDT (*Ber.*, 1912, 45, 1419—1429).—[With S. LINCK and M. DE SOUZA.]—The camphoramide, obtained by Winzer from ethyl camphorylmalonate and ammonia (*Abstr.*, 1890, 1150), is the *cis*-compound, since it yields *cis*-camphoric acid by treatment with nitrous acid.

By the action of saturated aqueous ammonia at 0° on *cis*-camphoryl chloride, the authors have obtained *sec*-cyanocamphoric acid (the formation of which indicates that *cis*-camphoryl chloride has the asymmetric constitution,  $C_8H_{14} \begin{smallmatrix} \diagup CCl_2 \\ \diagdown CO \end{smallmatrix} O$ ) and a *substance*,



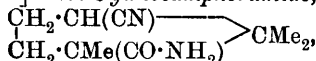
m. p. 132° (decomp.) (160° when anhydrous), which is shown to be *cis-trans*-camphoramide by its conversion into *cis-trans*-camphoric acid by nitrous acid. By treatment with bromine and potassium hydroxide it yields a *substance*, m. p. 158—159°, which contains bromine, whereas Winzer's amide yields a carbamide under these conditions (*Errera*, *Abstr.*, 1905, i, 383). Both camphoramides yield camphorimide when boiled with alcoholic potassium hydroxide. When *cis-trans*-camphoryl chloride is treated with saturated aqueous ammonia at 0°, a cyanocamphoric acid is not formed, the hydrated *cis-trans*-camphoramide alone being produced.

[With AUG. AMAN.]—Chlorocamphoryl chloride reacts with 11·6% aqueous ammonia at 0° to form *chloro-sec-cyanocamphoric acid*,



m. p. above 250° (decomp.), large, flat prisms, which is converted into camphanonitrile by warm aqueous sodium carbonate.

[With M. DE SOUZA.]—*sec-Cyanocamphoramide*,



m. p. 130°, long needles, obtained by heating *sec*-cyanocamphoric acid with phosphorus pentachloride in petroleum (low b. p.), removing the solvent and the phosphoryl chloride produced, and treating the residue with saturated, aqueous ammonia at 0°, is converted into *camphoronitrile*,  $C_8H_{14} \begin{smallmatrix} \diagup CN \\ \diagdown CN \end{smallmatrix}$ , m. p. 160°, by heating with phosphorus pentachloride on the water-bath. C. S.

**Existence of Liquid Racemates.** J. GRÖH (*Ber.*, 1912, 45, 1441—1447).—The problem whether fused methyl racemate exists as such or as a mixture of the tartrates has been attacked by measuring the velocity of crystallisation, the temperature-coefficient of the molecular surface-energy, the molecular heat of vaporisation, and by

Nernst's partition method. The last method proves unsuitable with the substance in question; the other methods prove, although not conclusively, that methyl racemate exists in the liquid state as a mixture of the tartrates. C. S.

**Preparation of Glutaric Acid by Knoevenagel's Method.** HENRI GAULT (*Bull. Soc. chim.*, 1912, [iv], 11, 380—382).—The improvement suggested consists in using 4 mols. of ethyl malonate to 2 mols. of formaldehyde in place of 2 mols. of the ester as used by Knoevenagel (*Abstr.*, 1894, i, 570). The mixture is cooled in melting ice, 1 to 1.5 grams of piperidine or diethylamine added, and the whole set aside during eighteen to twenty-four hours with frequent agitation. The mixture is then extracted with ether and the residue, left on distilling off the ether, fractionally distilled. Under these conditions the yield of ethyl methylenedimalonate is 81 to 82% with small amounts of ethyl pentanehexacarboxylate, and no ethyl methylenemalonate (compare Bottomley and Perkin, *Trans.*, 1900, 77, 294). Ethyl methylenedimalonate on boiling with diluted hydrochloric acid gives a quantitative yield of glutaric acid. T. A. H.

**Dibasic Ketonic Acids.  $\alpha$ -Ketoadipic Acid.** HENRI GAULT (*Bull. Soc. chim.*, 1912, [iv], 11, 382—389. Compare Blaise and Gault, *Abstr.*, 1911, i, 520, 664; Gault, this vol., i, 237).—A more detailed account of work already published (*Abstr.*, 1909, i, 362). Ethyl  $\alpha$ -oxalylglutarate,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CO}\cdot\text{CO}_2\text{Et})\cdot\text{CO}_2\text{Et}$ , yields a *phenylhydrazone*, m. p. 114—115°, and a *semicarbazone*, m. p. 128°. On hydrolysis by boiling diluted hydrochloric acid, the ester yields  $\alpha$ -ketoadipic acid,  $\text{CO}_2\text{H}\cdot\text{CO}\cdot[\text{CH}_2]_3\cdot\text{CO}_2\text{H}$ , m. p. 126—127°, which separates anhydrous from ether or alcohol, but sometimes as an unstable *hydrate*, m. p. 90—95° (approx.) from water. The salts are difficult to prepare. The *phenylhydrazone*, m. p. 141°, forms small, pale yellow crystals from dilute alcohol; the *semicarbazone* has m. p. 210—215° (approx.), and is sparingly soluble; the oxime, m. p. 151—152°, has been obtained already by Dieckmann (*Abstr.*, 1900, i, 297). The *ethyl ester*, b. p. 148°/9 mm. or 157°/16 mm., is a colourless liquid, giving a *phenylhydrazone*, m. p. 77°, crystallising from dilute alcohol in yellow needles, and a *semicarbazone*, m. p. 118°, forming colourless leaflets from warm water. Under the influence of sodium ethoxide, ethyl  $\alpha$ -ketoadipate undergoes lactonisation, forming the substance

$$\begin{array}{c} \text{CO}_2\text{Et}\cdot[\text{CH}_2]_3\cdot\text{CO}(\text{CO}_2\text{Et})\cdot\text{O} \\ \text{CO}_2\text{Et}\cdot[\text{CH}_2]_2\cdot\text{CH} \text{---} \text{CO} \end{array} \text{>CO} \quad (\text{compare } \text{Abstr.}, 1911, \text{i}, 709).$$

T. A. H.

**Citrophosphate Solutions.** UGO PRATOLONGO (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 363—364).—A reply to Quartaroli (this vol., i, 238). R. V. S.

**Condensation by means of Ultraviolet Light.** RICHARD PRIBRAM and ADOLF FRANKE (*Monatsh.*, 1912, 33, 415—439).—The authors have confirmed their previous conclusion (*Abstr.*, 1911, i, 420) that purified formaldehyde in aqueous solution when exposed to

ultraviolet light yields glycollaldehyde, the identity of which was proved by reducing it to ethylene glycol by means of aluminium amalgam. Control experiments showed that ethylene glycol is not produced in this manner in a solution of formaldehyde which has not been exposed to ultraviolet light. In addition higher condensation products are formed together with formic acid. The oxygen necessary for the production of the latter compound is not obtained from the water present, since the latter, under the experimental conditions chosen, is shown to suffer no decomposition; neither can it come from the air, since formic acid is still produced when air is completely excluded. It appears probable that a type of Cannizzaro reaction occurs, in which formaldehyde, under the influence of ultraviolet light, becomes decomposed into formic acid and methyl alcohol. The presence of the latter could not be proved, possibly owing to its reconversion into formaldehyde with liberation of hydrogen, which, however, is only partly evolved.

The condensation of formaldehyde is accompanied by slight decomposition, whereby carbon dioxide, carbon monoxide, hydrogen, and methane are formed.

H. W.

**The Polymerisation of Certain Aldehydes of the Series  $C_nH_{2n}O$ .** ADOLF FRANKE and HERMANN WOZELKA (*Monatsh.*, 1912, 33, 349—362).—The polymerisation products of *n*-butaldehyde, heptaldehyde, and of the so-called *i*-valeraldehyde have been studied.

When cooled dry hydrogen chloride is passed into *n*-butaldehyde cooled to  $-20^\circ$  until the temperature begins to rise, the aldehyde, after some time, becomes viscous and deposits slender needles of *n*-*meta*-butaldehyde, which can be separated from the oily *n*-*para*butaldehyde. The latter, on distillation, leaves a small residue of aldehyde resin, and is obtained as a colourless oil, b. p.  $105-108^\circ/12$  mm., which does not solidify at  $-20^\circ$ . When distilled under ordinary pressure, it yields the unimolecular aldehyde and aldehyde resin. Its molecular weight, determined in benzene solution and also by the Bleier-Kohn method, corresponds with the formula  $(C_4H_8O)_3$ . When treated with a minute quantity of sulphuric acid and distilled, it yields the unimolecular aldehyde, together with a small quantity of an oil, b. p.  $166-176^\circ$ , M.W. 117° (compare Gorghan, *Abstr.*, 1905, i, 171.). Depolymerisation is more readily accomplished by the use of a trace of hydrochloric acid. *n*-Metabutaldehyde separates from ether in long needles, m. p.  $173^\circ$ . It is stable at ordinary temperatures and sublimates at  $150^\circ$ . Determination of its molecular weight in benzene solution gives values intermediate between those required by the formulæ  $(C_4H_8O)_3$  and  $(C_4H_8O)_4$ . When heated at  $200^\circ$ , it forms the unimolecular aldehyde and its condensation products. Depolymerisation occurs more readily in the presence of a trace of acid.

Polymerisation of *n*-butaldehyde could also be brought about by sulphuric acid.

Heptaldehyde, when similarly treated, gives a small quantity of crystals of *meta*heptaldehyde, and an oil which, on distillation under diminished pressure, yields unchanged heptaldehyde, a fraction of indefinite b. p., *para*heptaldehyde, b. p.  $200-203^\circ/12$  mm., and alde-

hyde resin. Paraheptaldehyde is a colourless, viscous liquid, which, when cooled, solidifies to a fat-like mass, m. p.  $20^{\circ}$ . When preserved for some time or distilled, it yields unimolecular heptaldehyde and its condensation products as well as aldehyde resin. The molecular weight, determined in benzene solution, agreed with the formula  $C_{21}H_{42}O_3$ . Concentrated hydrochloric acid caused complete depolymerisation into the unimolecular aldehyde. Metaheptaldehyde forms long, silky needles, m. p.  $140^{\circ}$ . For its molecular weight in benzene solution, values were found intermediate between those required by the formulæ  $(C_7H_{14}O)_3$  and  $(C_7H_{14}O)_4$ . Depolymerisation occurs at  $200^{\circ}$ .

i-Valeraldehyde, a mixture of i-propylacetaldehyde and active methylethylacetaldehyde, obtained by the oxidation of commercial active amyl alcohol, has  $\alpha + 3.60^{\circ}$  ( $l = 100$ ). When treated as above with hydrogen chloride, polymerisation occurs, but without formation of metavaleraldehyde. The oily product yields mainly *paravaleraldehyde*, b. p.  $122-124^{\circ}/10$  mm., and aldehyde resin. The former is a colourless oil, which solidifies below  $-5^{\circ}$ . Its molecular weight, determined in benzene solution, corresponds with the formula  $C_{15}H_{30}O_3$ . Depolymerisation is readily effected by concentrated sulphuric acid, only a small quantity of resin being simultaneously formed.

Attempts were made to separate the two aldehydes by taking advantage of a possible difference in their velocities of polymerisation under the influence of hydrogen chloride. In these circumstances, i-valeraldehyde,  $\alpha_D + 3.60^{\circ}$ , yields an unpolymerised aldehyde,  $\alpha_D + 1.23^{\circ}$ . The polymerised portion was, however, found to be inactive, but on depolymerisation by means of a trace of hydrochloric acid gave a unimolecular aldehyde,  $\alpha_D + 1.78^{\circ}$ , which became inactive when preserved during six weeks in a vacuum. A second portion of the polymerised aldehyde was similarly preserved, and, after distillation, was also found to be inactive. Depolymerisation, however, yielded an active unimolecular aldehyde,  $\alpha_D - 0.66^{\circ}$ . This activity disappeared after fourteen days. A specimen of paravaleraldehyde was preserved during eight months, at the end of which it had become partly depolymerised. Both polymerised and depolymerised aldehyde are inactive, but depolymerisation of the former by means of concentrated sulphuric acid gives a unimolecular aldehyde,  $\alpha_D + 0.1^{\circ}$ .

H. W.

**Preparation of Methyleneacetone [ $\Delta^{\alpha}$ -Buten- $\gamma$ -one] and its Derivatives.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.P. 242612).— $\Delta^{\alpha}$ -Buten- $\gamma$ -one,  $COMe \cdot CH:CH_2$ , a colourless liquid, b. p.  $80^{\circ}$  with unpleasant odour and of therapeutic value, is prepared either by distilling  $\beta$ -acetylacrylic acid,  $COMe \cdot CH:CH \cdot CO_2H$ , at  $80-120^{\circ}$ , or by heating it with water under pressure. In a similar manner  $\beta$ -methylacetylacrylic acid,  $COMe \cdot CMe:CH \cdot CO_2H$  (prepared by elimination of hydrogen bromide from bromomethyl-lævulic acid,  $CH_3 \cdot CO \cdot CBrMe \cdot CH_2 \cdot CO_2H$ ), on distillation furnishes *methylene-ethyl-methyl ketone* [ $\beta$ -methyl- $\Delta^{\alpha}$ -buten- $\gamma$ -one],  $COMe \cdot CMe:CH_2$ , a colourless oil, with similar properties and b. p.  $96^{\circ}$ .

F. M. G. M.

**Syntheses Starting from Butyrone.** GAËTAN AMOUROUX and MARCEL MURAT (*Compt. rend.*, 1912, 154, 992-994).—Pure

butyrene has b. p. 144—145°/760 mm.,  $D^0$  0.8195,  $n_D$  1.414. When treated with magnesium isoamyl bromide, it yields *dipropylisoamylcarbinol*, b. p. 114—116°/17 mm.,  $D^0$  0.8548,  $D^{19}$  0.8388,  $n_D$  1.443; when the carbinol is passed over alumina at 300°, the unsaturated *hydrocarbon*,  $C_{12}H_{24}$ , b. p. 190—191°/760 mm., is obtained. The corresponding saturated *hydrocarbon*,  $C_{12}H_{26}$ , obtained by the catalytic method has b. p. 189°/760 mm.,  $D^{14}$  0.7538.

Butyrene and magnesium isobutyl chloride react, giving a 20% yield of *dipropylisobutylcarbinol*, b. p. 112—114°/20 mm.,  $D^0$  0.8577,  $D^{14}$  0.8445,  $n_D$  1.439; the unsaturated *hydrocarbon*,  $C_{11}H_{22}$ , has b. p. 180—183°/760 mm.

Butyrene and magnesium phenyl bromide yield *phenyldipropylcarbinol*, b. p. 134°/26 mm.,  $D^0$  0.9589,  $D^{15}$  0.9470,  $n_D$  1.516; the *acetate* has b. p. 160°/19 mm. (slight decomp.). *Phenylpropylbutylene* has b. p. 228°/760 mm., and yields a *nitrosochloride*, m. p. 112° (decomp.).

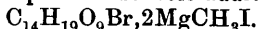
*Benzylidipropylcarbinol*, b. p. 161—163°/30 mm.,  $D^0$  0.9506,  $n_D$  1.513, forms an unsaturated *hydrocarbon*,  $C_{14}H_{20}$ , b. p. 246—248°/760 mm.,  $D^{19}$  0.902 (*nitrosochloride*, m. p. 115°); hydrogenation in presence of nickel gives  $\delta$ -*benzylheptane*, b. p. 241—243°/756 mm.,  $D^{14}$  0.854. Magnesium cyclohexyl chloride and butyrene furnish *cyclohexyldipropylcarbinol*, b. p. 128—130°/11 mm.,  $D^0$  0.9157,  $D^{19}$  0.9025,  $n_D$  1.469. The unsaturated *hydrocarbon*,  $C_{18}H_{28}$ , b. p. 226—228°/755 mm.,  $D^{21}$  0.8441, gives a *nitrosochloride*, m. p. 110° (decomp.), and on hydrogenation yields  $\delta$ -*cyclohexylheptane*, b. p. 228°/760 mm.

W. O. W.

**Reduction of  $\beta$ -Diketones.** ÉDOUARD BAUER (*Compt. rend.*, 1912, 154, 1092—1094).—Acetylacetone (60 grams) may be reduced to  $\beta\delta$ -dihydroxypentane by treatment with absolute alcohol (450 grams) and sodium (100 grams) until the latter is dissolved. Under these conditions benzoylacetone gives the aldol,  $OH \cdot CMe_2 \cdot CH_2 \cdot Ac$ , together with  $\gamma$ -hydroxy- $\alpha$ -phenylbutane and the corresponding glycol. Dibenzoylmethane likewise yields  $\alpha$ -hydroxy- $\beta\gamma$ -diphenylpropane and a *product*, b. p. 199—202°/13 mm., containing C 84.4, H 7.27%.

W. O. W.

**Compounds of Carbohydrate Derivatives with Magnesium Methyl Iodide.** EMIL FISCHER and KURT HESS (*Ber.*, 1912, 45, 912—915).—Acetobromoglucose reacts with magnesium methyl iodide, forming a colourless, amorphous insoluble additive product,



Water decomposes it with the formation of acetobromoglucose; alcohols, for example, methyl alcohol, give rises to methyl glucoside. Penta-acetylglucose, tetra-acetylglucose, and tetra-acetyl methyl-glucoside also form similar additive products with two molecules of magnesium methyl iodide.

E. F. A.

**Esters and Amides of Phosphoric Acid. III. Dihydroxyacetone- and Lævulose-phosphoric Acids.** KURT LANGHELD (*Ber.*, 1912, 45, 1125—1127).—Dihydroxyacetone dissolved in water was evaporated in a vacuum to a syrup and treated with ethyl metaphosphate

(less than 1 mol.). On cooling, the mixture solidified to a white mass, which was treated with chloroform to remove unchanged ester, and the residue dissolved in water and neutralised with barium hydroxide. After filtering off any barium phosphate, alcohol was added, and the *barium dihydroxyacetone-phosphate* separated as a white, amorphous compound,  $\text{C}_3\text{H}_5\text{O}_6\text{PBa}$ , which became crystalline after a time. The salt reduced Fehling's solution and silver nitrate, and gave with phenylhydrazine an *osazone* containing phosphorus and melting at  $143^\circ$ .

*Barium laevulose-phosphate*,  $\text{C}_6\text{H}_{11}\text{O}_9\text{PBa}\cdot\text{H}_2\text{O}$ , was obtained from laevulose in a similar manner. It was a crystalline compound, reduced Fehling's solution on warming, and yielded a *phenylosazone*,  $\text{C}_{18}\text{H}_{28}\text{O}_7\text{N}_4\text{P}$ , melting at  $158^\circ$ . These salts appear to be different from those obtained by Neuberg (Abstr., 1910, i, 610), in that the salts are crystalline and form osazones. Barium salts corresponding with diphosphoric esters of dihydroxyacetone and laevulose were obtained when excess of ethyl metaphosphate was employed.

Analysis of the laevulose compound agreed with the composition  $\text{C}_6\text{H}_{10}\text{O}_{12}\text{P}_2\text{Ba}_2\cdot\text{H}_2\text{O}$ . W. J. Y.

**Crystallographic Notes on Inosite, Potassium Nitrate, and Carbamide Nitrate.** THOMAS VIPOND BARKER (*Min. Mag.*, 1912, 16, 207—216).—New crystal-forms are noted on inosite, and a new orientation of the crystals is suggested. The rhombohedral modification of potassium nitrate fails to give a parallel growth on calcite.

Carbamide nitrate has the ratios  $a:b:c=0.9965:1:0.9142$ ;  $\beta=75^\circ 2\frac{1}{2}'$ . Crystals of the salt immersed in a saturated solution show marked differences in relief under the microscope, since the refractive index  $\alpha$  is approximately the same as that of the liquid, whilst  $\gamma$  is considerably higher. L. J. S.

**Cellulose. III. Xyloidins.** H. JENTGEN (*Zeitsch. angew. Chem.*, 1912, 25, 944—947).—It is proposed to classify under the group name "xyloidins," all substances formed by dissolving cellulose in nitric acid which are precipitated as amorphous masses from these solutions by water.

An account is given of a number of experiments dealing with the behaviour of different forms of cellulose (cotton wool, cotton waste, etc.) towards nitric acid of densities varying from 1.460 to 1.500.

The solution which first results from the action of nitric acid on cellulose is fairly viscous, but within twenty-four hours the viscosity falls, until it is about equal to that of water. In no case was it found possible to completely dissolve the cellulose in nitric acid; a few fibres always remained undissolved.

The results recorded show that the percentage of nitrogen in the product increases as the strength of the nitric acid employed in its preparation becomes greater, ranging from 6.2% to 11.0%. Similarly, the xyloidin becomes more readily soluble as the strength of the nitric acid is increased; thus, the nitrate obtained by the action of nitric acid (D 1.465) on cellulose is not affected by cold glacial acetic acid, but dissolves in the hot solvent, separating from the solution again when cold, whilst the nitrate resulting from the action of nitric acid

(D 1·470) swells up when brought into contact with cold glacial acetic acid, dissolves in the solvent when heated, and does not separate from the solution when cold. The products of the action of nitric acid of higher concentrations are readily soluble in acetic acid and acetic anhydride, whilst the higher nitrated products are soluble in most solvents.

The xyloidins decompose at 196—197°, and burn quite quietly when ignited; they contain from 2·5 to 4·0% of hygroscopic water, and, unlike collodion wool, become yellow to greenish-yellow when treated with potassium iodide. The xyloidins also differ from gun-cotton and collodion wool, in that they are much more readily attacked by hydrochloric acid, being converted in a few hours into acid-celluloses.

W. H. G.

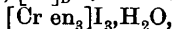
### Mirror Image Isomerism with Chromium Compounds.

II. ALFRED WERNER (*Ber.*, 1912, 45, 865—869. Compare Abstr., 1911, i, 951).—The author has succeeded in resolving triethylenediaminechromium salts into their optically active isomerides. Resolution by means of the tartrates, chloride and bromide tartrates, bromo-camphorsulphonates, or camphorsulphonates was not successful, since the aqueous solutions of the salts are so sensitive that they undergo change even on evaporation; as a rule, the yellow colour changes to violet, and triethylenediamine salts can no longer be obtained from the solution.

The salts formed with nitrocamphor, and which the author designates as camphornitronates, were found to resolve readily into their optical isomerides, *d*-triethylenediaminechromium *d*-camphornitronate being very sparingly soluble in water, whilst the corresponding *dl*-isomeride is readily soluble. No partial racemate is formed between the isomerides.

The resolution is carried out as follows: To a solution of 6 grams of triethylenediaminechromium chloride,  $[\text{Cr en}_3]\text{Cl}_3 \cdot 3\frac{1}{2}\text{H}_2\text{O}$ , in 20 c.c. of water is added a solution of 6 grams of sodium *d*-camphornitronate in 15 c.c. of water. The sparingly soluble *d*-triethylenediaminechromium *d*-camphornitronate immediately separates as a light yellow, powdery precipitate. After collecting the precipitate, further addition of sodium camphornitronate to the mother liquor produces, after two hours, another crop of small, yellow crystals. The mother liquor then contains the *l*-triethylenediaminechromium *d*-camphorsulphonate.

*d*-Triethylenediaminechromium iodide,  $[\text{Cr en}_3]\text{I}_3 \cdot \text{H}_2\text{O}$ , is obtained by triturating a thin aqueous paste of the *d*-camphornitronate with sufficient solid sodium iodide to cause it to set to a dark yellow mass. After washing this mass with a little water, alcohol and ether, it can be purified by re-precipitation from a concentrated aqueous solution of sodium iodide. It forms golden-yellow, flat, glistening crystals, and has  $[\alpha]_D + 60^\circ$ ,  $[\text{M}]_D + 378\cdot67^\circ$ . The *l*-iodide,



is obtained from the mother liquor from the *dd*-camphornitronate as follows: The addition of 5 grams of sodium iodide to the mother liquor gives a precipitate of an inactive iodide; after collecting this, the further addition of 8 grams of sodium iodide precipitates the active

*l*-iodide, which resembles the *d*-isomeride in appearance;  $[\alpha]_D - 60^\circ$ ,  $[M]_D - 378.67^\circ$ .

The *d*-thiocyanate,  $[\text{Cr en}_3](\text{SCN})_3 \cdot \text{H}_2\text{O}$ , was obtained from a concentrated solution of the *d*-iodide by precipitation with solid potassium thiocyanate. It is a yellow, crystalline powder, and has  $[\alpha]_D + 78^\circ$ ,  $[M]_D + 330.72^\circ$ . The *l*-thiocyanate,  $[\text{Cr en}_3](\text{SCN})_3 \cdot \text{H}_2\text{O}$ , was prepared similarly, from the *l*-iodide, and has  $[\alpha]_D - 80^\circ$ ,  $[M]_D - 339.2^\circ$ .

The racemic iodides and thiocyanates have the same composition as the active isomerides.

T. S. P.

**Mirror-Image Isomerism with Rhodium Compounds. I.**  
ALFRED WERNER (*Ber.*, 1912, 45, 1228—1236).—The similarity between the compounds of rhodium and cobalt (compare Abstr., 1906, i, 450) would indicate that triethylenediaminerhodium salts should form optical isomerides, as is the case with the corresponding cobalt compounds (this vol., i, 166). As a matter of fact the author has been successful in carrying out the resolution of the rhodium salts. Starting with triethylenediaminerhodium chloride, it was found that by precipitation with sodium camphornitronate (compare preceding abstract) the sparingly soluble *l*-triethylenediaminerhodium camphornitronate was obtained, the *d*-isomeride remaining in solution. An alternative method of resolution was to prepare a solution of the chloride tartrate from the chloride by interaction with silver tartrate. On concentration, the *l*-triethylenediaminerhodium chloride tartrate first separated in transparent, glistening crystals, the corresponding *d*-isomeride separating later as non-transparent, fibrous crystals. From the above compounds the various active salts could be obtained.

The active isomerides are very stable; their aqueous solutions can be evaporated down without loss of activity. They are also quite stable towards acids. It is noteworthy that the rotatory power of the rhodium compounds is of the opposite sign to that of the cobalt and chromium compounds, and from a consideration of the various active compounds which have been prepared, the author draws the conclusion that those asymmetric isomerides have corresponding configurations which give the more sparingly soluble salts with the same active acid. Cobalt and chromium give sparingly soluble *d*-isomerides, whilst rhodium gives sparingly soluble *l*-isomerides, so that rhodium has an optical effect exactly opposite to that of cobalt and chromium. Comparison of the rotatory powers of the triethylenediamine-rhodium and -chromium salts shows that they are of the same order; the rotation dispersion of rhodium salts is, however, very small, so that white light can be used in the optical measurements.

The present results, together with those previously obtained, indicate that the nature of the central atom is of decisive importance in determining the direction of rotation.

*Triethylenediaminerhodium chloride*,  $\text{YCl}_3 \cdot 2\frac{1}{2}\text{H}_2\text{O}$ , where  $\text{Y} = [\text{Rh en}_3]$ , was obtained in the impure condition by the interaction of 45 grams of ethylenediamine monohydrate with 100 grams of sodium rhodichloride. Repeated crystallisation from water does not free it from sodium chloride, with which it is isomorphous. The pure chloride is

obtained from the iodide by shaking a solution with excess of freshly precipitated silver chloride. It forms transparent, cubical crystals or small, glistening needles, and loses  $2\frac{1}{2}\text{H}_2\text{O}$  at  $120^\circ$ . The *iodide*,  $\text{YI}_3, \frac{1}{2}\text{H}_2\text{O}$ , was prepared from the impure chloride by precipitation with sodium iodide, and crystallises in transparent, rhombohedral crystals.

*l-Triethylenediaminerhodium camphornitronate* was obtained as a sparingly soluble precipitate by the interaction of 5 grams of the chloride with 4 grams of sodium camphornitronate in aqueous solution. When rubbed to a thin paste with water and solid sodium iodide, the *l-iodide*,  $\text{YI}_3, \frac{1}{2}\text{H}_2\text{O}$ , separated, and could be extracted with water and recrystallised. It crystallises in small, glistening cubes, and has  $[\alpha]_D - 50^\circ$ ,  $[\text{M}]_D - 336.5^\circ$ .

When the mother liquor from the *l*-camphornitronate was precipitated with sodium iodide, a white precipitate, containing chiefly inactive iodide, was formed. The filtrate from this precipitate was evaporated almost to dryness on the water-bath, and the residue extracted with boiling alcohol to remove sodium camphornitronate. The product remaining was dissolved in water and the solution precipitated with solid sodium iodide, whereby the pure *d-iodide*,  $\text{YI}_3, \frac{1}{2}\text{H}_2\text{O}$ , was obtained in cubical, efflorescent crystals, having  $[\alpha]_D + 48^\circ$  and  $[\text{M}]_D + 323^\circ$ ;  $[\alpha]_C + 40^\circ$ ,  $[\text{M}]_C + 269.2^\circ$ .

The *l-chloride d-tartrate*,  $\text{YCl}(\text{C}_4\text{H}_4\text{O}_6), 5\text{H}_2\text{O}$ , was obtained from the *r*-chloride and silver *d*-tartrate in the way already indicated, as was also the *d-chloride d-tartrate*,  $\text{YCl}(\text{C}_4\text{H}_4\text{O}_6), 4\text{H}_2\text{O}$ . The former crystallises in transparent, well-defined cubes, and has  $[\alpha]_D - 50^\circ$ ,  $[\text{M}]_D - 278.25^\circ$ ; the latter deposits in the form of spherical crusts, and has  $[\alpha]_D + 44^\circ$  and  $[\text{M}]_D 244.86^\circ$ . The *l*-iodide is readily obtained from the *l*-chloride *d*-tartrate by precipitation with sodium iodide, as also is the *d*-iodide from the *d*-chloride *d*-tartrate; in the latter case, however, fractional precipitation must be resorted to, since the inactive iodide is first deposited.

The *l-chloride*,  $\text{YCl}_3, 2\frac{1}{2}\text{H}_2\text{O}$ , was prepared from the *l*-iodide by a method similar to that used for obtaining the pure inactive chloride. It crystallises in long, white, efflorescent needles, and has  $[\alpha]_D - 80^\circ$ ,  $[\text{M}]_D - 347.6^\circ$ . The *d-chloride* forms similar crystals, and has  $[\alpha]_D + 78^\circ$ ,  $[\text{M}]_D + 338.9^\circ$ . The *l-thiocyanate*,  $\text{Y}(\text{SCN})_3$ , was obtained from the iodide by double decomposition with potassium thiocyanate. It forms large, dull, lancet-shaped crystals, and has  $[\alpha]_D - 72^\circ$ ,  $[\text{M}]_D - 329^\circ$ . The *d-thiocyanate* is similar, and has  $[\alpha]_D + 74^\circ$ ,  $[\text{M}]_D + 338^\circ$ .

T. S. P.

**Crystallography of Some New Organic Compounds.**  
 EDOARDO BILLOWS (*Zeitsch. Kryst. Min.*, 1912, 50, 504—509; from *Riv. Min. Crist. Ital.*, 1909, 39, 3—20).—The compounds of hexamethylenetetramine examined were prepared by G. A. Barbieri.  
 $\text{MgI}_2, 2\text{C}_6\text{N}_4\text{H}_{12}, 9\text{H}_2\text{O}$ , monoclinic,  $a : b : c = 0.8802 : 1 : 0.4951$ ;  $\beta = 90^\circ 1'$ .  
 $\text{Mg}(\text{NO}_3)_2, 2\text{C}_6\text{N}_4\text{H}_{12}, 10\text{H}_2\text{O}$ , orthorhombic,  $a : b : c = 0.8261 : 1 : 0.4813$ .  
 $\text{Mn}(\text{NO}_3)_2, 2\text{C}_6\text{N}_4\text{H}_{12}, 10\text{H}_2\text{O}$ , orthorhombic,  $a : b : c = 0.8388 : 1 : 0.4894$ .  
 $2\text{Mg}(\text{NO}_3)_2, 3\text{C}_6\text{N}_4\text{H}_{12}, 25\text{H}_2\text{O}$ , triclinic,  $a : b : c = 0.8461 : 1 : 0.8460$ ;  $\alpha = 126^\circ 5'$ ,  $\beta = 49^\circ 10'$ ,  $\gamma = 121^\circ 15'$ .

$\text{MgCl}_2 \cdot 2\text{C}_6\text{N}_4\text{H}_{12} \cdot 9\text{H}_2\text{O}$ , triclinic,  $a:b:c = 0.8321:1:0.8573$ ;  $\alpha = 125^\circ 43'$ ,  $\beta = 50^\circ 21'$ ,  $\gamma = 123^\circ 56'$ .  $\text{MgBr}_2 \cdot 2\text{C}_6\text{N}_4\text{H}_{12} \cdot 9\text{H}_2\text{O}$ , monoclinic,  $a:b:c = 0.9022:1:0.5111$ ;  $\beta = 90^\circ 40'$ .  $\text{Mg}(\text{CNS})_2 \cdot 2\text{C}_6\text{N}_4\text{H}_{12} \cdot 9\text{H}_2\text{O}$ , triclinic,  $a:b:c = 0.9342:1:0.9233$ ;  $\alpha = 134^\circ 12'$ ,  $\beta = 47^\circ 4'$ ,  $\gamma = 120^\circ 56'$ .  $\text{Mn}(\text{CNS})_2 \cdot 2\text{C}_6\text{N}_4\text{H}_{12} \cdot 4\text{H}_2\text{O}$ , tetragonal,  $a:c = 1:1.0366$ .  $\text{Co}(\text{CNS})_2 \cdot \text{C}_6\text{N}_4\text{H}_{12} \cdot 4\text{H}_2\text{O}$ , triclinic,  $a:b:c = 1.4232:1:1.6034$ ;  $\alpha = 128^\circ 23'$ ,  $\beta = 31^\circ 6'$ ,  $\gamma = 123^\circ 33'$ .  $\text{Ni}(\text{CNS})_2 \cdot \text{C}_6\text{N}_4\text{H}_{12} \cdot 4\text{H}_2\text{O}$ , triclinic. Mixed crystals of the last two compounds are also triclinic.

$\text{Fe}(\text{CNS})_2 \cdot \text{C}_6\text{N}_4\text{H}_{12} \cdot 4\text{H}_2\text{O}$ , triclinic,  $a:b:c = 1.4012:1:1.5723$ ;  $\alpha = 124^\circ 57'$ ,  $\beta = 29^\circ 54'$ ,  $\gamma = 121^\circ 36'$ .  $\text{Er}(\text{NO}_3)_3 \cdot 2\text{C}_6\text{N}_4\text{H}_{12} \cdot 10\text{H}_2\text{O}$ , monoclinic  $a:b:c = 1.501:1:1.4892$ ;  $\beta = 123^\circ 0'$ .

$\text{Nd}(\text{NO}_3)_3 \cdot 2\text{C}_6\text{N}_4\text{H}_{12} \cdot 8\text{H}_2\text{O}$ ,  
monoclinic,  $a:b:c = 0.7336:1:0.4329$ ;  $\beta = 122^\circ 30\frac{1}{2}'$ .

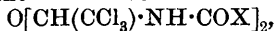
$\text{NdCl}_3 \cdot 2\text{C}_6\text{N}_4\text{H}_{12} \cdot 14\text{H}_2\text{O}$ , triclinic.

L. J. S.

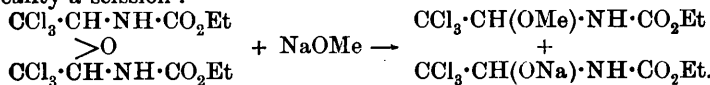
**Walden's Inversion.** EINAR BILLMANN (*Annalen*, 1912, 388, 330—344).—A theoretical paper in which the author points out that the explanations of Walden's inversion, recently advanced by Fischer (*Abstr.*, 1911, i, 418) and by Werner (*ibid.*, 424), and regarded by these authors as very similar to one another, are in reality so different that Fischer's explanation is not an explanation, whilst Werner's hypothesis presents a conception of the mechanism of the change which opens up entirely new possibilities.

The author's objections to Fischer's explanation are twofold. Taking as an example the reaction between ammonia and  $\alpha$ -bromopropionic acid, the explanation requires the splitting of the ammonia into hydrogen and the amino-group, and is, therefore, inapplicable in the case of the reaction between an organic halogen compound and a tertiary amine. The second objection is connected with the movements of the other atoms or groups in the molecule after the bromine atom has been loosened; if one of these atoms or groups moves into the place previously occupied by the halogen atom, the effect can be, in the author's opinion, at most racemisation, not inversion. C. S.

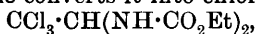
**The Condensation Products of Choral with Acid Amides.** FRANZ FEIST (*Ber.*, 1912, 45, 945—962).—Anhydrochloralurethane and its analogues are shown to have an ether-like structure,



instead of the structure  $\text{CCl}_3 \cdot \text{CH} : \text{N} \cdot \text{COX}$ , previously accepted (compare Moscheles, *Abstr.*, 1891, 1003; Hantzsch, *Abstr.*, 1894, i, 363; Diels and Seib, *Abstr.*, 1909, i, 885; Diels and Gukassianz, *Abstr.*, 1911, i, 24). The new formula contains two asymmetric carbon atoms, and so in the formation of these substances, meso- and racemic isomerides may be expected; isomerides have in some cases been isolated. The substances are neutral, very stable towards acids and towards potassium permanganate, sensitive towards alkalis, and frequently distillable without decomposition. The addition reaction of anhydrochloralurethane with sodium alcoholate (Diels and Seib, *loc. cit.*) is in reality a scission:



Chloralurethane,  $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , is converted into anhydrochloralurethane by treatment with cold sodium hydroxide solution and acetic anhydride; the product has m. p.  $149\text{--}150^\circ$ , but is very easily converted by acids into an *isomeride*, m. p.  $161\text{--}162^\circ$ ; the reverse change is caused by sodium hydroxide. Anhydrochloralurethane can be distilled (b. p.  $178^\circ/25\text{ mm.}$ , with slight decomp.); phosphorus pentachloride converts it into chloraldiurethane,



m. p.  $172^\circ$ ; it does not react with methyl sulphate.

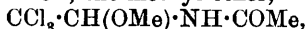
Chloralmethylurethane (from chloral and methyl carbamate) has m. p.  $125^\circ$ ; it is dehydrated similarly to the ethyl analogue, giving anhydrochloralmethylurethane, m. p.  $173\text{--}174^\circ$ , b. p.  $222^\circ/18\text{ mm.}$ ; it shows only slight indications of isomerisation. When treated with sodium methoxide solution the anhydro-compound yields *chloralmethylurethane methyl ether*, rectangular plates, m. p.  $67^\circ$ .

*Chloralisoamylurethane*, m. p.  $105\text{--}106^\circ$ , was dehydrated to *anhydrochloralisoamylurethane*, needles, m. p.  $81^\circ$ , which gave no indication of isomerism.

*Chloralmenthylurethane* was obtained from the interaction of menthylurethane and chloral in two isomeric forms, m. p.  $147\text{--}148^\circ$  and  $124\text{--}125^\circ$  respectively; both forms are resolved into their components by heating in a vacuum. It was not possible to obtain the anhydro-compounds.

Chloralformamide,  $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{NH}\cdot\text{COH}$ , m. p.  $118^\circ$ , obtained by interaction of chloral and formamide, is converted by sodium hydroxide solution and acetic anhydride into anhydrochloralformamide, m. p.  $194\cdot5\text{--}195^\circ$ ; the *methyl ether* of chloralformamide, obtained by the action of sodium methoxide on the anhydro-compound, forms prisms, m. p.  $139^\circ$ .

Chloralacetamide, m. p.  $158\text{--}159^\circ$ , is dehydrated to anhydrochloralacetamide, m. p.  $212\text{--}213^\circ$ ; the methyl ether,



obtained by the action of methyl sulphate on chloralacetamide, and of sodium methoxide on the anhydro-compound, has m. p.  $120^\circ$ .

Chloralbenzamide, m. p.  $150^\circ$ , by dehydration with sodium hydroxide solution and acetic anhydride and subsequent recrystallisation from alcohol yields an *anhydrochloralbenzamide*, m. p.  $199\text{--}200^\circ$ , together with the *ethyl ether*,  $\text{CCl}_3\cdot\text{CH}(\text{OEt})\cdot\text{NHBz}$ , m. p.  $144\text{--}145^\circ$ ; the latter is also obtainable from the anhydro-compound with sodium ethoxide in the usual way. If the crude anhydride is recrystallised without the use of alcohol there is obtained also the *acetyl* derivative,



m. p.  $151^\circ$ , b. p.  $163\text{--}165^\circ/25\text{ mm.}$  If the dehydration of chloralbenzamide is effected by sodium hydroxide solution and benzoyl chloride, the product is a mixture of the above anhydro-compound with an *isomeride*, m. p.  $138^\circ$ , together with *benzoylchloralbenzamide*,  $\text{CCl}_3\cdot\text{CH}(\text{OBz})\cdot\text{NHBz}$ , needles, m. p.  $168^\circ$ . The conversion of the more fusible isomeride into the less fusible is difficult to complete. On heating under reduced pressure, the more fusible isomeride (as also the other isomeride above its m. p.) forms *chloraldiibenzamide*,  $\text{CCl}_3\cdot\text{CH}(\text{NHBz})_2$ , colourless needles, m. p.  $272^\circ$ ; the easy formation of

this substance is a disproof of the structure previously assigned to these anhydro-compounds. The *methyl ether* of chloralbenzamide (m. p. 105—106°, b. p. ca. 200°/22 mm.) is obtainable from the anhydro-compound with sodium methoxide, and from chloralbenzamide itself with methyl sulphate. The *ethyl ether* is described above.

D. F. T.

**Derivatives of Monoamino-acids. Picrolonates of Glycine, *d*-Alanine, and *dl*-Leucine.** EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1912, 78, 150—155).—The monoamino-acids form sparingly soluble picrolonates, but these are all so similar as to be useless for the separation of mixtures of amino-acids.

*Glycine picrolinate*, which is composed of 2 mols. of amino-acid to 1 mol. of picrolonic acid, is prepared by mixing concentrated solutions of the components at the boiling point and heating for a few minutes. It crystallises in lustrous, orange, silky, soft needles, m. p. 208° (corr. decomp.).

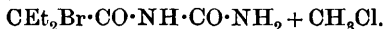
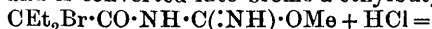
The corresponding *d-alanine picrolinate* (2 alanine + 1 picrolonic acid) has m. p. about 145° (decomp.). A second compound (1 alanine + 1 picrolonic acid) has m. p. 215° (decomp. 217°),  $[\alpha]_D^{20} + 11.8^\circ (\pm 0.74^\circ)$ .

*dl-Leucine picrolinate* (1 leucine + 1 picrolonic acid) crystallises in long, narrow prisms of greenish-yellow colour, which become yellow when dried, and soften at 130°, m. p. 150° (decomp.). E. F. A.

**Crystalline Form of Some Platinothiocyanates.** EDOARDO BILLOWS (*Zeitsch. Kryst. Min.*, 1912, 50, 509—510; from *Riv. Min. Crist. Ital.*, 1909, 39, 21—26).—The substances investigated were prepared by A. Minozzi. Potassium platinothiocyanate,  $K_2Pt(CNS)_6$ , hexagonal holohedral,  $a : c = 1 : 0.7829$ . Potassium platinothiocyanate dihydrate,  $K_2Pt(CNS)_6 \cdot 2H_2O$ , orthorhombic,  $a : b : c = 0.6224 : 1 : 0.9712$ . Ammonium platinothiocyanate,  $(NH_4)_2Pt(CNS)_6$ , hexagonal holohedral,  $a : c = 1 : 0.9340$ . Sodium platinothiocyanate,  $Na_2Pt(CNS)_6 \cdot 2H_2O$ : the microscopic crystals appear to be isomorphous with the corresponding potassium salt. These salts are isomorphous with the corresponding platinoselenocyanates (following abstract). L. J. S.

**Crystallography of Platinoselenocyanates.** EDOARDO BILLOWS (*Zeitsch. Kryst. Min.*, 1912, 50, 494—495; from *Riv. Min. Crist. Ital.*, 1909, 36, 49—55).—Potassium platinoselenocyanate,  $K_2Pt(CNSe)_6$ , orthorhombic hemimorphic,  $a : b : c = 0.5989 : 1 : 0.9565$ . Potassium platinoselenocyanate dihydrate,  $K_2Pt(CNSe)_6 \cdot 2H_2O$ , trigonal scalenohedral,  $\rho = 38^\circ 31\frac{1}{2}'$ . Ammonium platinoselenocyanate,  $(NH_4)_2Pt(CNSe)_6$ , orthorhombic,  $a : b : c = 0.6338 : 1 : 1.0444$ . L. J. S.

**Preparation of Bromo- $\alpha$ -ethylbutyrylcarbamide.** FARBEN-FABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 243233).—When bromo- $\alpha$ -ethylbutyrylisocarbamide methyl ether (this vol., i, 169) is heated with concentrated hydrochloric acid, it evolves methyl chloride and is converted into bromo- $\alpha$ -ethylbutyrylcarbamide :



F. M. G. M.

**Action of Hydroxycarbamide on Some  $\beta$ -Ketonic Esters.**  
 ANDRÉ MEYER (*Compt. rend.*, 1912, 154, 989—992).—On adding ethyl acetoacetate to an alcoholic solution of hydroxycarbamide, a very soluble additive *compound*,  $C_7H_{14}O_5N_2$ , m. p. 42—43°, is obtained, together with a *compound*,  $C_7H_{12}O_4N_2 \cdot 0.5H_2O$ , crystallising in slender needles, m. p. 45°. Ethyl benzoylacetate in the same way gives by condensation a *compound*,  $C_{12}H_{14}O_4N_2$ , silky needles, m. p. 98—99°. Ethyl oxalacetate furnishes a *compound*,  $C_9H_{14}O_6N_2$ , occurring in prisms, m. p. 77°, together with a small quantity of the *compound*,  $C_{18}H_{20}O_{13}N_4$ , probably a hydrate of the foregoing. W. O. W.

**Electrolytic Oxidation of Organic Sulphur Compounds**  
 FRITZ FICHTER and WALTER WENK (*Ber.*, 1912, 45, 1373—1383).—The authors have extended the observations of Fichter and Sjöstedt (*Abstr.*, 1911, i, 41). In all the experiments, with two exceptions, an anode of platinum gauze was used; in some cases it was not absolutely necessary to use a diaphragm. Except where stated the solvent used was a mixture of glacial acetic acid and concentrated hydrochloric acid.

At 15—20° ethyl thiocyanate is oxidised to ethanesulphonic acid. At 2°, using a current density (*C.D.*) of 0.02 ampere per sq. cm., thiocarbamide is oxidised in hydrochloric acid solution to the compound  $S_2[C(NH_2) \cdot NH_2]_2$  (compare Maly, *Abstr.*, 1890, 1399; Storch, *Abstr.*, 1891, 548), for which the authors adopt the name formamidine disulphide (compare Hector, *Abstr.*, 1892, 292). After electrolysis, the nitrate is readily precipitated from the solution by the addition of potassium nitrate.

*Formamidine disulphide sulphate*,  $C_2H_6N_4S_2 \cdot H_2SO_4$ , is similarly obtained from thiocarbamide in sulphuric acid (2*N*) solution, using a *C.D.* of 0.01 ampere per sq. cm. In hydrobromic acid solution the corresponding hydrobromide (compare MacGowan, *Trans.*, 1887, 51, 378) is obtained.

Ethyl sulphide behaves similarly to phenyl sulphide (Fichter and Sjöstedt, *loc. cit.*), ethyl sulfoxide being first formed, and then ethylsulphone. For the preparation of the sulphone it is best first to isolate the sulfoxide.

*o*-Nitrobenzyl sulphide is readily oxidised to the sulfoxide. The oxidation takes place best in glacial acetic acid-hydrochloric acid solution at 70—75°, using a *C.D.* of 0.06 ampere per sq. cm. If the temperature is raised to 100°, *o*-nitrobenzyl disulphoxide is produced; it is probable that the disulphide is first formed from the sulfoxide (compare Smythe, *Trans.*, 1909, 95, 349), and then oxidised to the disulphoxide. The production of sulfoxide also takes place when the hydrochloric acid is replaced by phosphoric or nitric acid, but it is then accompanied by some *o*-nitrobenzaldehyde. Oxidation to the sulphone does not take place at platinum anodes. *p*-Nitrobenzyl sulfoxide was obtained similarly from *p*-nitrobenzyl sulphide.

At 10°, with a *C.D.* of 0.02 ampere per sq. cm., acetonedithylmercaptole is oxidised to a mixture of acetone and ethanesulphonic acid. It is probable that the hitherto unknown diethylthionyl-2:2-propane,  $CM_e_2(SOEt)_2$ , is first produced, and then decomposed, in the presence of water, by chlorine evolved at the anode from the hydro-

chloric acid in the solvent, according to the scheme:  $\text{CMe}_2(\text{SOEt})_2 \rightarrow \text{CMe}_2\text{Cl}_2 + 2\text{Et}\cdot\text{SO}_2\text{Cl} \rightarrow \text{COME}_2 + 2\text{Et}\cdot\text{SO}_3\text{H}$ . This explanation is supported by the fact that when water was excluded from the solvent, which then consisted of glacial acetic acid containing 10% of acetic anhydride and continuously saturated with a current of dry hydrogen chloride, the mercaptol was oxidised to *diethylthionyl-2:2-propane*, when a graphite anode was used. This compound possesses a most objectionable odour, which is, however, quite different from that of the mercaptole. It is a colourless liquid, heavier than water, and has b. p.  $134-135^\circ/14$  mm. It is readily reduced to the mercaptole by tin and hydrochloric acid, and oxidised to sulphonol by permanganate in sulphuric acid solution.

Phenyl ethyl sulphide behaves quite differently from the symmetrical sulphides towards electrolytic oxidation, the products being benzenesulphonic acid and acetic acid. It is possible that it is first oxidised to the sulphoxide, but that this unites with hydrogen chloride, loses water, and then decomposes into phenyl mercaptan and acetaldehyde (compare Hilditch, this vol., i, 71), in accordance with the scheme:  $\text{SOEtPh} \rightarrow \text{OH}\cdot\text{SEtPhCl} \rightarrow \text{SPhCl}\cdot\text{CHMe} \rightarrow \text{PhSH} + \text{Me}\cdot\text{CHO}$ . The mercaptan and aldehyde are then oxidised to the sulphonic acid and acetic acid. A graphite anode was used in the electrolysis.

At  $40-50^\circ$ , with a *C.D.* of 0.04 ampere per sq. cm., phenyl disulphide is oxidised to two molecules of benzenesulphonic acid, behaving quite differently from benzyl disulphide. When water is excluded and graphite anodes are used, the disulphide is not acted on.

During the course of the investigation, it was found that acetone-diethylmercaptole readily gives *additive products* with mercuric nitrate and chloride, having the respective formulæ:  $\text{C}_7\text{H}_{16}\text{S}_2\cdot\text{Hg}(\text{NO}_3)_2$  and  $\text{C}_7\text{H}_{16}\text{S}_2\cdot\text{HgCl}_2$ . The former is insoluble in water, but from alcohol or acetone solution it is obtained as large, thin, flexible tablets with a silver glance; m. p.  $76^\circ$ . The latter is insoluble in water and organic solvents; from concentrated hydrochloric acid solution it is obtained as glistening, white flakes on the addition of water. When the mercaptole is shaken with a solution of mercurous nitrate, a black precipitate (delicate reaction) is obtained, consisting of mercury and the mercuric nitrate additive product. T. S. P.

**Methylated Guanidines.** MARTIN SCHENCK (*Zeitsch. physiol. Chem.*, 1912, 77, 328-393. Compare Abstr., 1910, i, 99; 1911, i, 842).—A summary of the subject. Eleven methylated guanidines are possible. Three of these, all containing the grouping  $\text{NMe}\cdot\text{C}(\text{NH}_2)_2\cdot\text{N}\cdot$ , could not be obtained. Attempts to prepare them led to the formation of guanidines with the grouping  $\text{NH}\cdot\text{C}(\text{NHMe})_2\cdot\text{N}\cdot$ , which appears to be the stable form.

*as*-Trimethylguanidine, the two tetramethylguanidines, and pentamethylguanidine are prepared for the first time. Other methylguanidines have been obtained by new methods. *s-aβγ*-Trimethylguanidine,  $\text{NMe}\cdot\text{C}(\text{NMe})_2$ , is formed whenever the conditions are in any way favourable, and in a number of unexpected cases; it is evidently very stable.

Dimethylamine behaves somewhat differently from ammonia or methylamine, carbamide derivatives being obtained with it instead of the methylated guanidines expected.

$\alpha$ -Methylguanidine,  $\text{NH}\cdot\text{C}(\text{NHMe})\cdot\text{NH}_2$ , forms a *platinichloride*, crystallising in plates, m. p. 194—195°.

$\gamma$ -Methylguanidine,  $\text{NMe}\cdot\text{C}(\text{NH}_2)_2$ , could not be prepared.

$\alpha\alpha$ -Dimethylguanidine,  $\text{NH}\cdot\text{C}(\text{NMe}_2)\cdot\text{NH}_2$ , forms an *aurichloride*, crystallising in dark yellow prisms, m. p. 248°, a *platinichloride*, crystallising in needles, m. p. 225°; the *picrate* has m. p. 230°.

$\alpha\beta$ -Dimethylguanidine,  $\text{NH}\cdot\text{C}(\text{NHMe})_2$ , may be prepared from methylamine and diethyl iminocarbonate or from methylamine and the methiodide of methylthiocarbamide. The *aurichloride* forms needles and plates, m. p. 122°; the *platinichloride* forms short, thick needles, m. p. 196—197°; the *picrate* gives prisms, m. p. 178°.

This guanidine was also obtained from *s*-dimethylthiocarbamide on treatment with mercury oxide in presence of ammonia, also on heating the ethiodide of *s*-dimethylthiocarbamide with alcoholic ammonia.

$\alpha\gamma$ -Dimethylguanidine,  $\text{NMe}\cdot\text{C}(\text{NHMe})\cdot\text{NH}_2$ , could not be obtained.

$\alpha\alpha\beta$ -Trimethylguanidine,  $\text{NH}\cdot\text{C}(\text{NMe}_3)\cdot\text{NHMe}$ , prepared by the action of dimethylamine on the methiodide of methylthiocarbamide in sealed tubes at 100° for twelve hours, forms an *aurichloride*, crystallising in needles and thin plates, m. p. 153—155°, and a *platinichloride*, crystallising in needles, m. p. 172—173°.

$\alpha\alpha\gamma$ -Trimethylguanidine,  $\text{NMe}\cdot\text{C}(\text{NMe}_2)\cdot\text{NH}_2$ , could not be prepared.

$\alpha\beta\gamma$ -Trimethylguanidine,  $\text{NMe}\cdot\text{C}(\text{NHMe})_2$ , can be obtained by a large variety of methods; the *hydriodide* forms long needles, m. p. above 290°; the *aurichloride* forms needles, m. p. 156°, and the *platinichloride*, needles and plates, m. p. 225—226°.

$\alpha\alpha\beta\beta$ -Tetramethylguanidine,  $\text{NH}\cdot\text{C}(\text{NMe}_2)_2$ , prepared by the action of ammonia on the methiodide of tetramethyl thiocarbamide, forms an *aurichloride*, crystallising in slender needles, m. p. 142—144°, a *platinichloride*, crystallising in needles, and a *picrate*, consisting of needles aggregated to form plates, m. p. 130°.

$\alpha\alpha\beta\gamma$ -Tetramethylguanidine,  $\text{NMe}\cdot\text{C}(\text{NMe}_2)\cdot\text{NHMe}$ , was obtained on treatment of  $\alpha\beta\gamma$ -trimethyl- $\psi$ -thiocarbamide with dimethylamine. The *aurichloride* forms needles, m. p. 115—117°; the *picrate* separates in short prisms, m. p. 158—160°.

*Pentamethylguanidine*,  $\text{NMe}\cdot\text{C}(\text{NMe}_2)_2$ , was obtained by treating  $\alpha\alpha\beta\gamma$ -tetramethyl- $\psi$ -thiocarbamide with dimethylamine. Attempts to prepare it from ethyl methyl iminocarbonate and dimethylamine or from ethyl methyl iminodithiocarbonate and dimethylamine were unsuccessful. The *aurichloride* forms slender needles, m. p. 130—132°; the *picrate* separates in long needles, m. p. 160—162°. E. F. A.

**The Formation of Triazomethylurethane from Triazoacetic Acid.** THEODOR CURTIUS and AUGUST BOCKMÜHL (*Ber.*, 1912, 45, 1033—1036)—An extension of the work of Curtius, Darapsky, and Bockmühl on the hydrazide and azide of triazoacetic acid is here described (compare Abstr., 1908, i, 144). It is found that those

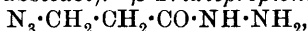
hydrazides which are only obtained as unstable syrups can readily be purified in the form of their condensation products with acetone, any excess of hydrazine hydrate being converted into the easily soluble dimethylketazine (compare the following abstracts). The acetone residue can easily be removed by hydrolysis.

*isoPropylidenetriazoacetohydrazide*,  $N_3 \cdot CH_2 \cdot CO \cdot NH \cdot N : CMe_2$ , produced by careful addition of acetone to the syrupy product from ethyl triazoacetate and hydrazine hydrate, crystallises in slender, white needles, m. p.  $114^\circ$ . The aqueous solution on shaking with benzaldehyde furnishes benzylidenetriazoacetohydrazide; with *p*-tolualdehyde, *p*-tolylidenetriazoacetohydrazide,  $N_3 \cdot CH_2 \cdot CO \cdot NH \cdot N : CH \cdot C_6H_4Me$ , is formed in white needles, m. p.  $157^\circ$ , whilst with benzoyl chloride in presence of sodium hydrogen carbonate, *benzoyltriazacetohydrazide*,  $N_3 \cdot CH_2 \cdot CO \cdot NH \cdot NHBz$ , forming slender, white needles from alcohol, m. p.  $145^\circ$ , is produced.

$\alpha$ -Phenylethylidenetriazoacetohydrazide,  $N_3 \cdot CH_2 \cdot CO \cdot NH \cdot N : CMePh$ , can be obtained by direct condensation with the syrupy triazoacetohydrazide, forming slender, white needles from alcohol, m. p.  $162^\circ$ . Triazoacetohydrazide hydrochloride, previously obtained from benzylidenetriazoacetohydrazide, is more readily prepared by the hydrolysis of the *isopropylidene*-hydrazide, whilst triazoacetic acid, usually made by hydrolysing its ethyl ester, has also been derived from benzylidenetriazoacetohydrazide. Triazoacetylazoimide (Abstr., 1908, i, 145) is converted by heat into the carbimide, which with alcohol produces *triazomethylurethane*,  $N_3 \cdot CH_2 \cdot NH \cdot CO_2Et$ , a mobile, yellow oil, which decomposes without explosion on heating; it has a faint odour, and is feebly acid. With ammonia, followed by silver nitrate, silver azoimide is immediately precipitated. J. C. W.

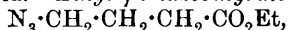
**The Hydrazide and Azoimide of  $\alpha$ - and  $\beta$ -Triazopropionic Acids.** THEODOR CURTIUS and HANS FRANZEN (*Ber.*, 1912, 45, 1037—1044).—The ethylesters of  $\alpha$ - and  $\beta$ -triazopropionic acids (Forster and Fierz, *Trans.*, 1908, 93, 669) react with hydrazine hydrate, the former with considerable development of heat, the latter only on warming, to give syrupy hydrazides which can also be isolated in the form of acetone condensation products (compare preceding abstract). *isoPropylidene- $\alpha$ -triazopropionohydrazide*,  $N_3 \cdot CHMe \cdot CO \cdot NH \cdot N : CMe_2$ , forms colourless, shining flakes, m. p.  $70^\circ$ ; the *benzylidene* derivative,  $N_3 \cdot CHMe \cdot CO \cdot NH \cdot N : CHPh$ , crystallises in colourless, silky needles from hot alcohol, m. p.  $92^\circ$ .  $\alpha$ -Triazopropionohydrazide *hydrochloride*,  $N_3 \cdot CHMe \cdot CO \cdot NH \cdot NH_2 \cdot HCl$ , is deposited on passing dry hydrogen chloride through the ethereal solution of the *isopropylidene*-hydrazide; it forms shining needles, m. p.  $107^\circ$  (decomp.). On treating the *isopropylidene*-hydrazide in the required quantity of *N*-hydrochloric acid with sodium nitrite, the very explosive  $\alpha$ -triazopropionylazoimide,  $N_3 \cdot CHMe \cdot CO \cdot N_3$ , is obtained as a yellow, mobile oil with a penetrating odour. The ethereal solution when evaporated with alcohol produces  $\alpha$ -triazomethylurethane,  $N_3 \cdot CHMe \cdot NH \cdot CO_2Et$ , with evolution of nitrogen; this is a dark, mobile oil, boiling with considerable decomposition at about  $100^\circ/15$  mm., and changing spontaneously into ethylidene-

diurethane (see later abstract).  $\beta$ -Triazopropionohydrazide,

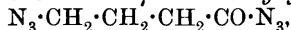


is a clear, colourless, viscid syrup, which also can be characterised in the form of its isopropylidene derivative,  $\text{C}_6\text{H}_{11}\text{ON}_5$ , which crystallises in colourless, shining leaflets, m. p.  $73^\circ$ . The benzylidene-hydrazide,  $\text{C}_{10}\text{H}_{11}\text{ON}_5$ , forms colourless, silky needles from hot alcohol, m. p.  $117^\circ$ ; the hydrochloride,  $\text{N}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2 \cdot \text{HCl}$ , is a very hygroscopic, crystalline mass, whilst the azoimide,  $\text{N}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{N}_3$ , is a mobile, yellow, very explosive oil, yielding  $\beta$ -triazopropionanilide, m. p.  $189^\circ$ , with aniline.  $\beta$ -Triazoethylurethane,  $\text{N}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$ , a faint yellow, mobile oil with pleasant odour, decomposes entirely, but without explosion when heated; it is feebly acid in warm water, and does not change with lapse of time. J. C. W.

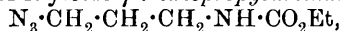
The Hydrazide and Azoimide of  $\gamma$ -Triazobutyric Acid. THEODOR CURTIUS and WILHELM GIULINI (*Ber.*, 1912, 45, 1045—1050).—Quite analogous to the foregoing substances are those derived from the new  $\gamma$ -triazobutyric acid. Ethyl  $\gamma$ -triazobutyrate,



prepared from ethyl  $\gamma$ -chlorobutyrate (Henry, *Abstr.*, 1886, 216), is a colourless, mobile liquid, b. p.  $102-104^\circ/22$  mm., miscible with organic solvents, but very slightly soluble in water; in all, 1050 grams of this substance were prepared. The contribution of the triazo-group to the molecular refraction, namely,  $M_r$  8.85, is normal, and agrees with similar values obtained by Philip (*Trans.*, 1908, 93, 918). The ester is easily hydrolysed by 20% sodium hydroxide to the acid,  $\text{C}_4\text{H}_7\text{O}_2\text{N}_3$ , a clear, colourless liquid solidifying below  $0^\circ$ , b. p.  $135^\circ/11$  mm.; the sodium, potassium, and silver salts are white. isoPropylidene- $\gamma$ -triazobutyrohydrazide,  $\text{N}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{N} \cdot \text{CMe}_2$ , is a white, crystalline mass, m. p.  $32.5^\circ$ . The benzylidene derivative,  $\text{C}_{11}\text{H}_{13}\text{ON}_5$ , crystallises in small, shining leaflets, m. p.  $47^\circ$ . The o-hydroxybenzylidene derivative forms slender needles from dilute alcohol, m. p.  $105.5^\circ$ , the hydrochloride being a yellow, gelatinous mass.  $\gamma$ -Triazobutyrylazoimide,

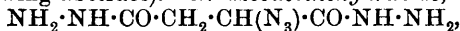


prepared from the hydrazide, is a faint yellow oil, exploding when heated; with alcohol it yields  $\gamma$ -triazopropylurethane,



as a mobile oil which cannot be distilled, but which does not change when kept. J. C. W.

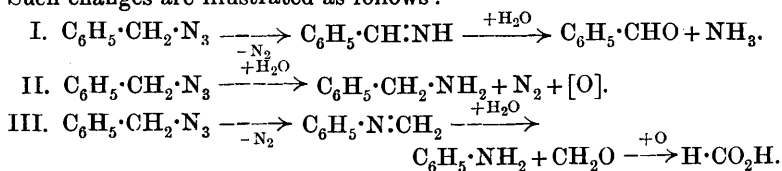
The Hydrazide and Azoimide of Triazosuccinic Acid. THEODOR CURTIUS and FRIEDRICH HARTMANN (*Ber.*, 1912, 45, 1050—1056).—The corresponding derivatives of succinic acid are in most respects similar to the substances described in the preceding abstracts. Diethyl triazosuccinate,  $\text{CO}_2\text{Et} \cdot \text{CH}_2 \cdot \text{CH}(\text{N}_3) \cdot \text{CO}_2\text{Et}$ , is obtained from the bromosuccinate and sodium azoimide under the influence of a little spongy palladium, considerable quantities of indefinite by-products being produced. It is a limpid liquid which solidifies at a very low temperature, and boils at  $90-92^\circ/0.01$  mm. It is very sensitive towards alkalis, giving fumaric and hydrazoic acids (compare following abstract). Triazosuccinohydrazide,



partly crystallises from the reaction mixture in colourless needles, m. p.  $122^{\circ}$ , readily soluble in cold water, dissolving less readily in alcohol. Hydrazine is eliminated on keeping the substance, and also on warming it with water; hence it is best converted into the *isopropylidene* compound,  $C_{10}H_{17}O_2N_7$ , a colourless, crystalline powder, m. p.  $182.5^{\circ}$ , soluble in hot water with decomposition. The *methylene* compound is a colourless powder almost insoluble in water, m. p.  $173^{\circ}$ ; the *benzylidene* derivative,  $C_{18}H_{17}O_2N_7$ , is a white powder, m. p.  $169^{\circ}$ ; the *o*-hydroxybenzylidene compound,  $C_{18}H_{17}O_4N_7$ , forms yellow flakes, m. p.  $204^{\circ}$ , whilst the *hydrochloride*,  $C_4H_9O_2N_7 \cdot 2HCl$ , is a colourless, very hygroscopic, crystalline powder, m. p.  $123^{\circ}$ . The *isopropylidene*-hydrazide yields with nitrous acid, *triazosuccinyl azoimide*,  $N_3 \cdot CO \cdot CH_2 \cdot CH(N_3) \cdot CO \cdot N_3$ , a yellow oil with penetrating odour; it is very unstable, exploding violently when touched or when the solution is evaporated. In the dry ethereal solution, aniline produces *triazosuccinoanilide*,  $C_{16}H_{15}O_2N_5$ , in colourless needles, m. p.  $175^{\circ}$ ; the *p*-toluidide,  $C_{18}H_{19}O_2N_5$ , forms colourless needles, m. p.  $201^{\circ}$ , whilst *triazoethylenediurethane*,  $CO_2Et \cdot NH \cdot CH_2 \cdot CH(N_3) \cdot NH \cdot CO_2Et$ , is a dark yellow oil, soluble in warm water, decomposing when kept.

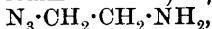
J. C. W.

**Hydrolytic Degradation of Triazo-acids, Triazo-acid-azoimides, and Triazourethanes (Formation of Triazo-alkylamines).** THEODOR CURTIUS (*Ber.*, 1912, 45, 1057—1093).—When hydrolysing agents are allowed to act on organic triazo-compounds, the azoimide nucleus is either eliminated as hydrazoic acid or in the form of nitrogen. Acid azoimides, which are analogous to acid chlorides, are very susceptible to the former change when attacked by sufficiently dissociated acids or alkalis. With water or alcohol, however, they lose nitrogen and undergo rearrangement to carbimides or urethanes. Aliphatic triazo-compounds, like aromatic azoimides, frequently resist simple hydrolysis, presenting marked contrast to the haloid analogues. With more powerful agents (strong acids or bases), they lose nitrogen and many of the possible changes which may occur have been observed. Such changes are illustrated as follows:



They consist in, therefore, (I) partial and transitory rearrangement of the residue; (II) addition of hydrogen, producing primary amines; and (III) complete rearrangement analogous to the acid-azoimides, followed by hydrolysis and oxidation.

Benzylazoimide itself has already been shown to give on hydrolysis benzaldehyde and ammonia (I) [Abstr., 1901, 574], also methylene-aniline (II) [Curtius, 1911]. Darapsky now proves the formation of formic acid (III) (private communication).  $\beta$ -Triazoethylamine,



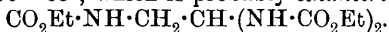
which is very stable towards strong alkalis, behaves in a similar manner

with concentrated hydrochloric acid, giving principally ethylenediamine (II) along with ammonia and glycine, traces of unoxidised glycinealdehyde being also recognisable (I). Scheme (III) would furnish a methylenediaminomethane,  $\text{CH}_2\cdot\text{N}\cdot\text{CH}_2\cdot\text{NH}_2$ , which would at once break down into ammonia and formaldehyde, the latter being oxidised to formic acid; the presence of carbon monoxide in the liberated gases would result from the decomposition of the latter. In neither of these two cases could nitrous oxide or free oxygen be found in the liberated gases, thus contradicting the view previously held by Curtius and Darapsky (Abstr., 1901, 574).

The various fatty triazo-acids are hydrolysed by strong acids or bases more especially according to scheme (I). Thus triazoacetic acid yields ammonia and glyoxylic acid (Abstr., 1908, i, 144);  $\alpha$ -triazopropionic acid,  $\text{CH}_3\cdot\text{CH}(\text{N}_3)\cdot\text{CO}_2\text{H}$  (b. p.  $121\cdot5^\circ/20$  mm.), when heated with strong hydrochloric acid furnishes pyruvic acid, whilst traces of an  $\alpha$ -amino-acid can be detected.  *$\beta$ -Triazopropionic acid*,  $\text{N}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , a yellow oil with rancid odour, could not be obtained from its ester by means of alkali, as this eliminates hydrazoic acid and leaves acrylic acid (Forster and Fierz, Trans., 1908, 93, 669); nevertheless, the ester, the hydrazide, or its acetone derivative may be smoothly hydrolysed by dilute acids. Strong hydrochloric acid degrades the ester to acetaldehyde and carbon dioxide, traces of glycine being also detected (III).  $\gamma$ -Triazobutyric acid, in the form of its ethyl salt, is hydrolysed by concentrated hydrochloric acid to ammonia, ethyl aldehydopropionate,  $\text{CHO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , and  $\beta$ -aldehydopropionic acid itself. This semialdehyde of succinic acid is easily converted into succinic acid (Perkin and Sprankling, Trans., 1899, 75, 11); the hydrolysis thus provides an interesting conversion of butyric into succinic acid. Probably  $\gamma$ -aminobutyric acid and  $\beta$ -alanine (II and III) are also produced. Ethyl triazosuccinate, when hydrolysed by means of sulphuric acid, furnishes ammonia, pyruvic acid, and carbon dioxide, the latter substances being the decomposition products of the expected ethyl aceto-oxalate (I). Towards alkalis, however, it is very sensitive, decomposing into fumaric and hydrazoic acids. With strong ammonia, fumaramide, ammonium azoimide and apparently ethyl imino-succinamate,  $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{C}(\text{NH})\cdot\text{CO}\cdot\text{NH}_2$ , are produced; the latter crystallises from alcohol in colourless tablets, m. p.  $120^\circ$ , is very sweet to the taste, and decolorises alkaline permanganate. Dilute alkalis liberate two molecules of ammonia, whilst sulphuric acid yields pyruvic acid and carbon dioxide, which arise from the intermediate ethyl oxalacetate. It is probably identical with Thomas-Mamert's "stereoisomeride" of ethyl aminofumaramate, (Abstr., 1895, i, 267).

Hydrolysis of those triazourethanes in which the triazo-group adjoins the urethane-nitrogen, yields hydrazoic acid and other degradation products. Thus, triazomethylurethane, even on boiling with water, gives (possibly) *hydroxymethylurethane*,  $\text{HO}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$ , as slender, white needles, m. p.  $64^\circ$ , which decompose with sulphuric acid into formaldehyde and carbon dioxide. It was not found possible to obtain such a substance directly from glycolylazoimide,  $\text{HO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}_3$ .  $\alpha$ -Triazoethylurethane undergoes a similar change with boiling water or dilute acids, giving acetaldehyde, etc.; it also suffers gradual

hydrolysis, the ethylidenediurethane of Nencki (*Ber.*, 1874, 7, 160), crystallising out from the oil with liberation of hydrazoic acid. Moist triazoethylenediurethane also decomposes after a time, yielding a substance, m. p. 60—65°, which is probably *ethanetriurethane*,



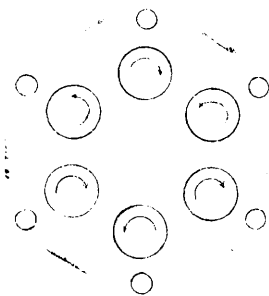
On the other hand, those urethanes in which the triazo-group is removed from the urethane-nitrogen furnish triazoalkylamines, which are remarkably stable towards strong alkalis, losing nitrogen when hydrolysed by acids and giving rise to diamines (scheme II.). Thus,  $\beta$ -triazoethylurethane yields with baryta the  $\beta$ -triazoethylamine of Forster and Newman (*Trans.*, 1911, 99, 1279), whilst  $\gamma$ -triazopropylurethane gives the  $\gamma$ -triazopropylamine recently described by Forster and Withers (*Trans.*, 1912, 101, 490). The *picrate* forms golden-yellow prisms from alcohol, m. p. 96°, and the contribution of the triazo group to the molecular refraction ( $M_p$  8.82) is normal. Hydrolysis with strong hydrochloric acid yields trimethylenediamine, whilst the liberated gas contains 1 mol. nitrogen, a small amount of carbon monoxide, but no oxygen or nitrous oxide.

J. C. W.

**Stereochemistry of the Aromatic Series.** EDMUNDO LOZANO (*Anal. Fis. Quim.*, 1912, 10, 81—82).—Polemical against the originality and validity of the formula proposed by Casares (compare *Abstr.*, i, 247).

G. D. L.

**The Configuration of Benzene, the Mechanism of Benzene Substitution, and the Contrast between the Formation of Para-, Ortho-, and of Meta-substitution Products.** JACOB BÖESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 14, 1066—1081).—The author has already pointed out that for the retention of two



homonymous atoms within a molecule, a certain inequality or contrast must be assumed which may possibly be caused by an adverse movement of the corpusculæ. By combining this idea with Werner's fundamental principle of the universal affinity he arrives at the annexed formula for benzene. This shows not only the contrast between the ortho-, para-, and meta-, but also the equality of the two ortho-placed carbon atoms.

The extreme slowness with which benzene undergoes substitution by halogens in the absence of a catalyst is attributed to the small chance of the molecules readily forming additive products of higher potential which will then eliminate halogen acid. Only the case of the formation of hexahalogen benzene compounds results in a condition the potential of which can be smaller than that of a mixture of benzene and halogen. In confirmation of this, van der Linden has noticed that when an insufficiency of halogen is added to benzene, hexahalogen benzene is obtained, which does not contain appreciable quantities of

lower additive products. The rôle of the catalyst in the formation of halogen substitution products of benzene is supposed to depend on its ability to promote the entrance of halogen into the benzene in such a manner that the simplest additive product is first formed.

Generally, a catalyst can cause a modification in the condition of benzene as well as in that of the acting molecule. Should the latter alone be affected, hexahalogen additive products result (action of benzene and halogen under influence of light or hypohalogenic acid). If, however, the benzene molecule is entered by the catalyst, then the second molecule, which may also have been made active, will be able to act there, and the formation of mono-substitution products is to be expected (action of  $\text{FeCl}_3, \text{AlCl}_3$ ). In the cases of nitration and sulphonation of benzene, which occur readily, the velocity is largely dependent on the concentration of the acid, so that it increases at a much greater rate than corresponds with the strength of the acid. Here it is assumed that nitrogen pentoxide and sulphur trioxide act as catalysts.

In considering the further substitution of mono-substituted derivatives of benzene, the author points out that two influences are operative, namely, the disturbance of equilibrium in the benzene molecule occasioned by the substituent already present, and the affinity of the group present towards the entering molecule. He distinguished three general cases: (1) The affinity of the entering molecule ( $B$ ) for the substituent present ( $X$ ) is very great.  $B$  will then act in the first place on  $X$ , and be retained therein, after which action ceases (reduction of the nitro-group, oxidation of the  $-\text{SH}$ -group, etc.). (2) The affinity of the acting molecule  $B$  for  $X$  is less considerable, so that, at most, labile additive products can be retained. The group  $B$  will then further accentuate the disturbance of the equilibrium caused by  $X$ , and the molecule enter into the nucleus in the ortho-para-position (chlorination of sulphides, amides, bromides, iodides; hydrogenation of phthalic and terephthalic acids, etc.). (3) The affinity of the acting molecule  $B$  for  $X$  is not present.  $X$  will then oppose the addition and substitution in the ortho-para-position, so that the influence of the disturbance of the equilibrium can be lessened or destroyed by this adverse action, thus the  $m$ -substitution can become predominant (nitration, sulphonation, and chlorination of nitro-compounds, sulphonic and carboxylic acids, hydrogenation of amino- and hydroxy-compounds). H. W.

**New Method for the Preparation of Hydrocarbons of the Styrene Group. I. Allylbenzene and its Homologues.** FRANZ KUNCKELL [and WILHELM DETTMAR] (*Ber. Deut. Pharm. Ges.*, 1912, 22, 180—199).—The paper consists of a re-statement of earlier results (Kunckell and Dettmar, *Abstr.*, 1903, i, 331; Kunckell, *Abstr.*, 1903, i, 617), together with some further details as to derivatives of the products.

Propenylbenzene gives  $\alpha\beta$ -dibromo propenylbenzene,  $\text{CHPhBr}\cdot\text{CHMeBr}$ , colourless needles, m. p. 66—67°. The action of alcoholic potash on  $\alpha$ -chloro- $\beta$ -bromopropenylbenzene apparently removes the elements of hydrogen chloride, giving a substance of unknown constitution, b. p. 232—238°, 122—130°/19 mm.

1-Methyl-4- $\alpha$ -dibromopropylbenzene is a colourless, oily liquid, b. p. 140—143°/10 mm.,  $D^{18}$  1.609; the nitrosochloride is a colourless solid, m. p. 135°.

1-Ethyl-4- $\alpha$ -dibromopropylbenzene has b. p. 162—165°/16 mm.,  $D^{18}$  1.574.

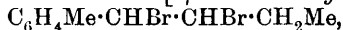
1-isoPropyl-4- $\alpha$ -dibromopropylbenzene has b. p. 169—172°/20 mm.,  $D^{18}$  1.512.

1-Methyl-4-iso-propyl-3- $\alpha$ -dibromopropylbenzene has b. p. 167—170°/19 mm.,  $D^{18}$  1.432.

1:2-Dimethyl-4- $\alpha$ -dibromopropylbenzene has b. p. 165—168°/16 mm.,  $D^{18}$  1.591. D. F. T.

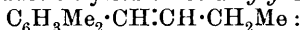
**New Method for the Preparation of Hydrocarbons of the Styrene Group. II.  $\alpha$ -Phenyl- $\Delta^{\alpha}$ -butylene and Its Homologues.** FRANZ KUNCKELL (*Ber. Deut. Pharm. Ges.*, 1912, 22, 242—251). —A recapitulation and extension of the results obtained in the preparation of derivatives of  $\alpha$ -phenyl- $\Delta^{\alpha}$ -butylene from phenyl propyl ketone derivatives (compare Kunckell and Siecke, *Abstr.*, 1903, i, 331; Kunckell, *Abstr.*, 1903, i, 617).

$\alpha$ -p-Tolyl- $\Delta^{\alpha}$ -butylene dibromide [ $\alpha\beta$ -dibromobutyltoluene],



is a pale yellow oil, b. p. 164—167°/18 mm.; the corresponding dichloride is a pale yellow liquid, b. p. 261—266°, or 124—129°/6 mm.; additive compound, with hydrogen chloride, a reddish-yellow oil; nitrosochloride, crystalline scales, m. p. 148° (decomp.).

*o*-, *m*-, and *p*-Xylene each give a set of derivatives. Three xyl- $\alpha$ -bromopropyl ketones,  $C_6H_3Me_2 \cdot CO \cdot CHBr \cdot CH_2Me$ , were obtained: 1:2:4, a liquid of irritating odour, b. p. 157—160°/8 mm.; 1:3:4, b. p. 167—172°/17 mm.; 1:4:3, b. p. 159—161°/16 mm. Three  $\alpha$ -chloro- $\beta$ -bromo- $\alpha$ -xyl- $\Delta^{\alpha}$ -butylenes,  $C_6H_3Me_2 \cdot CCl \cdot CBr \cdot CH_2Me$ : 1:2:4, colourless liquid of strong aromatic odour, b. p. 154—160°/17 mm.; 1:3:4, b. p. 144—154°/20 mm.; 1:4:3, b. p. 150—155°/16 mm. These by reduction yield three  $\alpha$ -xyl- $\Delta^{\alpha}$ -butylenes,



1:2:4, an oil with aniseed odour, b. p. 238—239°, 122—124°/18 mm.,  $D^{15}$  0.9114,  $n^{20}$  1.5458, dibromide, pale yellow oil, b. p. 155—157°/6 mm.; 1:3:4, colourless, aromatic liquid, b. p. 226—228°, or 109—111°/16 mm.,  $D^{18}$  0.8967,  $n^{20}$  1.5349, dibromide, pale yellow liquid, b. p. 167—169°/15 mm.; 1:4:3, liquid of aromatic odour, b. p. 221°, or 117—120°/17 mm.,  $D^{18}$  0.8958,  $n^{20}$  1.5280, dibromide, colourless leaflets, m. p. 75°, b. p. 166—168°/16 mm.

Ethylbenzene gives *p*-ethylphenyl  $\alpha$ -bromopropyl ketone, a very pale yellow liquid, b. p. 152—154°/7 mm.;  $\alpha$ -chloro- $\beta$ -bromo- $\alpha$ -*p*-ethylphenyl- $\Delta^{\alpha}$ -butylene, b. p. 140—145°/6 mm., and  $\alpha$ -*p*-ethylphenyl- $\Delta^{\alpha}$ -butylene, a colourless liquid of aniseed odour, b. p. 230—233°, or 98—102°/7 mm.,  $D^{20}$  0.9074,  $n^{20}$  1.5405; the dibromide of the last substance is almost colourless, b. p. 146—149°/6 mm.

Cumene gives  $\alpha$ -*p*-isopropylphenyl  $\alpha$ -bromopropyl ketone, b. p. 153—160°/8 mm.;  $\alpha$ -chloro- $\beta$ -bromo- $\alpha$ -*p*-isopropylphenyl- $\Delta^{\alpha}$ -butylene, a pale yellow oil, b. p. 145—155°/8 mm., and  $\alpha$ -*p*-isopropylphenyl- $\Delta^{\alpha}$ -butylene, a yellow oil, b. p. 242—243°, or 131—139°/17 mm.,  $D^{14}$  0.8932,  $n^{20}$  1.5330; the last-named gives a dibromide, b. p. 152—157°/10 mm.

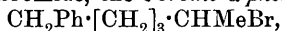
Cymene gives 3-methyl-6-isopropylphenyl  $\alpha$ -bromopropyl ketone, b. p. 152—155°/8 mm.;  $\alpha$ -chloro- $\beta$ -bromo- $\alpha$ -3-methyl-6-isopropylphenyl- $\Delta^{\alpha}$ -butylene, b. p. 152—159°/16 mm., and  $\alpha$ -3-methyl-6-isopropylphenyl- $\Delta^{\alpha}$ -butylene, a pale yellow liquid, b. p. 241—244°,  $D^{14}$  0.9353,  $n^{20}$  1.5274; the dibromide of the last has b. p. 150—152°/7 mm. D. F. T.

**New Applications of the Grignard Reaction.** JULIUS VON BRAUN, H. DEUTSCH, and A. SCHMATLOCH (*Ber.*, 1912, 45, 1246—1263).—It has already been observed that the conversion of phenoxyated iodides of the type  $C_6H_5 \cdot O \cdot (CH_2)_x \cdot I$  into phenoxyolefines by way of the quaternary ammonium iodides and the ammonium hydroxides does not proceed smoothly when the chain X has more than six members (compare Abstr., 1907, i, 28). It is now found that when the iodine is sufficiently removed from the phenol nucleus, the iodides give true Grignard compounds, which furnish the desired olefines when treated with allyl bromide, a reaction similar to that discovered by Tiffeneau, namely, that magnesium phenyl bromide and allyl bromide readily yield allylbenzene.

Two of the lowest members of the series, bromophenetole (Grignard, Abstr., 1904, i, 494) and  $\gamma$ -phenoxypropyl iodide, do not react in the normal way with magnesium, but already with  $\delta$ -phenoxybutyl iodide 70% of the substance does react, yielding with water *n*-phenoxybutane, 1 : 8-diphenoxyoctane also being formed by the synthetic action of the metal. Similarly,  $\epsilon$ -phenoxyamyl iodide furnishes *phenoxy-pentane*,  $C_6H_5 \cdot O \cdot [CH_2]_4 \cdot CH_3$ , a pleasant smelling oil, b. p. 111°/17 mm., volatile in steam, and non-volatile  $\alpha\kappa$ -diphenoxydecane,  $OPh \cdot [CH_2]_{10} \cdot OPh$ , m. p. 86°, whilst the action of oxygen on the magnesium compound produces  $\epsilon$ -phenoxyamyl alcohol,  $OPh \cdot [CH_2]_5 \cdot OH$ , as a glycerol-like liquid, b. p. 150—155°/11 mm., which gives an oily benzoyl derivative and a well-defined *phenylurethane*,  $OPh \cdot [CH_2]_5 \cdot O \cdot CO \cdot NHPh$ , m. p. 93°. The same magnesium compound reacts with trioxymethylene to give  $\zeta$ -phenoxyhexyl alcohol, a similar syrupy liquid, b. p. 175°/13 mm., the *phenylurethane*,  $C_{19}H_{23}ON_3$ , of which melts at 102°, but with ethylene chlorohydrin, however, it only yielded traces of phenoxyheptyl alcohol. Attempts to convert these Grignard compounds into acetals and thus into aldehydes by means of ethyl orthoformate have not succeeded, but the nitro-method which led to aliphatic dialdehydes and fatty-aromatic aldehydes (compare Abstr., 1911, i, 830; 1912, i, 265) may prove useful in the case of these iodides. From  $\gamma$ -phenoxypropyl iodide and silver nitrite,  $\gamma$ -nitro- $\alpha$ -phenoxypropane  $OPh \cdot [CH_2]_3 \cdot NO_2$ , is obtained as a pale yellow, pleasant smelling liquid, b. p. 171—177°/17 mm., which on reduction yields *phenoxypropionaldoxime*,  $OPh \cdot [CH_2]_3 \cdot CH : NOH$ , m. p. 142°;  $\epsilon$ -nitro- $\alpha$ -phenoxy-pentane,  $OPh \cdot [CH_2]_5 \cdot NO_2$ , b. p. 203—209°/16 mm., and *phenoxyvaleraldoxime*,  $OPh \cdot [CH_2]_4 \cdot CH : NOH$ , m. p. 112—113°, are prepared in the same way.

Tiffeneau's application of allyl bromide, which has also been made use of by de Rességuier in the preparation of allylcyclohexane (Abstr., 1910, i, 467), has now been extended to a variety of magnesium-halogen compounds, and is shown to be very valuable in the building up of aromatic compounds with long side-chains. Besides the allyl products,  $X \cdot C_3H_5$ , which are often produced in 70% yields, condensed hydrocarbons,  $X \cdot X$ , are also formed. Octyl bromide gives

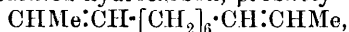
undecylene and hexadecane;  $\alpha\epsilon$ -di-iodopentane gives undecadiene, recently described by Reformatzky (Abstr., 1911, i, 597), oxidation to azelaic acid confirming the position of the unsaturated linking;  $\alpha\delta$ -di-iodobutane yields  $\Delta^{\alpha\delta}$ -decadiene,  $\text{CH}_2\text{:CH}\cdot[\text{CH}_2]_6\text{:CH:CH}_2$ , a sweet smelling liquid, b. p.  $170^\circ$ , which appears to be identical with the hydrocarbon from decamethylenebis(trimethylammonium) hydroxide (this vol., i, 165). In the same way phenylethyl bromide gives phenylamylene (Abstr., 1911, i, 613), the position of the ethenoid linking being shown by the fact that only after prolonged heating with saturated hydrobromic acid does addition take place, the resulting  $\delta$ -bromo- $\alpha$ -phenylpentane,  $\text{C}_6\text{H}_5\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{Br}$ , b. p.  $137\text{--}139^\circ/13\text{ mm.}$ , differing from the isomeric  $\epsilon$ -phenylamyl bromide (this vol., i, 106) in that it has a much less intense odour. The bromine atom is only exchanged for cyanogen after heating with potassium cyanide for many days; the nitrile,  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CN}$ , is a colourless, faintly smelling liquid, b. p.  $150\text{--}154^\circ$  in vacuum, which hydrolyses with difficulty to  $\delta$ -phenyl- $\alpha$ -methylvaleric acid,  $\text{C}_6\text{H}_5\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , b. p.  $178^\circ/8\text{ mm.}$ , giving a white silver salt, but not crystallising (compare Abstr., 1911, i, 969:  $\epsilon$ -phenylhexoic acid). From phenylpropyl bromide, magnesium and allyl bromide, the very pleasant smelling phenylhexylene,  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_3\text{:CH:CH}_2$ , is obtained, b. p.  $94\text{--}95^\circ/10\text{ mm.}$ ,  $D_4^{20} 0.8839$ ,  $n_D^{20} 1.5033$ . With similar difficulty it unites with hydrogen bromide, the  $\epsilon$ -bromo- $\alpha$ -phenylhexane,



boiling at  $152\text{--}156^\circ/10\text{ mm.}$ , and yielding a magnesium compound which decomposes with trioxymethylene, giving  $\zeta$ -phenyl- $\beta$ -methylhexyl alcohol,  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$ , b. p.  $160\text{--}163^\circ/13\text{ mm.}$ , which has a sweet odour, more intense than that of phenylheptyl alcohol and more pleasant than that of  $\zeta$ -phenylhexyl alcohol. Phenylamyl bromide,  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{CH}_2\text{Br}$ , b. p.  $144^\circ/12\text{ mm.}$ , from  $\epsilon$ -phenylamyl alcohol and hydrobromic acid, gives a somewhat poorer yield of phenyloctylene,  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_5\text{:CH:CH}_2$ , a pleasant smelling, colourless liquid, b. p.  $115\text{--}117^\circ/8\text{ mm.}$ ,  $D_4^{20} 0.8792$ ,  $n_D^{20} 1.4995$ . From  $\delta$ -phenoxybutyl iodide, besides some diphenoxyoctane, phenoxyheptene,  $\text{OPh}\cdot[\text{CH}_2]_5\text{:CH:CH}_2$ , is obtained; this readily absorbs bromine, the somewhat unstable dibromide being hydrolysed with difficulty by means of fuming hydrobromic acid, yielding  $\alpha\beta\eta$ -tribromoheptane,  $\text{CH}_2\text{Br}\cdot[\text{CH}_2]_4\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$ , a colourless liquid having a pleasant, spicy odour and boiling at  $150\text{--}155^\circ/8\text{ mm.}$  Similarly, phenoxyoctene,  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_5\text{:CH:CH}_2$ , from  $\epsilon$ -phenoxyamyl iodide, may be converted into  $\alpha\beta\theta$ -tribromo-octane,  $\text{CH}_2\text{Br}\cdot[\text{CH}_2]_5\cdot\text{CHBr}\cdot\text{CH}_2\text{Br}$ , b. p.  $160^\circ/10\text{ mm.}$

These tribromo-paraffins, like  $\alpha\beta\epsilon$ -tribromohexane (Abstr., 1911, i, 938), react with magnesium, losing the neighbouring bromine atoms and yielding unsaturated magnesium compounds, but the conversion of these into unsaturated iodides by means of iodine is unsatisfactory, the ethenoid linking absorbing the halogen to a great extent. It is now found, however, that iodoacetonitrile brings about the desired change and that it reacts generally like the free element, converting, for example, bromobenzene into iodobenzene and phenylpropyl bromide into phenylpropyl iodide, b. p.  $118\text{--}123^\circ/10\text{ mm.}$ , which is characterised by conversion into phenylbutyronitrile (Abstr., 1910, i, 843), and into

phenylbutyric acid itself. In the case of  $\alpha\beta\epsilon$ -tribromohexane, a certain amount of an unsaturated hydrocarbon, probably



is obtained, but the presence of iodoheptylene,  $\text{CHMe}:\text{CH}:[\text{CH}_2]_2:\text{CH}_2\text{I}$ , is shown by its conversion in the crude state into a nitrile and then into  $\Delta^5$ -heptenoic acid,  $\text{CH}_3:\text{CH}:\text{CH}:[\text{CH}_2]_3:\text{CO}_2\text{H}$ . The formation of iodoheptylene from  $\alpha\beta\gamma$ -tribromoheptane is also proved by treating the crude product with trimethylamine, when, besides a small amount of *trimethylcyanomethylammonium iodide*,  $\text{NMe}_3\text{I}:\text{CH}_2:\text{CN}$ , m. p.  $196^\circ$ , from unchanged iodoacetoneitrile, the recently described trimethyl- $\Delta^5$ -heptenylammonium iodide (Abstr., 1912, i, 165) is obtained; this confirms the position of the three bromine atoms, and hence of the ethylene linking in phenoxyheptene. For synthetic purposes it appears unnecessary to isolate the unsaturated iodide from the crude product.

J. C. W.

**The Action of Aluminium Chloride on the Homologues of Benzyl Chloride.** JULIUS VON BRAUN and H. DEUTSCH (*Ber.*, 1912, 45, 1267—1274).—Inspired by Kipping's discovery that fatty-aromatic acid chlorides produce cyclic ketones under the influence of aluminium chloride (see *Trans.*, 1894, 65, 480; 1899, 75, 144; 1901, 79, 602), the authors have tried the action of this reagent on their oxygen-free fatty-aromatic chlorides, with the hope of finding the conditions for ring formation. They have found that the substitution of  $-\text{CH}_2$  for  $-\text{CO}$  in the side-chain is of enormous influence, considerably diminishing the tendency to the formation of benzene derivatives of five- or seven-membered rings.

Phenylbutyl chloride was converted by this means into pure tetrahydronaphthalene previously obtained from naphthalene in a less pure form by Bamberger and Kitschelt (Abstr., 1890, 1146); contrary to this earlier notice, it was found to have an odour like hydrindene, did not change in the air, nor decolorise bromine, and was only slowly attacked by permanganate; b. p.  $205^\circ$ ,  $D_4^{20}$  0.957,  $n_D^{20}$  1.5370. Phenylpropyl chloride, however, gave only a trace of hydrindene, although phenylpropionyl chloride is converted to the extent of 95% into  $\alpha$ -hydrindone (Thiele and Wanscheidt, Abstr., 1910, i, 831); the chief product, which is not volatile in steam, is a viscid, chlorine-free, red oil, probably a combination of several molecules of the chloride with elimination of hydrogen chloride. A mixture of such compounds is the only result in the case of phenylethyl chloride. Phenylamyl chloride in light petroleum or carbon disulphide solution is converted into a similar mixture (35%), but chiefly into a peppermint-like oil which distilled in steam (60%); potassium permanganate removed a small amount of unsaturated hydrocarbons from this, leaving phenylcyclopentane (compare Borsche and Menz, Abstr., 1908, i, 149). In benzene solution, however, the portion not volatile in steam was not a complicated mixture, but  $\alpha\epsilon$ -diphenylpentane,  $\text{CH}_2(\text{CH}_2:\text{CH}_2\text{Ph})_2$ , a glycerol-like liquid, b. p.  $190$ — $200^\circ/12$  mm. The formation of phenylcyclopentane, the constitution of which is confirmed by oxidation to benzoic acid and not to phthalic acid, as the latter would agree with benzosuberane, is a case in which aliphatic hydrogen is removed in an

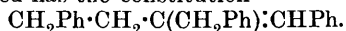
elimination of hydrogen chloride, and instances a new course of the Friedel and Craft's reaction. That the *cyclopentane* ring does not hinder substitution in the benzene ring is shown by the formation of *p*-(?)-nitrophenylcyclopentane,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_5\text{H}_9$ , a yellow oil with pleasant odour, b. p. 162—169°/13 mm. J. C. W.

**Electrolytic Reduction of Nitrobenzene without a Diaphragm.** E. F. FARNAU (*J. Physical Chem.*, 1912, 16, 249—252. Compare Snowdon, this vol., i, 100).—Snowdon's method of electrolyzing an emulsion of nitrobenzene between iron electrodes when carried out at ordinary temperatures (25°, rising to 35°) with sodium sulphate solution as electrolyte instead of ferrous chloride gives a good yield of aniline.

Both cathodic hydrogen and ferrous sulphate act as reducing agents. In the author's experiments the reduction was not carried to completion, and the average current efficiency calculated on the aniline produced was 78%. It is stated that no reduction product other than aniline was obtained, but about 12% of the nitrobenzene was unaccounted for. R. J. C.

**Nitration of *o*-Tolyl *p*-Toluenesulphonate.** FRÉDÉRIC REVERDIN (*Bull. Soc. chim.*, 1912, [iv], 11, 447; *Ber.*, 1912, 45, 1450).—In a previous paper with P. Crépieux (*Abstr.*, 1902, i, 435), the author described *o*-tolyl *p*-toluenesulphonate as yielding on nitration 3:5-dinitro-*o*-tolyl *p*-toluenesulphonate, m. p. 108—109°. He now finds that the substance so described was really 5-nitro-*o*-tolyl 2-nitro-*p*-toluenesulphonate (compare Ullmann and Sané, this vol., i, 104). T. A. H.

**Unsaturated Compounds. I. Elimination of Hydrogen Chloride from Unsymmetrical Carbinyl Chlorides.** ALEX. ORECHOFF and R. KONOWALOFF (*Ber.*, 1912, 45, 861—865).—On elimination of hydrogen chloride from dibenzylphenylethylcarbinyl chloride,  $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{CCl}(\text{CH}_2\text{Ph})_2$ , by heating with pyridine, the formation of two unsaturated hydrocarbons is possible. By oxidation of the product with ozone, benzaldehyde is obtained, proving that the hydrocarbon obtained has the constitution



The nearest phenyl radicle in this case has the strongest displacing influence on the hydrogen of the methylene group. It is proposed to test whether this is a general rule.

*Dibenzylphenylethylcarbinol*, prepared by the interaction of ethyl phenylpropionate with benzyl chloride and ether, crystallises in small, colourless needles, m. p. 62—63°.

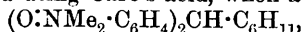
*Dibenzylphenylethylcarbinyl chloride*, obtained by the action of dry hydrogen chloride on the carbinol dissolved in ether, forms colourless needles, m. p. 108°.

*$\beta$ -Phenyl- $\alpha$ -benzyl- $\alpha$ -phenylethylethylene* [ *$\alpha\delta$ -Diphenyl- $\beta$ -benzyl- $\Delta^{\alpha}$ -butylene*] crystallises in well-formed, colourless needles in stellate aggregates, m. p. 57—58°. E. F. A.

**Hexahydrotriphenylmethane and its Derivatives.** JULIUS SCHMIDLIN and ROBERT VON ESCHER (*Ber.*, 1912, 45, 889—899).—Hexahydrotriphenylmethane [diphenylcyclohexylmethane] is obtained by reduction of hexahydrotriphenylcarbinol or from diphenylcyclohexylidenemethane. The hydroxyl group of hexahydrotriphenylcarbinol is very mobile, but substitution is prevented by the proximity of the cyclohexane ring; in such cases, water is eliminated and diphenylcyclohexylidenemethane obtained. No carbinyl chloride could be isolated after the mild action of hydrogen chloride. When hydrogen chloride is allowed to act directly on the unsaturated hydrocarbon or on the carbinol at a higher temperature, diphenylchlorocyclohexylmethane,  $\text{CHPh}_2 \cdot \text{CCl} < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{CH}_2$ , isomeric with the carbinol chloride is readily obtained. The instability of the carbinol chloride points to a similar instability in the dyes derived from hexahydrotriphenylmethane.

To prepare hexahydroleucomalachite-green (Zelinsky and Gutt, *Abstr.*, 1907, i, 709), magnesium cyclohexyl bromide is caused to react with *p*-dimethylaminobenzaldehyde, and the *p*-dimethylaminophenylcyclohexylcarbinol formed (Schmidlin and Escher, *Abstr.*, 1908, i, 163) is condensed with dimethylaniline.

Crystalline oxidation products of hexahydroleucomalachite-green could only be obtained using Caro's acid, when a dioxide,



is formed.

On oxidation in acetic acid solution with very little lead peroxide or ozone, a fairly marked bluish coloration is produced, which in time vanishes, particularly on the addition of mineral acids.

*Diphenylcyclohexylmethane* forms prismatic crystals, m. p. 56.5°.

*Diphenylchlorocyclohexylmethane* crystallises in colourless leaflets, m. p. 120—122° (corr.).

*Diphenylbromocyclohexylmethane* separates in colourless, lustrous crystals, m. p. 125° (corr.).

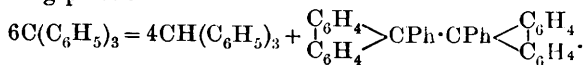
The dioxide of hexahydroleucomalachite-green crystallises in lustrous, colourless plates, m. p. 165° (corr.).

*p*-Methoxyphenylcyclohexylcarbinol,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{C}_6\text{H}_{11}$ , prepared from bromocyclohexane, magnesium, and anisaldehyde, forms long, colourless needles, m. p. 92° (corr.).

*p*-Methoxyphenylcyclohexylcarbinyl chloride separates in crystals, m. p. 104° (corr.); when boiled with water, it is converted into the carbinol.

E. F. A.

**Autoreduction of Triphenylmethyl under the Action of Light.** JULIUS SCHMIDLIN and ANTONIO GARCIA-BANÚS (*Ber.*, 1912, 45, 1344—1350).—Complete decolorisation occurs when a benzene solution of pure triphenylmethyl is exposed to diffused light, quantitative decomposition into triphenylmethane and diphenyldi-biphenylene-ethane taking place:



The reaction appears to depend on the reduction of hexaphenylethane to diphenyldi-biphenylene-ethane by the triphenylmethyl. Complete decolorisation is only observed when pure triphenylmethyl is employed. When heat or impure metal is used in the preparation of the latter substance, yellow impurities, stable towards light, are readily introduced.

Pure triphenylmethyl dissolved in benzene was exposed to light during forty-five days. The colourless solution had deposited crystals of diphenyldi-biphenylene-ethane, which were filtered and exposed to air in benzene solution, whereby phenyldiphenylenecarbonyl peroxide,  $C_{38}H_{26}O_2 \cdot 2C_6H_6$ , m. p.  $209^\circ$  (corr.), was obtained, the identity of which was proved by comparison with phenyldiphenylenecarbonyl peroxide obtained from phenyldiphenylenecarbinol. The mother liquor yielded triphenylmethane, together with a small additional quantity of diphenyldi-biphenylene-ethane. Solutions of triphenylmethyl remained unchanged when preserved in the dark during three months.

Triphenylmethyl, when heated during forty-eight hours in xylene solution, yielded triphenylmethane, together with a large quantity of a non-crystalline, fluorescent, yellow substance. When heated in benzene solution at  $100^\circ$  during four months, it yielded only crystalline products, chiefly a substance, m. p.  $165^\circ$ , which is coloured red by concentrated sulphuric acid. No triphenylmethane could be detected.

H. W.

**The Behaviour of Monohalogenanilines.** OTTO FISCHER and PETER NEBER (*Ber.*, 1912, 45, 1093—1098).—The behaviour of *o*-chloroaniline is in many respects peculiar. With regard to the formation of benzylidene compounds, and the action of nitrous acid on *o*-halogenmono-methylanilines or *o*-chloroacetanilide, however, these substances behave similarly to, for example, *m*-chloroaniline.

By the condensation of *o*-chloroaniline with the respective aldehydes, the following derivatives were obtained: benzylidene-*o*-chloroaniline, m. p.  $33\text{--}34^\circ$ ; *o*-hydroxybenzylidene-*o*-chloroaniline, m. p.  $79^\circ$ ; *p*-hydroxybenzylidene-*o*-chloroaniline, m. p.  $162^\circ$ ; *o*-nitrobenzylidene-*o*-chloroaniline, m. p.  $111^\circ$ ; *p*-nitrobenzylidene-*o*-chloroaniline, m. p.  $121^\circ$ ; *p*-methoxybenzylidene-*o*-chloroaniline, m. p.  $58^\circ$ ; from *o*-bromoaniline were obtained *o*-hydroxybenzylidene-*o*-bromoaniline, m. p.  $84^\circ$ , and *p*-hydroxybenzylidene-*o*-bromoaniline, m. p.  $162^\circ$ .

*o*-Chloro-*N*-nitrosoacetanilide, m. p.  $47^\circ$ , was prepared by passing nitrous fumes into a well-cooled solution of *o*-chloroacetanilide in glacial acetic acid.

*o*-Chloroaniline was treated successively with methyl sulphate and nitrous acid. The oily nitrosoamine, when acted on by concentrated hydrochloric acid, was transformed into *o*-chloro-*p*-nitrosomethylaniline, m. p.  $131\text{--}132^\circ$ , which gave *o*-chloro-*p*-nitrosophenol, m. p.  $148^\circ$  (decomp.), when heated with sodium hydroxide. *o*-Bromoaniline, when similarly treated, yielded *o*-bromo-*p*-nitrosomethylaniline, m. p.  $104^\circ$ . Similarly, from *m*-chloroaniline, *m*-chlorophenylmethylnitrosoamine, m. p.  $37\text{--}38^\circ$ , was prepared, which was transformed into *m*-chloro-*p*-nitrosomethylaniline, m. p.  $134\text{--}136^\circ$  (decomp.), by the action of cold hydrochloric acid.

H. W.

**The Nitrosoamine Rearrangement with Hydrobromic Acid.** OTTO FISCHER [with HANS GROSS] (*Ber.*, 1912, 45, 1098—1103).—Nitrosoamines are converted into *p*-nitroso-bases by means of hydrochloric acid in alcoholic, aqueous, or glacial acetic acid solution. It is advisable to choose that solvent in which the hydrochloride of the nitroso-base is least soluble. Disturbing factors arise through the oxidation of the eliminated nitric oxide by means of air, and the reaction of the nitrogen peroxide with hydrochloric acid, resulting in the liberation of chlorine and the formation of chlorinated by-products. These disturbing influences are more marked when hydrobromic acid is substituted for hydrochloric acid.

A cold ethereal solution of phenylmethylnitrosoamine, when acted on by an alcoholic solution of hydrobromic acid, precipitated the hydrobromides of methylaniline, *p*-nitrosomethylaniline, *p*-bromomethylaniline, and *o*-*p*-dibromomethylaniline, the latter in very small quantity, whilst the mother liquor contained phenylmethylnitrosoamine, *p*-bromophenylmethylnitrosoamine, together with the hydrobromides of methylaniline, *p*-bromomethylaniline, and *p*-nitrosomethylaniline. Larger quantities of the above-mentioned *o*-*p*-dibromomethylaniline can be obtained when phenylnitrosoamine is added to a well-cooled aqueous solution of hydrobromic acid (D 1.78). *o*-*p*-Dibromophenylmethylnitrosoamine has m. p. 50°.

If the para-position in the nitrosoamine be already occupied, an almost quantitative transformation into the secondary base can be brought about by hydrobromic acid; thus *p*-bromophenylmethylnitrosoamine yields *p*-bromomethylaniline.

Diphenylnitrosoamine, when dissolved in a mixture of alcohol and ether and treated with alcoholic hydrobromic acid, yielded diphenylamine and di-*p*-bromodiphenylamine. H. W.

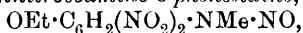
**Action of Methyl Iodide and Alkali on *p*-Nitrosodimethylaniline.** OTTO FISCHER and EDUARD HEPP (*Ber.*, 1912, 45, 1103—1104).—Contrary to the statement of von Pechmann and Seel (*Abstr.*, 1898, i, 309), the authors find that tetramethyldiaminoglyoxime *N*-phenyl ether is formed when the methiodide of *p*-nitrosodimethylaniline is treated with sodium hydroxide. H. W.

**Action of Concentrated Sulphuric Acid on Some Aromatic Nitrosamines.** III. FRÉDÉRIC REVERDIN and FRANZ LIEBL (*Arch. Sci. phys. nat.*, 1912, [iv], 33, 332—338.\* Compare *Abstr.*, 1910, i, 255; 1911, i, 123).—With the object of determining whether the reduction of secondary nitroamines to nitrosoamines by sulphuric acid is general, derivatives of *o*- and *p*-phenetidine have been prepared. These readily undergo oxidation, so although the formation of nitrosoamines does indeed take place, the yields are very poor, being much less than in the former cases. The course of the reaction is not clear, although the liberation of carbon dioxide, oxygen, nitrogen, and sometimes oxides of nitrogen would suggest a complete destruction of part of the substance; slight changes in the experimental conditions modify the result to such an extent that comparative studies are well-nigh impossible. It may be that the nitro-group is set free to oxidise a part of the molecule

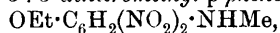
\* and *Bull. Soc. chim.*, 1912, [iv], 11, 485—490.

and then becomes fixed as a nitroso-group, for it is found that such resistant nitroamines as the highly oxidised trinitromethylnitroaniline scarcely react, whilst in the case of those nitroamines which are only slightly substituted, the nitro-group is free to wander in the nucleus and the formation of nitrosoamines is likewise avoided.

*Dimethyl-o-phenetidine*,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$ , is obtained as a colourless oil by the action of hot methyl sulphate on *o*-phenetidine. It boils at  $218\text{--}220^\circ$ , has a characteristic odour, and becomes pink in the light. Concentrated nitric acid converts it into Blanksma's 3 : 5-dinitromethylnitroamino-*o*-phenetidine (Abstr., 1905, i, 431), from which phenol removes the *N*-nitro-group, producing 3 : 5-dinitromonomethyl-*o*-phenetidine (Blanksma, *loc. cit.*). This secondary amine yields with nitrous acid, 3 : 5-dinitromethylnitrosoamino-*o*-phenetidine,



which crystallises from alcohol in yellow needles, m. p.  $71^\circ$ . The nitroamine forms a green solution in a little cold sulphuric acid, giving the same nitrosoamine (20% yield), accompanied by a small quantity of the dinitromethyl-*o*-phenetidine, only the latter being recovered when excess of acid is used, or the temperature is allowed to rise. Methyl sulphate also methylates *p*-phenetidine, yielding Knorr's dimethyl-*p*-phenetidine (Abstr., 1897, i, 108), which cold concentrated nitric acid converts into 3 : 5-dinitromethylnitroso-*p*-phenetidine,  $\text{OEt}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{NMe}\cdot\text{NO}$ . This separates in shining leaflets, m. p.  $108^\circ$ , and is oxidised by fuming nitric acid to 3 : 5-dinitromethylnitroamino-*p*-phenetidine,  $\text{OEt}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2\cdot\text{NMe}\cdot\text{NO}_2$ , which crystallises in pale yellow needles from alcohol, m. p.  $95^\circ$ , and furnishes with phenol, 3 : 5-dinitromethyl-*p*-phenetidine,



in jagged, dark red crystals, m. p.  $98^\circ$ , the position of the nitro-groups being confirmed by the formation of a *m*-diamine. The nitroamine dissolves in cold sulphuric acid with an intense red colour, yielding the nitrosoamine; these characteristic colours serve to detect the presence of small traces of nitroamines in impure nitrosoamines. J. C. W.

**A New Method of Preparing Thiocarbimides.** LUDWIG KALUZA (*Monatsh*, 1912, 33, 363—371. Compare Andreasch, Abstr., 1907, 1, 233; Kalaza, Abstr., 1910, i, 130).—Good yields of thiocarbimides are obtained by the interaction of ethyl chloroformate and the potassium or ammonium salts of alkyl (or aryl) dithiocarbamic acids. Symmetrical di-substituted carbamides are formed at the same time, the removal of which is impossible in certain cases.

Methylthiocarbimide, m. p.  $35^\circ$ , b. p.  $118^\circ$ , and ethylthiocarbimide were obtained in yields of 78—85% by the interaction of ethyl chloroformate with potassium methylthiocarbamate and potassium ethylthiocarbamate respectively. In each case, only traces of the corresponding carbamide derivatives were present. Phenylthiocarbimide and *o*- and *p*-tolylthiocarbimides were similarly prepared, but contained 12—25% of disubstituted carbamide derivatives, from which they could not be satisfactorily separated. In the cases of the tolylthiocarbimides these impurities were identified as di-*o*-tolylcarbamide, m. p.  $251^\circ$ , and di-*p*-tolylcarbamide, m. p.  $263^\circ$ . Andreasch (*loc. cit.*) has shown that phenylthiocarbimide deposits diphenylcarbamide.

[With R. HAID.]—*o*-Anisylthiocarbimide was readily obtained from ethyl chloroformate and ammonium *o*-anisylthiocarbamate. It deposits di-*o*-anisylcarbamide when preserved for some time.

$\alpha$ -Naphthylthiocarbimide, m. p.  $58^{\circ}$ , and  $\beta$ -naphthylthiocarbimide, m. p.  $62$ — $63^{\circ}$ , were similarly obtained in yields of 85—86% and 88% respectively. The small amounts of *s*-dinaphthylcarbamide simultaneously formed were readily removed by recrystallisation from alcohol.

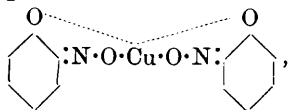
H. W.

Catalysis of Cyclic Alcohols by the Wet Way by means of Sulphuric Acid; Preparation of *cyclo*Hexenes. JEAN B. SENDERENS (*Compt. rend.*, 1912, 154, 1168—1170. Compare this vol., i, 331).—*cyclo*Hexanol and its homologues may be converted into the corresponding unsaturated hydrocarbons by distillation with 3—4% of their volume of sulphuric acid. The yields are not so good as those obtained in the dry way, but the method is more convenient. *cyclo*-Hexanol gave 89% of the theoretical yield of hydrocarbon.

On distilling menthol with 1—2% of its volume of sulphuric acid, menthene was obtained in the same yield as that given by the dry catalytic method (compare this vol., i, 406). As the use of 4—5% of the acid, diluted with twice its volume of water, does not diminish the yield, it would appear that the process is strictly catalytic and does not depend on absorption of water by the acid. Anhydrous aluminium sulphate, a good catalyst for menthol in the dry way, is inefficient in the wet method.

W. O. W.

*o*-Nitrosophenol. OSKAR BAUDISCH and NIKOLAUS KARZEFF (*Ber.*, 1912, 45, 1164—1171).—*o*-Nitrophenol was converted into *o*-nitrophenyl *p*-toluenesulphonate, and this reduced by means of hydrogen sulphide and ammonia to the corresponding hydroxylamine compound, which was converted by means of amyl nitrite and ammonia into the ammonium salt of the corresponding nitrosohydroxylamine compound,  $C_6H_4 \cdot SO_2 \cdot O \cdot C_6H_4 \cdot N(NO) \cdot O \cdot NH_4$ . On hydrolysis with boiling sodium hydroxide, sodium *o*-hydroxy-*m*-nitrosophenylhydroxylamine,  $OH \cdot C_6H_4 \cdot N(NO) \cdot ONa$ , is formed. This forms an internally complex copper salt,  $(OH \cdot C_6H_4 \cdot N \begin{smallmatrix} \diagup NO \\ \diagdown O \end{smallmatrix})_2 Cu$ , which dissolves in organic solvents with a bluish-green coloration and crystallises from acetone in pale grey needles. In presence of traces of acid, it becomes deep red, and on precipitation of the red solution with light petroleum an almost black, crystalline precipitate is obtained of a salt:



Reddish-brown fumes of  $N_2O_3$  are evolved during the transformation of the grey into the red copper salt. The calcium salt corresponding with the red salt consists of a deep red crust with a strong greenish-gold reflex, and gives a deep red solution in water. When this is extracted with light petroleum after being made acid with metaphosphoric acid, an emerald-green extract is obtained, which on

evaporation leaves greenish-yellow needles of *o*-nitrosophenol. These have a strong odour, and are very volatile. The *iron* salt forms lustrous, greenish-black crystals; the *cobalt* salt is almost black, but gives red solutions.

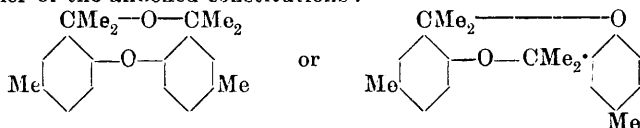
*o*-Nitrosophenol is more quickly prepared by oxidation of *o*-hydroxylaminophenyl *p*-toluenesulphonate with silver oxide to *o*-nitroso-phenyl *p*-toluenesulphonate, which exists in green and colourless modifications, the green form being labile. On boiling with calcium hydroxide, the calcium salt of *o*-nitrosophenol is formed.

*o*-Hydroxylaminophenyl *p*-toluenesulphonate crystallises in snow-white needles, m. p. 112.5°.

The ammonium salt of *o*-nitrosohydroxylaminophenyl *p*-toluenesulphonate has m. p. 119°; it becomes yellow and dirty brown on exposure to the air for a few hours. When decomposed with metaphosphoric acid, *o*-nitrosohydroxylaminophenyl *p*-toluenesulphonate,  $C_6H_4Me \cdot SO_2 \cdot O \cdot C_6H_4 \cdot N(NO) \cdot OH$ , is obtained in colourless crystals, m. p. 76.5°.

*o*-Nitrosophenyl *p*-toluenesulphonate forms green crystals, m. p. 45°, and colourless, lustrous needles, m. p. 87.5–88.5°. E. F. A.

**Condensation Products of *m*- and *p*-Cresol with Acetone.** THEODOR ZINCKE and W. GAEBEL (*Annalen*, 1912, 388, 299–312).—The condensation of *o*-cresol with acetone is similar to that of phenol; the product, on account of its behaviour with bromine, doubtless has the constitution  $CMe_2(C_6H_3Me \cdot OH)_2$ . When a mixture of *m*- or *p*-cresol (six parts) and acetone (one part) is saturated with hydrogen chloride in the cold, and is heated at 100° for thirty hours, or when the mixture is heated on the water-bath for a long time with phosphoryl chloride (0.1 part), condensation products are obtained, which are probably ethers on account of their chemical indifference and insolubility in alkalis. The condensation product from *m*-cresol is identical with the substance obtained by the action of hydriodic acid on hydroxythymol (Fries and Fickewirth, *Abstr.*, 1908, i, 822); it is dimorphous, crystallising from alcohol in monoclinic prisms, m. p. 132°, and from glacial acetic acid in rhombic plates, m. p. 126°. The condensation product of *p*-cresol and acetone, which probably has one or other of the annexed constitutions:



is likewise dimorphous, crystallising in needles, m. p. 138°, or plates, m. p. 144°.

When heated with phosphorus pentachloride at 130°, both condensation products yield amorphous, yellowish-white powders having approximately the composition  $C_{20}H_{16}O_2Cl_8$ ; the m. p. of the meta-derivative is 90–110°, that of the para-derivative, 73–85°. By chlorination in the presence of iron, the condensation product of *m*-cresol and acetone yields an impure *tetrachloro*-derivative, m. p. 198–201°, in glacial acetic acid, and a *hexachloro*-derivative,  $C_{20}H_{18}O_2Cl_6$ , m. p. 208° in chloroform. Under similar conditions, the condensation

product of *p*-cresol yields in either solvent an *octachloro*-derivative, m. p. 105—115°, which is probably identical with the preceding. By bromination, the condensation product of *m*-cresol forms an impure *tetrabromo*-derivative, m. p. 190°, or a *hexabromo*-derivative, m. p. 252°, whilst the condensation product of *p*-cresol yields an impure *dibromide*, m. p. 213°, or *hexabromo*-derivative, m. p. 300° (decomp.). The reduction of the condensation products by zinc dust at 320—350° yields a gas (probably propane), *m*- or *p*-cresol, and *substances*,  $C_{10}H_{14}O$ , b. p. 230—240° and 240—250° respectively, which are probably tertiary alcohols,  $OH \cdot CMe_2 \cdot C_6H_4Me$ .

Oxidation of the condensation products by chromic acid yields definite results only in the case of the para-derivative. In this case an *acid*,  $C_{20}H_{20}O_6$ , m. p. above 270°, white needles, is obtained; the *sodium*, *barium*, and *silver* salt, and the *methyl* and *ethyl* esters, m. p. 215° and 180° respectively, are described. C. S.

**A New Synthesis of Hordenine.** HUGO VOSWINCKEL (*Ber.*, 1912, 45, 1004—1006).—Hordenine,  $OH \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot NMe_2$ , can be synthesised (compare Barger, *Trans.*, 1909, 95, 2193; Rosenmund, *Abstr.*, 1910, i, 241) by the following steps which provide a general process for the synthesis of hydroxyphenylethylamine bases.

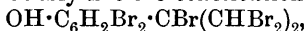
*p*-Methoxyphenyl dimethylaminomethyl ketone,  
 $OMe \cdot C_6H_4 \cdot CO \cdot CH_2 \cdot NMe_2$ ,

is prepared by the action of an alcoholic solution of dimethylamine on *p*-methoxyphenyl chloromethyl ketone (Kunckell and Johansen, *Abstr.*, 1897, i, 522); it forms a colourless oil, m. p. about 30°. The *hydriodide* (colourless needles, m. p. 150°) on boiling with hydriodic acid (D 1·7) and phosphorus gives *p*-hydroxyphenyl dimethylaminomethyl ketone, colourless, prismatic crystals, m. p. 142°; the *hydriodide* of this base (needles, m. p. 176°) when heated in a sealed tube with hydriodic acid (D 1·96) and phosphorus gives hordenine (m. p. 118°; methiodide, m. p. 228—229°). D. F. T.

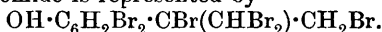
**Preparation of *p*-Hydroxyphenylisopropylamine.** KARL W. ROSENMUND, CARL MANNICH, and WILLY JACOBSON (D.R.-P. 243546).—*p*-Methoxyphenylisopropylamine,  $OMe \cdot C_6H_4 \cdot CH_2 \cdot CHMe \cdot NH_2$ , a strongly basic oil, b. p. 158°/25 mm., is readily prepared by reducing *p*-methoxybenzyl methyl ketoxime,  $OMe \cdot C_6H_4 \cdot CH_2 \cdot CMe : NOH$ , with sodium amalgam; the *hydrochloride*, colourless leaflets, has m. p. 210°. When the foregoing base is boiled during fifteen minutes with three parts of hydriodic acid (D 1·7), it furnishes *p*-hydroxyphenylisopropylamine *hydriodide*, m. p. 155°; this base forms colourless rosettes, has m. p. 125—126°, and is of therapeutic value. F. M. G. M.

**Constitution of the Bromides of *p*-isoPropylphenol and *p*-sec Butylphenol.** THEODOR ZINCKE (*Annalen*, 1912, 388, 294—298).—The constitutions ascribed to the hexa- and heptabromo-derivatives of *p*-isopropylphenol obtained by the action of bromine on 3:5:3':5'-tetrabromo-*p*-diphenoldimethylmethane (*Abstr.*, 1906, i, 172) were given to these substance in consequence of the constitution given by Baeyer and Seuffert to the hexabromothymol obtained from menthone (*Abstr.*, 1901, i, 216). Since, however, Fries has shown (*Abstr.*, 1910, i, 333) that the hexabromothymol contains only two bromine atoms in

the nucleus, the constitutions of the hexa- and the heptabromoderivatives of *p*-isopropylphenol become open to doubt. It is now shown that the hexabromo-*p*-isopropylphenol obtained from the acetylated heptabromide (*loc. cit.*) yields with alkali and methyl sulphate a *methyl ether*,  $\text{OMe}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{C}(\text{CHBr}_2)\cdot\text{CBr}_2$ , m. p.  $127^\circ$ , which is oxidised to 3:5-dibromo-4-methoxybenzoic acid, m. p.  $213^\circ$ , by boiling nitric acid, D 1.4, and water (2:3 by volume). The heptabromide, therefore, probably has the constitution



whilst the hexabromide is represented by



The constitutions previously ascribed to the hexa- and heptabromoderivatives of *p*-sec-butylphenol (Abstr., 1908, i, 780) must be altered in a corresponding manner; the hexabromide probably has the constitution  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CBr}(\text{CHBr}_2)\cdot\text{CHMeBr}$ , and the heptabromide the constitution  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Br}_2\cdot\text{CBr}(\text{CHBr}_2)\cdot\text{CMeBr}_2$ . C. S.

**Amidosulphonic Acid.** KARL A. HOFMANN and E. BIESALSKI (*Ber.*, 1912, 45, 1394—1398).—The authors recommend the employment of amidosulphonic acid as a standard in acidimetry. Its gradual hydrolysis in aqueous solution to acid ammonium sulphate has little influence on most titrations.

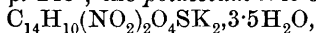
It may also be used in the preparation of aryl-sulphuric acids and phenol-sulphonic acids, and possesses the advantage over sulphuric acid that no separation of the product from excess of sulphonating agent is necessary. Thus ammonium phenol-*p*-sulphonate results when phenol is heated with amidosulphonic acid at  $150$ — $160^\circ$ , whilst at  $100^\circ$  ammonium phenyl sulphate is obtained. From the above it might appear that the latter compound is formed as an intermediate step in the preparation of ammonium phenol-*p*-sulphonate. Against this view, however, is the fact that ammonium anisole-*p*-sulphonate is obtained in good yield when anisole and amidosulphonic acid are heated at  $140$ — $150^\circ$  during six hours. Similarly, *o*-, *m*-, and *p*-cresols, and 1:2:4- and 1:3:4-xenols are sulphonated by amidosulphonic acid at  $150^\circ$ .  $\beta$ -Naphthol at  $160^\circ$  is similarly transformed into ammonium 2-naphthol-6-sulphonate.

In all these cases no dehydrating agent is necessary, since the eliminated water is absorbed in the hydrolysis of the amino-group with the formation of an ammonium salt. This intramolecular redistribution of water is particularly obvious when amidosulphonic acid is brought into contact with the carbinol base of malachite-green, whereupon the dye is at once produced. H. W.

***o*-Hydroxytolylsulphone.** JOSEF ZEHENTER (*Monatsh.*, 1912, 33, 333—347).—*o*-Hydroxytolylsulphone was obtained in good yield by heating *o*-cresol (2 parts) with sulphuric acid containing 8% sulphur trioxide (1 part) during three to four hours at  $160$ — $180^\circ$ . It separates from alcohol in colourless prisms, m. p.  $263$ — $265^\circ$ . Its identity with the compound prepared by Tassinari (Abstr., 1889, 245) follows from its m. p., and that of its diacetyl derivative. Salts of it could not be prepared, nor could any definite oxidation product be isolated. Its constitution has not been proved, but the  $\cdot\text{SO}_2$  group is in the ortho- or para-position to the hydroxyl group. *o*-Cresol-

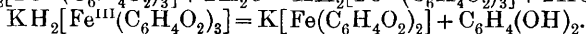
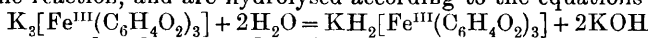
*p*-sulphonic acid was isolated as by-product in the above reaction, and its potassium and barium salts were analysed.

Bromine in hot ethereal solution transforms *o*-hydroxytolylsulphone into *dibromo-o-hydroxytolylsulphone*,  $C_{14}H_{12}O_4Br_2S$ , m. p. 254—256°, whilst, in the absence of a solvent, tetrabromo-*o*-cresol, m. p. 207—208°, is formed. When heated on the boiling water-bath with nitric acid (D 1·2), *o*-hydroxytolylsulphone yields *dinitro-o-hydroxytolylsulphone*,  $C_{14}H_{12}(NO_2)_2O_4S$ , m. p. 243°, the potassium salt of which,



was analysed. At the ordinary temperature, concentrated sulphuric acid converts *o*-hydroxytolylsulphone mainly into *o*-cresol-3-sulphonic acid [isolated in the form of its barium salt,  $(OH \cdot C_6H_3Me \cdot SO_3)_2Ba \cdot 3H_2O$ ], which when oxidised with nitric acid forms 3:5-dinitro-*o*-cresol, m. p. 85·5°; at 100—110°, this acid together with *o*-cresol-3:5-disulphonic acid is formed, whilst at 160—170° practically only the latter acid is obtained. Its potassium and barium salts were analysed. Oxidation with concentrated nitric acid converts the potassium salt into 3:5-dinitrocresol. H. W.

**The Ferric Chloride Reaction with Catechol. II. Violet Iron-Catechol Compounds.** RUDOLF FRIEDRICH WEINLAND and KARL BINDER (*Ber.*, 1912, 45, 1113—1124).—The authors have already shown (*Abstr.*, 1912, i, 184) that the deep red solutions formed when ferric salts and catechol are mixed in alkaline solution contain the salts of an acid,  $H_3[Fe^{III}(C_6H_4O_2)_3]$ . These solutions when diluted become reddish-violet and then violet, and contain salts of a new acid,  $H[Fe(C_6H_4O_2)_2]$ . Aqueous solutions of salts of the red acid have an alkaline reaction, and are hydrolysed according to the equations:



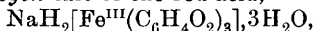
The ammonium salts of the violet acid may be obtained by boiling a dilute aqueous solution of the ammonium salt of the red acid, since the liberated ammonia is volatilised. In the case of non-volatile bases, the addition of acetic acid is necessary. Salts of the violet acid may also be prepared by mixing solutions of catechol, ferric acetate, and alkali acetate.

The free violet acid and its salts are black, microcrystalline substances, soluble in water, insoluble in alcohol. All contain water, which, in the case of the normal potassium salt, was retained after preservation in a vacuum over sulphuric acid during four weeks. Their aqueous solutions are immediately decolorised by the addition of mineral acids, whilst addition of alkali results in the formation of salts of the red acid, one-third of the iron being precipitated as ferric hydroxide. In certain circumstances, the addition of acetic acid to the solutions of normal salts of the red acid causes the formation of acid salts of the same acid, which consist of brownish-black or black, crystalline powders soluble in water or alcohol with the formation of violet solutions. Alkali dissolves them with formation of red solutions and without precipitation of ferric hydroxide.

The free violet acid,  $H\left[Fe(C_6H_4O_2)_2\right] \cdot H_2O$ , was obtained as a black

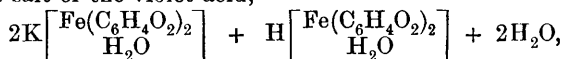
powder, sparingly soluble in water or alcohol, by mixing aqueous solutions of catechol, ferric acetate, and sodium acetate.

The *sodium dihydrogen* salt of the red acid,



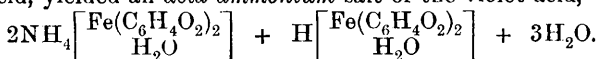
prepared by the addition of one or two equivalents of acetic acid to the normal sodium salt of the red acid and evaporation of the solution over sulphuric acid, is readily transformed into the *normal sodium* salt of the violet acid,  $\text{Na}\left[\text{Fe}\left(\frac{\text{C}_6\text{H}_4\text{O}_2}{\text{H}_2\text{O}}\right)_2\right]$ , by evaporating its aqueous solution on the water-bath. By the action of three equivalents of acetic acid on the normal sodium salt of the red acid, an *acid sodium* salt of the violet acid was obtained as a black powder.

The *normal potassium* salt of the violet acid,  $\text{K}\left[\text{Fe}\left(\frac{\text{C}_6\text{H}_4\text{O}_2}{\text{H}_2\text{O}}\right)_2\right]$ , was prepared by addition of one or two equivalents of acetic acid to a solution of the normal potassium salt of the red acid. The *acid potassium* salt of the violet acid,

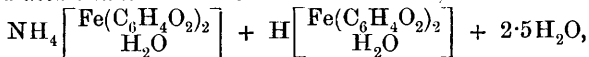


was formed when three equivalents of acetic acid were used.

The *normal ammonium* salt of the violet acid,  $\text{NH}_4\left[\text{Fe}\left(\frac{\text{C}_6\text{H}_4\text{O}_2}{\text{H}_2\text{O}}\right)_2\right]$ , was obtained on evaporating a solution of the normal ammonium salt of the red acid. The latter, when treated with three equivalents of acetic acid, yielded an *acid ammonium* salt of the violet acid,



A second *acid ammonium* salt of the violet acid,



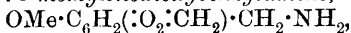
was obtained by mixing solutions of catechol, ammonium acetate, and ferric acetate. When larger quantities of ammonium acetate were employed (7—12 equivalents instead of 3.5), an *ammonium* salt of the red and violet acid,  $4\text{NH}_4\left[\text{Fe}\left(\frac{\text{C}_6\text{H}_4\text{O}_2}{\text{H}_2\text{O}}\right)_2\right] + (\text{NH}_4)_3[\text{Fe}^{\text{III}}(\text{C}_6\text{H}_4\text{O}_2)_3] + (\text{NH}_4)_2\text{H}[\text{Fe}^{\text{III}}(\text{C}_6\text{H}_4\text{O}_2)_3] + 13\text{H}_2\text{O}$ , was obtained. From the mother liquor left in this experiment, the *diammonium hydrogen* salt of the red acid,  $(\text{NH}_4)_2\text{H}[\text{Fe}^{\text{III}}(\text{C}_6\text{H}_4\text{O}_2)_3], 4\text{H}_2\text{O}$ , was prepared. H. W.

**A Contribution to the Knowledge of Phloroglucinol.**  
A. GÖSCHKE and JOSEF TAMBOR (*Ber.*, 1912, 45, 1237, 1239).—Although resacetophenone, quinacetophenone, and gallacetophenone are now easily obtainable hydroxy-ketones, 2 : 4 : 6 - trihydroxyacetophenone or phloroacetophenone has not yet been synthesised. Many flavone and flavonol colouring matters possess the same carbon skeleton, and recently Semmler and Schossberger have found its dimethyl ether in some ethereal oils (Abstr., 1911, i, 1002), whilst Rupe has suggested that cyanomaclurin may be a pentahydroxychalkone, that is, a condensation product of phloroacetophenone and resorcinolaldehyde. As the present authors have found that polyhydroxychalkones are coloured (compare Abstr., 1912, i, 30), whereas cyanomaclurin is a

colourless powder, they have attempted to apply Nencki's method (Abstr., 1899, 879) to the synthesis of phloroacetophenone. Two substances have been obtained, but they proved to be the triacetyl-*cyclohexantrione* (Abstr., 1909, i, 656) and diacetyl-*cyclohexantrione* (Abstr., 1912, i, 274) of Heller. From the former an *as-phenylmethylhydrazone*,  $C_{15}H_{16}O_3N_2$ , has been obtained in very small, yellow prisms, m. p.  $165^\circ$ . Further studies on the action of acid chlorides on phloroglucinol and on aromatic hydroxy-acids are in progress.

J. C. W.

**3-Methoxy-4:5-methylenedioxybenzylamine.** LEOPOLD RÜGHEIMER and G. RITTER (*Ber.*, 1912, 45, 1340—1343).—Myristinaldehyde (Semmler, Abstr., 1891, 311) was converted into the *oxime* (m. p.  $159$ — $160^\circ$ ), which could be reduced by zinc dust and acetic acid to 3-methoxy-4:5-methylenedioxybenzylamine,



a strong base, b. p.  $172.5^\circ/16.5$  mm.; *hydrochloride*, m. p.  $222^\circ$ , gives solutions with green fluorescence; *double salt* with mercuric chloride, needles, m. p.  $215^\circ$ ; *platinichloride*, yellow needles and leaflets; *picrate*, leaflets.

The acetal compound,  $\text{OMe} \cdot \text{C}_6\text{H}_2(\text{:O}_2\text{CH}_2) \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{CH}(\text{OEt})_2$ , unlike that of 3:4-dimethoxybenzylamine (compare Rügheimer and Schön, Abstr., 1908, i, 153; 1909, i, 605), does not condense to an *isoquinoline* derivative.

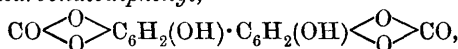
The amine reacts with phenylcarbimide, giving *phenyl-3-methoxy-4:5-methylenedioxybenzylcarbimide*,  $(\text{C}_6\text{H}_5\text{O}_2)\text{NH} \cdot \text{CO} \cdot \text{NHPh}$ , slender needles, m. p.  $174^\circ$ ; phenylthiocarbimide similarly gives the corresponding *thiocarbimide*, plates, m. p.  $143^\circ$ . It readily condenses with acetylacetone, giving  $\beta$ -3-methoxy-4:5-methylenedioxybenzyliminopropyl *methyl ketone*,  $\text{CMe}[\text{:N} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_2(\text{:O}_2\text{CH}_2) \cdot \text{OMe}] \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$ , m. p.  $73^\circ$ .

D. F. T.

**Derivatives of 3:4:5:3':4':5'-Hexahydroxydiphenyl.** CARL LIEBERMANN and E. HERRMUTH (*Ber.*, 1912, 45, 1218—1227).—Hexahydroxydiphenyl is readily converted by oxidising agents into the bluish-violet sparingly soluble tetrahydroxydiphenoquinone. 2:6:2':6'-Tetrabromohexahydroxydiphenyl, however, cannot be oxidised to the corresponding quinone.

The possibility of the molecule being half the size, namely,  $\text{C}_6\text{HBr}_2(\text{OH})_3$ , is discussed; it is shown that it is not identical with dibromopyrogallol, and that the resistance to oxidation is due to the influence of the substituting groups.

*Dihydroxydicarbonatodiphenyl*,



forms slender needles, m. p.  $312^\circ$  (decomp.).

Hexa-acetoxydiphenyl,  $\text{C}_{12}\text{H}_4(\text{OAc})_6$ , crystallises in colourless needles, m. p.  $236^\circ$  (previously given  $145^\circ$ ).

Tetrahydroxydiphenoquinone, prepared by the action of alcoholic iodine solution on the aqueous solution of hexahydroxydiphenyl, is obtained as a deep blue precipitate, dissolving in concentrated sulphuric acid with a brown coloration.

*Tetrabromohexa-acetoxydiphenyl*,  $C_6Br_2(OAc)_3 \cdot C_6Br_2(OAc)_3$ , crystallises in platelets, m. p.  $231^\circ$ . On hydrolysis, *tetrabromohexahydroxydiphenyl* is obtained in colourless leaflets, which darken at  $260^\circ$ , m. p.  $270$ — $276^\circ$  (decomp.). The solution in dilute alkali is at first colourless; it becomes red at the surfaces of contact with the air, and finally a deep red all through.

Dibromopyrogallol as prepared either by Einhorn (Abstr., 1904, i, 238) or by Perkin and Simonsen (Trans., 1905, 87, 863) has m. p.  $158^\circ$  (decomp.); the acetate has m. p.  $143^\circ$ , and shows other differences in its behaviour from tetrabromohexahydroxydiphenyl.

E. F. A.

**Optically Active Phenylmethylcarbinols.** BROR HOLMBERG (*Ber.*, 1912, 45, 997—1003).—In order to discover, if possible, any directing influence in the Walden inversion exerted by the groups already attached to the asymmetric atom, the author has selected for investigation  $\alpha$ -phenylethyl alcohol as a structurally simple substance.

$\alpha$ -Phenylethylamine was prepared from acetophenoneoxime and then resolved (compare Lovén, Abstr., 1905, i, 875); the *l*-form has  $D_4^{20}$  0.952; the two forms had  $\alpha_D^{19}$  + and  $-38.73^\circ$  respectively, and b. p.  $77$ — $77.5/16$  mm. (compare Markwald and Meth, Abstr., 1905, i, 272).

Treatment of the *l*-form with sulphuric acid and sodium nitrite gave  $\alpha$ -phenylethyl nitrite, an unstable, yellow oil, b. p.  $72.5$ — $73/19$  mm.,  $D_4^{20}$  1.045,  $\alpha_D^{17}$   $+6.80^\circ$ , together with  $\alpha$ -phenylethyl alcohol, a colourless liquid, b. p.  $98.5$ — $99/20$  mm.,  $D_4^{20}$  1.018,  $\alpha_D^{15}$   $+5.00^\circ$  (compare Emmerling and Engler, this Journ., 1874, 74; Markwald and Meth, *loc. cit.*). The *d*-base on similar treatment, but with less careful cooling, gave the stereoisomeric *l*-alcohol and nitrite, of similar properties to the enantiomorphs, but with lower optical activity, evidently due to partial racemisation.

*d*- $\alpha$ -Phenylethyl alcohol was converted by hydrogen bromide into the bromide, b. p.  $94.5/19$  mm.,  $D_4^{20}$  1.311 (compare Bernthsen and Bender, Abstr., 1883, 70); the product was completely inactive. The action of phosphorus pentabromide on an ethereal solution of the *l*-alcohol produced a feebly *d*-bromide, whilst the action of nitric oxide and bromine on the hydrobromide of *d*- $\alpha$ -phenylethylamine gave a very small quantity of a *d*-liquid (presumably the bromide ester).

When *d*-phenylethyl bromide was treated in alcoholic solution with moist silver oxide, *phenylethyl ethyl ether* was produced, b. p.  $71.5$ — $72/15$  mm.,  $\alpha_D^{15}$   $-0.20^\circ$ , and also a smaller amount of another laevorotatory substance, apparently  $\alpha$ -phenylethyl alcohol.

D. F. T.

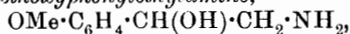
**Preparation of Phenyl-, Alkyloxyphenyl-, and Dialkyloxyphenyl-ethanolamines and their Alkyl Ethers.** KARL W. ROSENMUND (D.R.-P. 244321. Compare Abstr., 1911, i, 34).—Compounds having the general formula  $R \cdot CH(OR_1) \cdot CH_2 \cdot NH_2$  (where R is phenyl, alkyloxyphenyl, or dialkyloxyphenyl, and  $R_1$  hydrogen or an alkyl group) are readily prepared by the condensation of benzaldehyde (or its alkyloxy- or dialkyloxy-substitution products)

with nitromethane in the presence of alkali and subsequent reduction of the nitro-group.

$\beta$ -Hydroxy- $\beta$ -phenylethylamine,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NH}_2$ , is obtained by treating a cooled alcoholic mixture of benzaldehyde and nitromethane with sodium ethoxide (1.5 mols.), followed by reduction with sodium amalgam. The hydrochloride is an oil; the intermediate nitro-alcohol, an oil, has b. p.  $164\text{--}167^\circ/20\text{ mm.}$ , with partial decomposition.

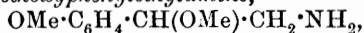
$\alpha$ -Nitro- $\beta$ -methoxy- $\beta$ -phenylethane,  $\text{OMe}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{NO}_2$ , an oil, b. p.  $140\text{--}141^\circ/15\text{ mm.}$ , is prepared in a similar manner from nitro-styrene in methyl-alcoholic solution, and on reduction furnishes  $\beta$ -methoxy- $\beta$ -phenylethylamine, which was isolated in the form of its crystalline hydrochloride, m. p.  $158\text{--}159^\circ$ .

$\beta$ -Hydroxy- $\beta$ -p-methoxyphenylethylamine,



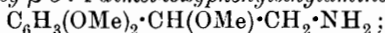
obtained from anisaldehyde and nitromethane, was isolated as its hydrochloride, m. p.  $168\text{--}173^\circ$ .

$\beta$ -Methoxy- $\beta$ -p-methoxyphenylethylamine,



prepared from p-methoxynitrostyrene, furnishes a hydrochloride, m. p.  $165\text{--}166.5^\circ$ , decomp.  $186\text{--}187^\circ$ .

$\beta$ -Nitrodimehoxystyrene (*loc. cit.*) is converted by the action of sodium methoxide into the corresponding  $\alpha$ -nitro- $\beta$ -methoxy- $\beta$ -3:4-dimehoxyphenylethane, an unstable, yellow oil, which on reduction furnishes  $\beta$ -methoxy- $\beta$ -3:4-dimehoxyphenylethylamine,



its hydrochloride has m. p.  $182\text{--}183^\circ$ .

F. M. G. M.

**Dehydration of Diphenyl- $\psi$ -butylcarbinol.** (Mme.) PAULINE RAMART-LUCAS (*Compt. rend.*, 1912, 154, 1088—1090. Compare Abstr., 1911, i, 636).—The tertiary alcohol,  $\text{C}_{17}\text{H}_{20}\text{O}$ , previously described behaves normally with thionyl chloride, giving a chloride,  $\text{C}_{17}\text{H}_{19}\text{Cl}$ , m. p.  $72\text{--}73^\circ$ , but yields an isomeric of this substance, m. p.  $109^\circ$ , when treated with acetic anhydride and acetyl chloride; dehydration also occurs, however, with production of benzophenone and  $\beta$ -methylpropane. Oxidation of the alcohol with chromic acid, leads to the formation of carbon dioxide, acetophenone, and benzophenone, whilst the corresponding unsaturated hydrocarbon,  $\text{C}_{17}\text{H}_{18}$ , under the same conditions yields the same substances together with an acid, crystallising in needles, m. p.  $173^\circ$ . The constitution of the hydrocarbon cannot be settled without a further examination of this oxidation product.

W. O. W.

**The Behaviour of Some Degradation Products of Cholesterol on Heating.** ADOLF WINDAUS (*Ber.*, 1912, 45, 1316—1321).—On account of the stability of the structure of cholesterol towards heat (compare Diels and Linn, Abstr., 1908, i, 164, 263), it is probable that many reactions occurring at elevated temperatures may provide trustworthy evidence as to the constitution of this substance.

The dibasic acid,  $\text{C}_{27}\text{H}_{44}\text{O}_4$  (Diels and Abderhalden, Abstr., 1904, i, 880), when covered with acetic anhydride, the mixture distilled under ordinary pressure, and the residue under reduced pressure, loses carbon dioxide and water with the formation of a cyclic ketone,

$C_{26}H_{42}O$ , needles, m. p.  $95-96^\circ$ ; *oxime*, m. p.  $176^\circ$ . This behaviour indicates that in the original acid the two carboxyl groups must be in a 1:6- or 1:7-position to each other.

The tribasic acid,  $C_{25}H_{40}O_6$ , obtained from the previous acid (Windaus, Abstr., 1908, i, 264, 728; 1909, i, 920) under similar treatment loses carbon dioxide and water with the formation of a cyclic ketonic carboxylic acid,  $C_{24}H_{38}O_3$ , which separates from dilute acetic acid in hexagonal tablets, m. p.  $146-147^\circ$ ; *semicarbazone*, leaflets, m. p.  $249-250^\circ$  (decomp.). From analogy to the conversion of homocamphoronic acid into camphononic acid (Lapworth and Chapman, Trans., 1899, 75, 986), the disappearing carboxyl groups must likewise be in the 1:6- or 1:7-position.

The acid,  $C_{24}H_{38}O_3$ , on oxidation with chromic acid in acetic acid solution gives a tricarboxylic acid,  $C_{24}H_{38}O_6$ , slender, prismatic crystals containing water of crystallisation, m. p. (anhydrous)  $216^\circ$ ; the sodium salt is sparingly soluble. An isomeric acid, m. p. ca.  $201^\circ$ , is simultaneously produced. By comparison of this behaviour with that of camphononic acid (Lapworth and Chapman, *loc. cit.*), the carbonyl group in the acid,  $C_{24}H_{38}O_3$ , must be adjacent to a  $-CH_2$  group.

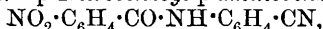
The acid,  $C_{24}H_{38}O_6$ , when subjected to similar distillation produces (with loss of water and carbon dioxide) a cyclic ketonic acid,  $C_{23}H_{36}O_3$ , thin, prismatic crystals from acetic acid, m. p.  $170^\circ$ ; *semicarbazone*, leaflets, m. p.  $226^\circ$  (decomp.). D. F. T.

**Preparation of Chloro-substituted Derivatives of Anthranilic Acid.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 244207. Compare Trans., 1902, 81, 1324).—When polychlorobenzoic acids are heated at  $100-150^\circ$  during twelve to fifty hours with 30% ammonium hydroxide in the presence of copper, the chlorine atom in the ortho-position to the carboxyl group is replaced by an amino-group.

4-Chloro-2-aminobenzoic acid was thus obtained in quantitative yield from 2:4-dichloro-benzoic acid, whilst 2:4:5-trichlorobenzoic acid furnished 4:5-dichloro-2-aminobenzoic acid, colourless needles, m. p.  $210^\circ$  (approx.). F. M. G. M.

***p*-Aminobenzonitrile and Certain of its Derivatives. III.** MARSTON T. BOGERT and LOUIS ELSBERG WISE (*J. Amer. Chem. Soc.*, 1912, 34, 693—702).—An account is given of a continuation of the study of derivatives of *p*-aminobenzonitrile (Bogert and Kohnstamm, Abstr., 1903, i, 559; Bogert and Wise, Abstr., 1911, i, 46).

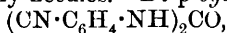
*p*-Aminobenzonitrile *picrate*, m. p.  $150.5^\circ$  (corr.), forms long, silky, golden-yellow needles. *p*-Nitrobenzoyl-*p*-aminobenzonitrile,



m. p.  $258-259^\circ$  (uncorr.), obtained by the action of *p*-nitrobenzoyl chloride on *p*-aminobenzonitrile, crystallises in long, pale yellow, lustrous needles. *p*-Cyanophenylurethane,  $CN \cdot C_6H_4 \cdot NH \cdot CO_2Et$ , m. p.  $116-117^\circ$  (corr.), prepared by treating *p*-aminobenzonitrile with ethyl chloroformate in presence of sodium carbonate, forms colourless needles with a faint, pineapple-like odour, and when heated with hydrogen peroxide solution is converted into *p*-carbamylphenylurethane,

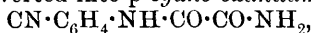


m. p. about  $232.5^{\circ}$  (uncorr.), which crystallises in slender, colourless, silky needles. *p*-Cyanophenylcarbamide,  $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ , m. p.  $207.5$ — $208.5^{\circ}$  (uncorr.), from *p*-aminobenzonitrile hydrochloride and potassium cyanate, forms minute, colourless needles. *p*-Cyanocarb-anilide,  $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ , m. p.  $198.5^{\circ}$  (corr.), obtained by the action of phenylcarbimide on *p*-aminobenzonitrile, crystallises in clusters of colourless, silky needles. *Di-p-cyanocarb-anilide*,



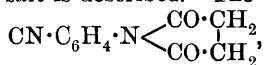
m. p.  $273^{\circ}$  (uncorr.), from *p*-aminobenzonitrile and carbonyl chloride, forms small, colourless needles.

When ethyl *p*-cyano-oxanilate is heated with concentrated solution of ammonia, it is converted into *p*-cyano-oxanilamide,



m. p. above  $300^{\circ}$ , which forms minute, colourless crystals. *p*-Cyano-oxanilanilide,  $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CO}\cdot\text{NHPh}$ , m. p.  $246^{\circ}$  (uncorr.), obtained by the action of aniline and zinc chloride on ethyl *p*-cyano-oxanilate, forms small, colourless crystals.

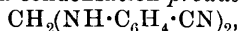
*p*-Cyanosuccinanilic acid,  $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p.  $213$ — $214^{\circ}$  (uncorr.), obtained by the action of succinic anhydride on *p*-aminobenzonitrile, crystallises in minute, colourless prisms; its methyl and ethyl esters have m. p.  $155$ — $156^{\circ}$  (corr.) and  $111^{\circ}$  (corr.) respectively; the silver salt is described. The anil,



m. p.  $170^{\circ}$  (corr.), forms opaque crystals.

*p*-Cyanophthalanilic acid,  $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , crystallises in nearly colourless, silky needles; its m. p. varies with the rate of heating, but if the substance is placed in a bath at  $145^{\circ}$ , it melts at about  $163^{\circ}$ . The anil,  $\text{CN}\cdot\text{C}_6\text{H}_4\cdot\text{N} \begin{array}{c} \text{CO} \\ \text{CO} \end{array} \text{C}_6\text{H}_4$ , m. p.  $187^{\circ}$  (corr.), forms feathery clusters of slender, silky needles.

When solution of formaldehyde is added to a solution of *p*-aminobenzonitrile in acetone, a condensation product, probably



m. p.  $158^{\circ}$ , is produced, which forms microscopic, colourless crystals.

*Bromo-p-acetylaminobenzonitrile*,  $\text{NHAc}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CN}$ , m. p.  $161.5$ — $162.5^{\circ}$  (corr.), crystallises in colourless needles. *3-Nitro-4-acetylaminobenzamide*,  $\text{NHAc}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{CO}\cdot\text{NH}_2$ , m. p.  $239.5^{\circ}$  (uncorr.), obtained by the action of an alkaline solution of hydrogen peroxide on 3-nitro-4-acetylaminobenzonitrile, forms flat, yellow needles. *3:4-Diacetylaminobenzonitrile*,  $(\text{NHAc})_2\text{C}_6\text{H}_3\cdot\text{CN}$ , m. p.  $238$ — $238.5^{\circ}$  (uncorr.), forms colourless, silky, hair-like crystals.

*Cyano-a-methylbenziminazole*,  $\text{CN}\cdot\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \text{N} \end{array} \text{CMe}$ , m. p.  $241^{\circ}$  (uncorr.), prepared by the action of acetic acid on 3:4-diaminobenzonitrile or by the action of heat on 3:4-diacetylaminobenzonitrile, forms clusters of microscopic crystals or of opaque needles. *Carbamyl-2-methylbenziminazole*,  $\text{NH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_3 \begin{array}{c} \text{NH} \\ \text{N} \end{array} \text{CMe}$ , obtained by the

reduction of 3-nitro-4-acetylaminobenzonitrile with tin and acetic acid, forms colourless needles, and decomposes at about  $270^{\circ}$  (uncorr.).

E. G.

**Preparation of Mercury Compounds of Sulphamidobenzoic Acid.** JOHANNES KERB (D.R.-P. 242571 and 242572).—When the alkali derivatives of *o*- or *m*-sulphamidobenzoic acids are warmed in aqueous solution with one molecule of mercuric oxide (or carbonate) and the solution filtered and evaporated to dryness in a vacuum, it furnishes the *compound*,  $\text{CO}_2\text{Na}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_2\cdot\text{NH}\cdot\text{Hg}\cdot\text{OH}$ .

The second patent describes the preparation of the *compound*,  $\text{CO}_2\text{Na}\cdot\text{C}_6\text{H}_3(\text{SO}_2\cdot\text{NH}\cdot\text{Hg}\cdot\text{OH})_2$ , from 2:4-disulphamidobenzoic acid with mercuric oxide (2 mols.).

F. M. G. M.

**New Transformations of *m*-Sulphamidobenzoic Acid under the Influence of Heat.** ROKURO NAKASEKO (*Amer. Chem. J.*, 1912, 47, 429–453).—*m*-Sulphamidobenzoic acid has m. p.  $237\text{--}238^{\circ}$ , but on prolonged heating melts at a much lower temperature. If the acid is kept in the fused state for several hours at  $220\text{--}230^{\circ}$  and is then rapidly cooled, about four-fifths of the product consists of the insoluble, amorphous modification of the acid. Another modification, m. p.  $233\text{--}235^{\circ}$ , is simultaneously produced, which is crystalline and easily soluble in water. Both these modifications were described by Limpricht and Uslar (*Annalen*, 1858, 106, 36).

If *m*-sulphamidobenzoic acid is maintained in the fused condition for only twenty to thirty minutes and is then cooled slowly, an *ammonium hydrogen m-sulphobenzoate* is produced, together with another substance isomeric with *m*-sulphobenzoic diamide. The former product crystallises in hexagonal plates containing  $1\text{H}_2\text{O}$ , and differs in this respect from the ordinary form of ammonium hydrogen *m*-sulphobenzoate which has never been obtained with water of crystallisation. A new *barium m-sulphobenzoate*,  $(\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3)_2\text{Ba}\cdot 4\text{H}_2\text{O}$ , is also described. The *substance* isomeric with the diamide crystallises in prisms, does not melt when heated to  $253^{\circ}$ , and is probably *m*-sulphobenzoylamidine,  $\text{SO}_3\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{:NH})\cdot\text{NH}_2$ .

Wilson (Abstr., 1904, i, 51) has shown that *o*-sulphobenzamide can be prepared by heating potassium hydrogen *o*-sulphobenzoate with ammonium thiocyanate. Attempts to obtain *m*-sulphobenzamide in a similar manner were not successful, but resulted in the formation of two substances, one crystallising in plates and the other in needles, which were not identified.

E. G.

[Preparation of *m*-Acetylaminophenylthiolacetic and *m*-Amino-*o*-tolylthiolacetic Acids.] KALLE & Co. (D.R.-P. 244615 and 244616).—*m*-Acetylaminophenylthiolacetic acid, a yellowish-white, crystalline powder prepared by previously described methods (this vol., i, 354) from acetyl-*m*-phenylenediamine, furnishes a vat dye when treated with chlorosulphonic acid. The second patent states that *m*-amino-*o*-tolylthiolacetic acid (or its acetyl derivative), obtained from 4-acetyl-amino-2-toluidine in a similar manner, yields a blue vat dye when treated with condensing reagents.

F. M. G. M.

[Preparation of *s*-Xylylthiolacetic Acid.] KALLE & Co. (D.R.-P. 242997. Compare this vol., i, 126).—*m*-Xylyl-5-thiolacetic acid, needles, m. p. 85°, prepared from *m*-5-xylidine by known methods, requires a higher temperature to convert it into a dye than does the previously-described 4-carboxy-*m*-xylyl-5-thiolacetic acid.

F. M. G. M.

Unsaturated Compounds. IX. Addition of Hydroxylamine to Unsaturated Acids and Esters of the Cinnamic Acid Series and to Analogous Compounds. THEODOR POSNER (*Annalen*, 1912, 389, 1—120. Compare Abstr., 1907, i, 212).—The mechanism of additive processes and the influence of groups in the molecule of the unsaturated compound (especially those containing conjugated double linkings) and of the distribution of the affinity in the molecule of the addendum on the course of the addition are still very obscure, despite numerous researches on the subject. With the object of discovering any existent regularities in such processes, the author has examined very thoroughly the addition of hydroxylamine to cinnamic acid and its derivatives and allied substances. The influence of substituents in the nucleus, in the  $\alpha$ - and  $\beta$ -positions, and in place of the acidic hydroxyl group on the additive process has been examined, but regularities have not been discovered.

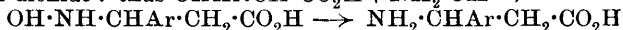
It has been shown previously (Abstr., 1904, i, 160; *loc. cit.*) that, in the case of cinnamic acid itself, hydroxylamine in alcoholic solution forms a hydroxylamine salt in the cold,  $\beta$ -hydroxylamino- $\beta$ -phenylpropionic acid after boiling for three-quarters of an hour, and  $\beta$ -amino- $\beta$ -phenylpropionic acid after boiling for ten hours, whilst in the case of methyl or ethyl cinnamate, alcoholic hydroxylamine forms  $\beta$ -hydroxylaminophenylpropionic hydroxamoxime hydrate in the cold, and  $\beta$ -amino- $\beta$ -phenylpropionic acid after prolonged boiling. In the present comparative experiments, therefore, the alcoholic hydroxylamine solution of approximately normal concentration has been used in slight excess ( $2\frac{1}{2}$ —3 mols. in the case of the acids, and  $3\frac{1}{2}$ —4 mols. in that of the esters), and the reacting mixture has been boiled for three-quarters of an hour, ten hours, or two hundred and forty hours in the case of the acids, and kept at 0° for eight days or boiled for ten hours or two hundred and forty hours in the case of the esters. Since the products of the reaction are generally easily separated from the original materials by their solubility in dilute acids, many of the experiments have been performed quantitatively. Unfortunately, this method was discovered only after the research had been in progress for some time, so that the earlier experiments are qualitative in nature, the ease of addition of hydroxylamine to cinnamic acid itself being taken as a standard of comparison. With regard to nuclear-substituted cinnamic acids and their esters, the most that can be said from the results of the experiments is that the nature and the position of the substituent have a very marked influence on the additive capacity of the C:C group of the side-chain (so far as the final product of the reactions is concerned, it will be noted that in most cases the addition of hydroxylamine has taken place at this C:C group). A certain parallelism appears to exist between the ease of addition of hydroxyl-

amine to a nuclear-substituted cinnamic acid and the dissociation constant (of the corresponding benzoic acid; data are not available for the dissociation constants of the substituted cinnamic acids). The three nitrocinnamic acids, the three methoxycinnamic acids, *m*-aminocinnamic acid, and *o*-coumaric acid do not react with hydroxylamine after boiling for three-quarters of an hour; the dissociation constants of the corresponding benzoic acids are all greater than that of benzoic acid itself. *m*- and *p*-Hydroxycinnamic acids react with hydroxylamine as easily as cinnamic acid; the dissociation constants of the corresponding benzoic acids are about the same. The ester of a nuclear-substituted cinnamic acid reacts with hydroxylamine, sometimes more readily, in other cases less so, than the acid itself.

Regularities have not been observed in the addition of hydroxylamine to  $\alpha$ - or  $\beta$ -substituted cinnamic acids or their esters. The most interesting result in the case of the  $\alpha$ -substituted acids is that the chemical nature, not the molecular weight, of the substituent appears to influence the addition of hydroxylamine; when the substituent is an alkyl or aryl group, the order with regard to increasing hindering effect is ethyl, phenyl, methyl.  $\alpha$ -Substituted cinnamic acids and their esters unite with hydroxylamine decidedly less readily than do cinnamic acid and its esters;  $\alpha$ -benzoylcinnamic acid and its esters, however, react as readily as cinnamic acid and its esters.  $\beta$ -Substituted cinnamic acids show still smaller tendency to react with hydroxylamine; with alkyl or aryl substituents the influence appears to be steric, the order of increasing hindrance being methyl, ethyl, phenyl.

So far as the final product in each case is concerned, the results of all the experiments may be summed up as follows:  $\alpha\beta$ -Unsaturated acids and their esters, anhydrides, amides, hydroxamic acids, and  $\omega$ -nitrostyrene add the constituents of hydroxylamine at the C:C group; cinnamaldehyde and cinnamionitrile add on hydroxylamine at the CO or CN group, not at all or only with very great difficulty at the C:C group; unsaturated hydrocarbons,  $\beta\gamma$ -unsaturated acids, unsaturated alcohols, and  $\omega$ -halogenostyrenes do not form additive compounds with hydroxylamine.

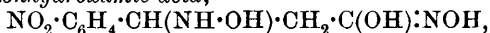
The experimental results, although not fulfilling the author's expectations, have led to several interesting discoveries. One of these is a general method for the preparation of  $\beta$ -aminocarboxylic acids; another is an apparently general method of obtaining aryl methyl ketones. By prolonged boiling of a cinnamic acid (except *o*- or *p*-aminocinnamic acids) with alcoholic hydroxylamine, the initially formed  $\beta$ -hydroxylamino-derivative is partly reduced to the  $\beta$ -amino-acid and partly oxidised to an oximino-compound, which may either condense to an isooxazolone derivative or yield an arylmethylketoxime by loss of carbon dioxide: thus  $\text{CHAr}:\text{CH}\cdot\text{CO}_2\text{H} + \text{NH}_2\cdot\text{OH} \rightarrow$



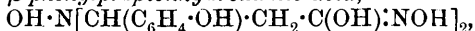
and  $\text{NOH}\cdot\text{CAr}\cdot\text{CH}_2\cdot\text{CO}_2\text{H} \rightarrow \text{CArMe}\cdot\text{NOH}$  or  $\text{O} < \begin{array}{c} \text{N}=\text{CAr} \\ \text{CO}\cdot\text{CH}_2 \end{array}$ . The

$\beta$ -amino-acids are most conveniently obtained by starting with the esters of the cinnamic acids, and the aryl methyl ketones by starting with the acids themselves.

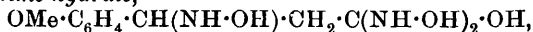
The following experimental results are recorded. The numbers after the names of the acids denote the duration in hours of the boiling with alcoholic hydroxylamine. *o*-Nitrocinnamic acid (240) yields *o*-nitro- $\beta$ -amino- $\beta$ -phenylpropionic acid, m. p. 222° (decomp.). Ethyl *o*-nitrocinnamate (two days at 0°) yields *o*-nitro- $\beta$ -hydroxylamino- $\beta$ -phenylpropionhydroxamic acid,



m. p. 135°, and (ten hours) *o*-nitro- $\beta$ -amino- $\beta$ -phenylpropionic acid. *m*-Nitrocinnamic acid yields ( $\frac{3}{4}$ ) hydroxylamine *m*-nitrocinnamate, m. p. 150° (decomp.), and (10) *m*-nitro- $\beta$ -amino- $\beta$ -phenylpropionate, m. p. 236° (decomp.), yellow needles. Ethyl *m*-nitrocinnamate yields (four days at 0°) *m*-nitro- $\beta$ -hydroxylamino- $\beta$ -phenylpropionhydroxamic acid, m. p. 163—164° (decomp.), and (ten hours) *m*-nitro- $\beta$ -amino- $\beta$ -phenylpropionic acid. *p*-Nitrocinnamic acid (240) yields *p*-nitro- $\beta$ -amino- $\beta$ -phenylpropionic acid, m. p. 226° (decomp.), and *p*-nitroacetophenoneoxime, m. p. 172—173°. Ethyl *p*-nitrocinnamate (shaken for one hundred and ten hours) yields *p*-nitro- $\beta$ -hydroxylamino- $\beta$ -phenylpropionhydroxamic acid, m. p. 140° (decomp.), and (ten hours) *p*-nitro- $\beta$ -amino- $\beta$ -phenylpropionic acid. *o*-Aminocinnamic acid ( $\frac{3}{4}$  or 10) and its ethyl ester, (thirty days' keeping or ten hours' boiling) yield only carbostyrl. *m*-Aminocinnamic acid (10) yields *m*- $\beta$ -diamino- $\beta$ -phenylpropionic acid, m. p. 228° (decomp.). Ethyl *m*-aminocinnamate yields (five days at 0°) *m*-amino- $\beta$ -hydroxylamino- $\beta$ -phenylpropionhydroxamic acid, m. p. 100—101° (decomp.), and (ten hours) *m*- $\beta$ -diamino- $\beta$ -phenylpropionic acid. *o*-Coumaric acid yields (3)  $\beta$ -aminodihydro-*o*-coumaric acid, which is also obtained from the ethyl ester (10). *m*-Hydroxycinnamic acid yields ( $\frac{3}{4}$ ) hydroxylamine  $\beta$ -hydroxylamino-*m*-hydroxy- $\beta$ -phenylpropionhydroxamate (?), decomp. 129—130°, and (10)  $\beta$ -amino-*m*-hydroxy- $\beta$ -phenylpropionic acid, m. p. 235—236° (decomp.). Methyl *m*-hydroxycinnamate yields (10)  $\beta$ -hydroxylimino-*bis*-*m*-hydroxy- $\beta$ -phenylpropionhydroxamic acid,



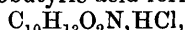
m. p. 187—188° (decomp.), and (24)  $\beta$ -amino-*m*-hydroxy- $\beta$ -phenylpropionic acid. *p*-Hydroxycinnamic acid yields ( $\frac{3}{4}$ )  $\beta$ -hydroxylamino-*p*-hydroxy- $\beta$ -phenylpropionic acid, m. p. 166° (decomp.), and (10)  $\beta$ -amino-*p*-hydroxy- $\beta$ -phenylpropionic acid, m. p. 198° (decomp.), which is also obtained from the methyl ester (10). *cis*-*o*-Methoxycinnamic acid ( $\frac{3}{4}$ ) yields *trans*-*o*-methoxycinnamic acid and  $\beta$ -amino-*o*-methoxy- $\beta$ -phenylpropionic acid, m. p. 209—210° (decomp.) [benzoyl derivative,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{NH} \cdot \text{Bz}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 201°], which is also obtained from methyl *cis*-*o*-methoxycinnamate (10), *trans*-*o*-methoxycinnamic acid (10), and its methyl ester (10). *m*-Methoxycinnamic acid (10) yields  $\beta$ -amino-*m*-methoxy- $\beta$ -phenylpropionic acid, m. p. 216° (decomp.), which is also obtained from the methyl ester (10). *p*-Methoxycinnamic acid (10) yields  $\beta$ -amino-*p*-methoxy- $\beta$ -phenylpropionic acid, m. p. 243° (decomp.). Methyl *p*-methoxycinnamate yields (three days at 0°)  $\beta$ -hydroxylamino-*p*-methoxy- $\beta$ -phenylpropionhydroxamoxime hydrate,



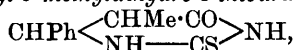
decomp. 125—129°, and (10)  $\beta$ -amino-*p*-methoxy- $\beta$ -phenylpropionic acid. Caffeic acid (15) yields  $\beta$ -aminodihydrocaffeic acid, m. p. 196°

(decomp.). Ferulic acid (240) and its methyl ester (10) each yield  $\beta$ -aminodihydroferulic acid, m. p. 182° (decomp.). Piperonylacrylic acid (15) yields  $\beta$ -aminopiperonylpropionic acid, m. p. 233° (decomp.), and acetopiperoneoxime,  $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_5\cdot\text{CMe}\cdot\text{NOH}$ , m. p. 156—157°, by the hydrolysis of which acetopiperone is obtained most conveniently. Methyl piperonylacrylate (15) yields only  $\beta$ -aminopiperonylpropionic acid, which is converted into  $\beta$ -carbamidopiperonylpropionic acid, m. p. 178—179° (decomp.), by boiling aqueous potassium cyanate.

In part, with AUGUST STIRNUS.]— $\alpha$ -Methylcinnamic acid (100) yields  $\beta$ -amino- $\beta$ -phenylisobutyric acid,  $\text{NH}_2\cdot\text{CHPh}\cdot\text{CHMe}\cdot\text{CO}_2\text{H}$ , m. p. 243° (decomp.), which is also obtained from the methyl ester (90).  $\beta$ -Amino- $\beta$ -phenylisobutyric acid forms a hydrochloride,

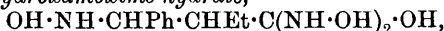


m. p. 227° (decomp.), and a benzoyl derivative, m. p. 205°, reacts with boiling aqueous potassium cyanate to form  $\beta$ -carbamido- $\beta$ -phenylisobutyric acid, m. p. 153° (decomp.) (which yields 4-phenyl-5-methyldihydrouracil,  $\text{CHPh}\langle\begin{smallmatrix} \text{CHMe}\cdot\text{CO} \\ \text{NH}—\text{CO} \end{smallmatrix}\rangle\text{NH}$ , m. p. 185°, at 160°), and by treatment with boiling dilute hydrochloric acid and potassium thiocyanate yields, after evaporation of the solution and heating the residue at 140°, 4-phenyl-5-methyldihydro-3-thiouracil,

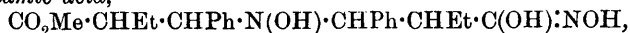


m. p. 186°. The presence of the amino-group in the  $\beta$ -position in  $\beta$ -amino- $\beta$ -phenylisobutyric acid, which is proved by the formation of the preceding uracil derivatives, is confirmed by the behaviour of the acid towards nitrous acid, whereby  $\beta$ -hydroxy- $\beta$ -phenylisobutyric acid is formed.

$\beta$ -Methylcinnamic acid (240) yields  $\beta$ -amino- $\beta$ -phenylbutyric acid,  $\text{NH}_2\cdot\text{CPhMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , m. p. 225° (decomp.), which is also obtained from the methyl ester (10) or the ethyl ester (240), and is converted into 4-phenyl-4-methyldihydrouracil, m. p. 240—241°, by treatment with boiling aqueous potassium cyanate and acidifying.  $\alpha$ -Ethylcinnamic acid yields ( $\frac{3}{4}$ ) hydroxylamine  $\alpha$ -ethylcinnamate and (10)  $\beta$ -amino- $\beta$ -phenyl- $\alpha$ -ethylpropionic acid, m. p. 227° (decomp.). Methyl  $\alpha$ -ethylcinnamate (several days at 0°) yields  $\beta$ -hydroxylamino- $\beta$ -phenyl- $\alpha$ -ethylpropionhydroxamoxime hydrate,



m. p. 121° (decomp.), and after thirty-five or thirty-one hours, according to the experimental conditions, either an impure substance, m. p. 190—215°, or methyl hydroxyliminobis- $\beta$ -phenyl- $\alpha$ -ethylpropionate-hydroxamic acid,

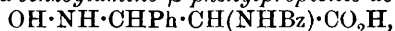


m. p. 228° (decomp.), or  $\beta$ -amino- $\beta$ -phenyl- $\alpha$ -ethylpropionic acid. The last substance is obtained, together with some unchanged ester, from methyl  $\alpha$ -ethylcinnamate (190).  $\beta$ -Ethylcinnamic acid (240) yields  $\beta$ -amino- $\beta$ -phenylvaleric acid, m. p. 217° (decomp.), which is also obtained from the methyl ester (10) or ethyl ester (240), forms a pale blue copper salt,  $2\text{Cu}(\text{C}_{11}\text{H}_{14}\text{O}_2\text{N})_2\cdot\text{C}_{11}\text{H}_{15}\text{O}_2\text{N}\cdot\text{H}_2\text{O}$ , and is converted into 4-phenyl-4-ethyldihydrouracil, m. p. 220—221°, by boiling aqueous potassium cyanate and subsequent acidification.

$\alpha$ -Phenylcinnamic acid yields (2) stilbene and (240)  $\beta$ -amino- $\alpha\beta$ -diphenylpropionic acid, m. p. 225° (decomp.) (hydrochloride, m. p. 238°), which is also obtained from the methyl ester (10).  $\beta$ -Carbamido- $\alpha\beta$ -diphenylpropionic acid,  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$ , m. p. 141° (decomp.), is converted at 145—150° into 4:5-diphenyldihydrouracil, m. p. 268°.

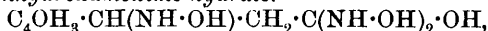
$\beta$ -Phenylcinnamic acid (240) yields  $\beta$ -amino- $\beta\beta$ -diphenylpropionic acid, m. p. 208° (decomp.). Methyl  $\beta$ -phenylcinnamate yields (10) 3:3-diphenylisooxazolidone,  $\text{O} \begin{array}{c} \text{CO}-\text{CH}_2 \\ | \\ \text{NH}\cdot\text{CPh}_2 \end{array}$ , m. p. 199—199·5°,

and (240) a mixture of diphenylisooxazolidone and  $\beta$ -amino- $\beta\beta$ -diphenylpropionic acid.  $\alpha$ -Benzoylamino- $\alpha\beta$ -cinnamic acid yields ( $\frac{3}{4}$ )  $\beta$ -hydroxylamino- $\alpha$ -benzoylamino- $\beta$ -phenylpropionic acid,



m. p. 195° (decomp.). Ethyl  $\alpha$ -benzoylamino- $\alpha\beta$ -cinnamate (two days at 0°) yields  $\beta$ -hydroxylamino- $\alpha$ -benzoylamino- $\beta$ -phenylpropionhydroxamic acid,  $\text{OH}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CH}(\text{NHBz})\cdot\text{C}(\text{OH})\cdot\text{NOH}$ , m. p. 128° (decomp.). This hydroxamic acid is converted by boiling water into  $\beta$ -amino- $\alpha$ -benzoylamino- $\beta$ -phenylpropionic acid, m. p. 193° (decomp.), from which  $\beta$ -carbamido- $\alpha$ -benzoylamino- $\beta$ -phenylpropionic acid, m. p. 205°, is obtained by boiling aqueous potassium cyanate.

Furylacrylic acid (288) yields a substance, m. p. 102·5°, which appears to be Bouveault's acetylfuranoxime. Methyl furylacrylate (many days at the ordinary temperature) yields  $\beta$ -hydroxylamino- $\beta$ -furylpropionhydroxamoxime hydrate.



m. p. 109°. This substance, which is also obtained from ethyl furylacrylate (6), is converted by boiling water into  $\beta$ -amino- $\beta$ -furylpropionic acid, m. p. 205° (decomp.) (benzoyl derivative, m. p. 180°).  $\beta$ -Carbamido- $\beta$ -furylpropionic acid and 4- $\alpha$ -furyldihydroureacil have m. p. 175° and 210° respectively; the latter is obtained from the former at about 180°.

Atropic acid (1) yields  $\beta$ -amino- $\alpha$ -phenylpropionic acid, not  $\alpha$ -amino- $\alpha$ -phenylpropionic acid as stated previously (Abstr., 1904, i, 160; 1905, i, 577); the  $\beta$ -amino- $\alpha$ -phenylpropionic acid ( $\beta$ -aminohydratropic acid) of the literature is really  $\alpha$ -phenyl- $\beta$ -lactamide. Phenylisocrotonic acid (five minutes) yields hydroxylamine phenylisocrotonate, not  $\gamma$ -hydroxylamino- $\gamma$ -phenylbutyric acid (Abstr., 1904, i, 160).

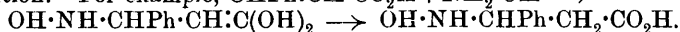
[With OTTO UNVERDORFEN.]—Styrene, stilbene,  $\omega$ -bromostyrene,  $\omega$ -chlorostyrene, allyl alcohol, and amylene do not form additive compounds with hydroxylamine.  $\omega$ -Nitrostyrene (many days at 0° or boiling for one hour) yields  $\alpha$ -nitro- $\beta$ -hydroxylamino- $\beta$ -phenylethane,  $\text{NO}_2\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{NH}\cdot\text{OH}$ , m. p. 99—100°, colourless crytals.

Cinnamic anhydride yields ( $\frac{3}{4}$ )  $\beta$ -hydroxylamino- $\beta$ -phenylpropionhydroxamoxime hydrate, or, by longer boiling,  $\beta$ -amino- $\beta$ -phenylpropionic acid. The same results are obtained with cinnamamide and with cinnamhydroxamic acid. Cinnamionitrile (three days at 0°, or boiling for five hours) yields cinnamamideoxime.

[With KARL RÖHDE.]—Cinnamaldehyde yields (at 0°, or by boiling for twenty hours) cinnamaloxime and (200) a substance, m. p. 205—206°, which does not contain nitrogen.

Only towards the end of the research was the discovery made that methylarylketoximes are frequently obtained by the reaction of hydroxylamine with cinnamic acids. A further communication on the subject is promised.

Other investigators have shown that ammonia, hydrogen cyanide, ethyl malonate, or ethyl acetoacetate can be added at a carbonyl group, but not at a C:C group, and, conversely, that halogens or halogen acids can be attached to a C:C group, but not to the carbonyl group. When both groups are present in the form C:C·CO, all addenda are apparently attached at the C:C group in such a manner that, if the addendum is a substance containing hydrogen and another atom or group, the hydrogen is attached in the  $\alpha$ -, and the other constituent of the addendum in the  $\beta$ -, position. The author is of opinion, however, that an addendum (consisting of strongly positive hydrogen or alkali metal and another atom or group of less highly pronounced polar character, such as  $\text{NH}_2$ ,  $\text{NH}\cdot\text{OH}$ ,  $\text{CN}$ , etc.) is attached at a double linking or to a conjugated system, only when the terminal atom is oxygen or nitrogen. The CO or the CN group, alone or conjugated with C:C, is able to combine with such addenda; the C:C group, alone or in conjugation with another C:C, is unable to do so. This leads to the theory that the necessary condition for the attachment of such addenda to an unsaturated system, whether simple or conjugated, is the presence in the unsaturated system of a terminal oxygen or nitrogen atom, which is the first point of attack during the addition. For example,  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H} + \text{NH}_2\cdot\text{OH} \rightarrow$



The influence, on the course of the addition, of addenda containing like or unlike atoms of strongly polar character is discussed, and generalisations are stated which serve to account for many instances of abnormal addition.

C. S.

**Menthyl Esters of  $\alpha$ -Phenyldihydrocinnamic [ $\alpha\beta$ -Diphenylpropionic] Acids.** HANS RUPE and W. KERKOVUS (*Ber.*, 1912, 45, 1398—1403).—*r*- $\alpha\beta$ -Diphenylpropionic acid, like *r*- $\beta$ -phenylbutyric acid (Abstr., 1909, i, 927), is resolved into its active constituents by esterification with menthol. The mixture of esters, obtained by the action of the alcohol on the acid chloride in the presence of pyridine and benzene, is separated by alcohol into the more fusible and more soluble menthyl *l*- $\alpha\beta$ -diphenylpropionate, m. p. 58—62°,  $[\alpha]_D^{20} - 84.99^\circ$  (*loc. cit.*), and the less fusible and less soluble menthyl *d*- $\alpha\beta$ -diphenylpropionate, m. p. 100—101°,  $[\alpha]_D^{20} - 21.97^\circ$ . The same two esters are produced by resolving *r*- $\alpha\beta$ -diphenylpropionic acid by means of its strychnine salt and esterifying the active acid chlorides.

The hydrolysis of the esters by alcoholic potassium hydroxide is accompanied by extremely rapid racemisation, since the resulting acids are optically inactive.

C. S.

**Preparation of Esters of Salicylic Acid.** ACTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 244208).—*Allyl salicylate*, a colourless liquid with a cabbage-like odour, b. p.

247—250° or 105—106°/5 mm.,  $D^{15}_D$  1.100, is prepared by either heating salicylic acid with allyl alcohol in the presence of a condensing agent, or by the action of allyl iodide on potassium salicylate in allyl alcoholic solution.

F. M. G. M.

[Preparation of Triphenylmethane Derivatives.] FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 243086).—A description of the preparation of dyes obtained by condensing *oo'*-methylenedioxydibenzoic acids in concentrated sulphuric acid solution with derivatives of salicylic acid in the presence of an oxidising agent.

The tinctorial properties of the following condensation products are tabulated in the original.

*s*-Xylenol-2-carboxylic acid with (1) 2:2'-methylenedioxy-di-*m*-toluic acid, with (2) 2:4'-methylenedioxy-di-*m*-toluic acid, (3) with 2:2'-methylenedioxydibenzoic acid; and of 2:2'-methylenedioxy-di-*m*-toluic acid with (1) 3-hydroxy-*p*-toluic acid, with (2) *m*-chlorosalicylic acid, and with (3) 6-chloro-2-hydroxy-*m*-toluic acid.

F. M. G. M.

**Homogentisic Acid.** I. CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1912, 78, 306—326. Compare Abstr., 1911, i, 56).—*Benzoquinone-2-acetic acid*,  $C_6H_3O_2 \cdot CH_2 \cdot CO_2H$ , prepared by oxidation of homogentisic acid with sodium dichromate and sulphuric acid, crystallises in thin rhombohedric or quadratic plates having the same colour as lead iodide, m. p. 130° (decomp.). It tastes and reacts acid, and has the oxidising action of quinones. The clear reddish-yellow aqueous solution becomes darker when kept, and finally deposits a black sediment, characterised as homogentisic acid. On addition, first of potassium iodide and then cautiously of sodium hydroxide, a cherry-red colour is formed, which becomes olive-green on further addition of sodium hydroxide.

*Homogentisic acid quinhedrone*, prepared by the interaction of homogentisic acid and benzoquinoneacetic acid in acetone, forms a dark bluish-violet powder (decomp. 144°).

Benzoquinoneacetic acid also results when homogentisic acid is oxidised with ferric chloride.

E. F. A.

**Derivatives of 5-Nitro Eugenol and of Nitrated Methoxybenzoic Acids.** ALFONS KLEMENC (*Monatsh.*, 1912, 33, 375—392).—The work is in continuation of that by Wegscheider and Klemenc (Abstr., 1911, i, 541).

Fuming nitric acid was added to a solution of eugenol in ether, the solution boiled, and the crude potassium salt of 5-nitro Eugenol precipitated by addition of methyl-alcoholic potassium hydroxide. This salt was dissolved in water, and the solution treated with carbon dioxide, which precipitated 5-nitro Eugenol together with a small quantity of an *acid potassium* salt of 5-nitro Eugenol. Separation of these substances was effected by means of ether. The acid potassium salt of 5-nitro Eugenol,  $C_{10}H_{11}O_3N_2K$ , is a red, crystalline substance, which decomposes at 215°. Concentrated hydrochloric acid very

slowly transforms it into 5-nitro Eugenol. When boiled with water it is decomposed, and, on cooling, 5-nitro Eugenol separates. Boiling alcohol (96%) also decomposes it with separation of the normal potassium salt of 5-nitro Eugenol. It can also be obtained by adding 5-nitro Eugenol to an aqueous solution of the normal potassium salt of 5-nitro Eugenol. Methylation and subsequent oxidation of the oil so formed yields 5-nitroveratric acid.

5-Nitro Eugenol methyl ether can be obtained by methylation of the normal potassium salt of 5-nitro Eugenol by methyl iodide, or, better, by treating an ethereal solution of 5-nitro Eugenol with diazomethane. Methylation by means of methyl sulphate is difficult. Oxidation of 5-nitro Eugenol methyl ether in dilute acetic acid solution by means of potassium permanganate gives a mixture of 5-nitroveratric acid and 5-nitrohomoveratric acid. Oxidation in alkaline solution yields 5-nitroveratric acid.

5-Nitrohomovanillic acid, m. p.  $217^{\circ}$  (decomp.), was obtained by the oxidation of 5-nitroacetyleneugenol by means of potassium permanganate in very dilute acetic acid solution. Its ammonium and silver salts were examined. The crude oxidation product generally contains also 5-nitrovanillic acid. If smaller quantities of water are employed, the yield of 5-nitrohomovanillic acid is less, whilst if the oxidation is performed in glacial acetic acid solution, still less 5-nitrohomovanillic acid and more 5-nitrovanillic acid is produced.

Methyl 5-nitrohomovanillate, m. p.  $101-102^{\circ}$ , was transformed into its potassium salt, and the latter boiled with methyl iodide in methyl alcoholic solution. The crude oil was cautiously saponified by potassium hydroxide, and the liberated acids recrystallised from benzene, whereby 5-nitrohomoveratric acid, m. p.  $113-114^{\circ}$ , was obtained. Its ammonium, silver, uranyl, and copper salts were examined. The methylation of 5-nitrohomovanillic acid is more readily accomplished by means of diazomethane. Methyl sulphate is without action on the acid or its ester.

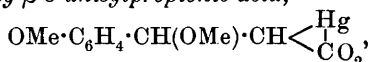
5-Nitroveratric acid was boiled with aniline during thirty minutes, whereby it was transformed into 5-nitrovanillic acid and 6-nitroguaiacol. More prolonged boiling increased the yield of 6-nitroguaiacol at the expense of the 5-nitrovanillic acid, a black mass, insoluble in alkali, being simultaneously formed. 5-Nitroveratric acid was stable towards boiling concentrated hydrochloric acid. Boiling concentrated potassium hydroxide caused slow elimination of a methoxy-group.

Methyl 5-nitrovanillate forms yellow needles, m. p.  $154-155^{\circ}$ .

5-Nitroveratric acid, when treated with cold fuming nitric acid (D 1.52), yields 3:4:5-trinitroveratrole and 5:6-dinitroveratric acid, m. p.  $193^{\circ}$ . This acid is also obtained by cautious saponification of its methyl ester. Its ferric, ammonium, and copper salts were examined. When the ammonium salt is heated at  $180-200^{\circ}$ , methyl 5:6-dinitroveratrate, m. p.  $133-134^{\circ}$ , is obtained. Distillation of a mixture of the potassium salt and lime leads to the formation of methyl 5:6-dinitroveratrate and 5:6-dinitrovanillic acid, m. p.  $215^{\circ}$  (decomp.). Nitration of methyl 5-nitroveratrate by means of fuming nitric acid (D 1.52) at  $60^{\circ}$  gives an almost quantitative yield of methyl

5 : 6-dinitroveratrate, m. p. 133—134·5°. This, when saponified by boiling potassium hydroxide, yields 5 : 6-dinitrovanillic acid, the *ferric* salt of which was examined. The acid could not be acetylated by acetic anhydride and sulphuric acid. H. W.

**The Coumarin Group.** EINAR BIILMANN (*Annalen*, 1912, 388, 259—279).—Despite numerous researches on coumarin and its derivatives, satisfactory explanations have not yet been given of the slight activity of its ethylenic linking and of the conversion of coumarin into coumaric acid. In connexion with the first problem, the author utilises the fact that ethylene derivatives containing two negative groups do or do not form complex mercuri-compounds according as the two groups have the *cis*- or the *trans*-configuration (Abstr., 1902, i, 665; 1910, i, 346). Methylcoumarinic acid reacts with mercuric acetate in methyl alcohol to form an *inner* salt of *α*-mercuri-*β*-methoxy-*β*-o-anisylpropionic acid,



a white, microcrystalline substance which is converted into *β*-methoxy-*β*-o-anisylpropionic acid, m. p. 82°, by hydrogen sulphide in alkaline solution. Coumarin does not react with methyl alcoholic mercuric acetate, a fact which, taken in conjunction with the unstable character of the additive compounds of coumarin and bromine and hydrogen bromide (Clayton, *Trans.*, 1908, 93, 524), indicates that coumarin does not contain an ordinary ethylenic linking.

[With ULLA STARCKE].—Contrary to expectation, coumaric acid and methylcoumaric acid each react with mercuric acetate in methyl alcohol. The former yields the *inner* salt of *α*-mercuri-*β*-methoxymelilotic acid,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OMe}) \cdot \text{CH} < \begin{array}{c} \text{Hg} \\ | \\ \text{CO}_2 \end{array}$ , which is converted into *β*-methoxy-melilotic acid,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OMe}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 123° (decomp.), by hydrogen sulphide in alkaline solution. Methylcoumaric acid yields an *inner* salt isomeric with that obtained from methylcoumarinic acid; it is converted into the same acid, m. p. 82°, by hydrogen sulphide.

[With AGNES HOFF].—It is known that the conversion of coumarin into coumaric acid is effected very slowly by boiling aqueous alkali, but proceeds very rapidly when the lactone is heated with alcoholic sodium ethoxide and the solution is treated with water and acidified after removal of the alcohol; ethyl coumarate is formed as an intermediate product (Fries and Klostermann, *Abstr.*, 1908, i, 820). The following three experiments throw light on the course of the change: (1) Coumarin dissolves in cold methyl alcoholic sodium methoxide with an intense yellow colour; acidification by dilute acetic acid regenerates coumarin. (2) Coumarin and sodium methoxide (2 mols.) are kept in methyl alcoholic solution at the ordinary temperature for a few hours. Ice-water and acetic acid are then added, whereby a mixture of coumarin, methyl coumarate, and an oil (which yields *β*-methoxymelilotic acid by hydrolysis, and is almost certainly its methyl ester) is obtained. (3) Same as (2) except that after the addition of the

water the mixture is kept for twelve to thirty-six hours before acidifying. A mixture of coumarin, coumaric acid, and  $\beta$ -methoxymelilotic acid is thus obtained.

These results are interpreted as follows: The yellow substance obtained in (1) is the additive compound,  $\text{ONa}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$ . The product of acidification is methyl coumarinate, which at once regenerates coumarin. In the presence of an excess of sodium methoxide, the additive compound takes up another molecule of methyl alcohol, and forms the sodium derivative of methyl  $\beta$ -methoxymelilotate,  $\text{ONa}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OMe})\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ , by the acidification of which the oil (methyl  $\beta$ -methoxymelilotate?) is formed. (*Methyl- $\beta$ -methoxymelilotate*, obtained from the silver salt and methyl iodide, is an oil very similar to the preceding, and is converted into methyl coumarate by methyl alcoholic sodium methoxide.) By long keeping before acidification, however, the sodium derivative of methyl  $\beta$ -methoxymelilotate loses methyl alcohol, and forms the sodium derivative of, not methyl coumarinate, but methyl coumarate, so that coumaric acid is finally obtained by acidification and the accompanying hydrolysis.

When experiments similar to the preceding are performed with sodium methoxide and ethyl alcohol, ethyl coumarate, coumaric acid, and  $\beta$ -ethoxymelilotic acid, m. p. 98°, are obtained. C. S.

**Cyanohydrins, and the Corresponding Benzoylamides and Alcohols.** JULES ALOY and CH. RABAUT (*Bull. Soc. chim.*, 1912, [iv], 11, 389—393).—The authors have applied the methods of Francis and Davis (*Trans.*, 1909, 95, 1403; 1910, 97, 949) for the preparation of acyl derivatives of aldehyde-cyanohydrins to a number of phenolic aldehydes, and in some cases have prepared the corresponding benzoyl amides and hydroxy-acids.

*p*-Hydroxybenzaldehyde with benzoyl chloride and potassium cyanide yields *p*-benzoyloxybenzoylmandelonitrile [*a*:4-dibenzoyloxyphenylacetone nitrile], m. p. 143—144°, which crystallises from chloroform on addition of ether. 4-Benzoyloxybenzoyl-*m*-tolylglycollonitrile [*a*:4-dibenzoyloxy-*o*-tolylacetone nitrile],  $\text{OBz}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CH}(\text{OBz})\cdot\text{CN}$ , m. p. 124—125°, similarly obtained from 4-hydroxy-*m*-tolualdehyde, forms colourless crystals. The corresponding substance obtained from vanillin has m. p. 146—147°. Salicylaldehyde gives a liquid compound. All these products are stable, and do not decompose when heated at 100° for several hours.

Benzoylmandelonitrile in contact with fuming hydrochloric acid at atmospheric temperature furnishes benzoylmandelamide. In the case of the dibenzoylcyanohydrins derived from the phenolic aldehydes it is better to heat them at 100° in closed tubes with hydrochloric acid. Under these conditions, *p*-benzoyloxybenzoylmandelonitrile furnishes the corresponding amide,  $\text{OBz}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OBz})\cdot\text{CO}\cdot\text{NH}_2$ , m. p. 183—184°, colourless crystals, soluble in alcohol, insoluble in water, which on hydrolysis by sodium hydroxide solution gives *p*-hydroxymandelic acid. It is not always necessary to isolate the amide in order to convert it into the corresponding hydroxy-acid; thus the benzoylcyanohydrin derived from anisaldehyde on long keeping

with fuming hydrochloric acid at atmospheric temperature, yields *p*-methoxymandelic acid.

T. A. H.

**Esterification of Unsymmetrical Di- and Poly-basic Acids.**  
**XXIV. Esterification of Amino- and Acetamino-terephthalic Acids.** RUDOLF WEGSCHEIDER and FRANZ FALTIS (*Monatsh.*, 1912, 33, 185—205. Compare Cahn Speyer, *Abstr.*, 1907, i, 849).—When the amino-group in aminoterephthalic acid is regarded as positive, the carboxyl group in position 4 is the stronger acid, and the least affected by steric hindrance. According to Wegscheider's rule, when esterified by alcohol, with or without mineral acids, or by methyl iodide, aminoterephthalic acid should give salts of the 4-ester acid, whereas on partial hydrolysis of the neutral ester, the 1-ester acid should be formed. Experiment shows that this hydrolysis gives rise likewise to the 4-ester acid, affording an exception to the rule.

In the case of acetylaminoterephthalic acid, the acetyl-amino-group is negative; accordingly, when esterified by methyl iodide, the 1-ester acid should result, as is actually the case. On esterification with methyl alcohol, the 4-ester acid is formed; in both cases the acetyl group is eliminated during the process. Hydrolysis of the neutral ester of acetylaminoterephthalic acid yields the 4-ester acid instead of the 1-ester acid forecasted by Wegscheider's rule.

Acetylaminoterephthalic acid has decomp.  $272^{\circ}$  (corr.); it crystallises +  $\text{CH}_3\text{OH}$  from solution in methyl alcohol in large, lustrous, golden-yellow aggregates.

4-Methyl 1-hydrogen 2-acetylaminoterephthalate crystallises in colourless, stunted needles, m. p.  $207\text{--}208^{\circ}$  (corr.), becoming solid again at  $245^{\circ}$ , and finally melting at  $305^{\circ}$  (compare Cahn-Speyer, *loc. cit.*).

*Methyl acetylanthranilcarboxylate*, formed on prolonged heating of the 2-acetyl-amino-4-ester acid with a large excess of acetic anhydride, has m. p.  $148\text{--}149^{\circ}$  (corr.), becoming solid at about  $265^{\circ}$ .

E. F. A.

**Esterification of Unsymmetrical Di- and Poly-basic Acids.**  
**XXV. Esterification of Dimethylaminoterephthalic Acid.** RUDOLF WEGSCHEIDER and SIEGMUND BLACK (*Monatsh.*, 1912, 33, 207—221).—According to Wegscheider's rule the main product on esterification of dimethylaminoterephthalic acid with alcohols, with or without mineral acids, or by means of alkyl iodides should be the 4-ester acid, whereas on partial hydrolysis of the neutral ester the 1-ester acid should result.

This is the case when methyl-alcoholic potassium hydroxide is used for hydrolysis, but when the neutral ester is hydrolysed in neutral or acid, and probably also in alkaline, aqueous solution, the 4-ester acid predominates. This is the first time on which such a pronounced influence of the solvent on hydrolysis has been recorded.

The following salts of dimethylaminoterephthalic acid are described: *potassium hydrogen salt* +  $2\text{H}_2\text{O}$ , decomp.  $160^{\circ}$ ; *silver hydrogen salt*, which is faintly yellow-coloured, decomp.  $200^{\circ}$ ; *silver salt*, which is at first colourless, but becomes deep blue overnight and black when dried.

4-Methyl 1-hydrogen 2-dimethylaminoterephthalate forms colourless, slender crystals, m. p. 172—174°.

1-Methyl 4-hydrogen 2-dimethylaminoterephthalate crystallises in slender, golden-yellow needles, m. p. 132—133°. E. F. A.

Esterification of Unsymmetrical Di- and Poly-basic Acids. XXVI. Esterification of Methyl Aminoterephthalic Acid. RUDOLF WEGSCHEIDER and OSKAR HUPPERT (*Monatsh.*, 1912, 33, 223—234).—Contrary to the behaviour of aminoterephthalic acid and its dimethylamino-derivative, methyl aminoterephthalic acid behaves quite normally when its neutral ester is partly hydrolysed with potassium hydroxide or hydrogen chloride in aqueous or methyl alcoholic solution, forming the 1-ester acid. By the action of methyl iodide on the normal silver or acid potassium salts, 4-methyl 1-hydrogen dimethylaminoterephthalate is obtained.

The silver salt of methylaminoterephthalic acid is light yellowish-brown when freshly precipitated, but quickly becomes darker.

The potassium hydrogen salt crystallises in lustrous, silvery plates; it is yellow after drying at 100°.

The normal ester has m. p. 89—90°; it is triclinic [ $a:b:c = 0.643:1:0.9907$ ]. It has a citron-yellow colour with a blue fluorescence.

1-Methyl 4-hydrogen 2-methylaminoterephthalate crystallises in platelets, m. p. 208.5—209.5° (corr.).

The 4-methyl ester acid of 2-dimethylaminoterephthalic acid (compare Wegscheider and Black, preceding abstract), m. p. 178—179°, forms measureable triclinic crystals [ $a:b:c = 0.7908:1:0.8297$ ].

E. F. A.

Action of Oxalyl Chloride on Aromatic Hydrocarbons. CARL LIEBERMANN [with M. KARDOS, W. RAHTS, PROFULLA MITTER, and D. BUTESCU] (*Ber.*, 1912, 45, 1186—1217. Compare Abstr., 1911, i, 202, 387).—Whereas diphenyl with oxalyl chloride yields mainly monocarboxylic acid, 4:4'-dimethyldiphenyl with the same reagent yields mainly dicarboxylic acid with a considerable proportion of quinone (dimethylphenanthraquinone). Other 4:4'-derivatives have now been studied: 4:4'-dinitrodiphenyl does not react with oxalyl chloride and aluminium chloride; 4:4'-dibromodiphenyl only gives very little acid, whilst 4:4'-dimethoxydiphenyl gives very little monocarboxylic acid. With 3:3'- and 2:2'-dimethyldiphenyl considerable quantities of dicarboxylic acid and a little monocarboxylic acid were obtained, but no quinone.

With 2:4:2':4'-dixylyl, which contains methyl groups in the para- and ortho-positions, dicarboxylic acid and no quinone was obtained.

Anthracene derivatives, substituted in the benzene nucleus, yielded in every case *meso*-anthracenemonocarboxylic acids and aceanthrene-quinones.

Phenyl radicles joined through a methane or aliphatic group give rise to acids and not quinones with oxalyl chloride. In these cases the higher carboxylic acids are formed; thus triphenylmethane yields

tri- and di-carboxylic acids. From stilbene, carboxylic acids of a polymerised stilbene were obtained.

Increase of the number of methyl groups in the benzene nucleus has no effect; the three isomeric xylenes give monocarboxylic acids.

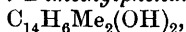
On oxidation of 4:4'-dimethylphenanthraquinone with chromic acid the methyl groups are oxidised to carboxyl, and one of the latter is eliminated, so that phenanthraquinonemonocarboxylic acid is obtained, which could not be further oxidised without complete decomposition.

It was possible, however, to convert dimethylphenanthraquinone-oxime into 4:4'-dimethyldiphenyl-2:2'-dicarboxylic acid, isomeric with 4:4'-dimethyldiphenic acid.

These compounds are further oxidised to tetracarboxylic acids, which differ mainly in the melting points of their methyl esters, and in the fluorescein reaction with resorcinol without zinc chloride. The exact position of the groups is discussed; it has not yet been established with certainty.

Oxalyl chloride affords a very satisfactory means of introducing carboxyl groups into aromatic hydrocarbons, and when methyl groups are also present in the phenyl radicle, higher carboxylic acids are readily obtained on oxidation. Oxalyl chloride differs in its action from phosgene, which mainly yields ketones and probably acts in virtue of the complex  $\text{CO}\cdot\text{COCl}$ .

[With M. KARDOS.]—2:7-Dimethylphenanthrene-9:10-diol,



obtained from the corresponding quinone by reduction with zinc dust and acetic acid, crystallises in well-formed, long, colourless needles in the tube, but it is soon darkened on access of air, m. p. 175—180°; the *quinhydrone* could not be obtained pure.

2:7-Dimethylphenanthraquinonemono-oxime crystallises in lustrous, silky, yellow needles, m. p. 180—181°, and dissolves in concentrated sulphuric acid with a faint violet coloration. When dissolved in acetic anhydride and heated with hydrogen chloride, it undergoes rearrangement, and 4:4'-dimethyldiphenyl-2:2'-dicarboxylic acid is obtained in microscopic platelets, m. p. 258—260°. It does not give a fluorescein reaction with resorcinol; the *methyl* ester has m. p. 91—92°.

Diphenyl-2:4:2':4'-tetracarboxylic acid,  $\text{C}_{12}\text{H}_6(\text{CO}_2\text{H})_4$ , obtained on oxidation with potassium permanganate, is not melted at 325°, and does not form an anhydride; the *tetramethyl* ester has m. p. 181—182°.

4:4'-Dimethyldiphenylcarboxylic acid,  $\text{C}_{12}\text{H}_7\text{Me}_2\cdot\text{CO}_2\text{H}$ , has m. p. 197°.

4:4'-Dimethyldiphenyl-2:3'(1)-dicarboxylic acid forms an *ethyl* ester, m. p. 66—67°, a *methyl* ester, m. p. 113—115°, and a crystalline *chloride*,  $\text{C}_{12}\text{H}_6\text{Me}_2(\text{COCl})_2$ , m. p. 170—171°.

4:4'-Dimethyldiphenyldicarboxylic anhydride, prepared by heating the acid with acetic anhydride at 160—170°, crystallises in long needles, m. p. 286°.

Diphenyl 4:4':2:3'(1)-tetracarboxylic acid has m. p. 290°, and sublimes at this temperature. When heated with acetyl chloride, it appears to form mono- and di-anhydrides. On fusion with resorcinol an orange fluorescein is obtained. The *methyl* ester has m. p. 99—100°.

3:3'-Dimethyldiphenyl-4:4'-dicarboxylic acid, obtained from 3:3'-dimethyldiphenyl and oxalyl chloride, has m. p. above 300° (compare Loewenherz, Abstr., 1892, 852); the *methyl* ester crystallises in lustrous, silky needles, m. p. 137°; the *ethyl* ester has m. p. 77—78°. Diphenyl-3:3':4:4'-tetracarboxylic acid, obtained on oxidation, has m. p. above 300°; the *methyl* ester crystallises in transparent prisms, m. p. 99—100°. The acid (compare Loewenherz, *loc. cit.*) sublimes with difficulty in snow-like flakes; on heating at 100—115° the dianhydride is readily formed.

2:4:2':4'-Tetramethyldiphenyldicarboxylic acid, prepared from the corresponding tetramethylphenyl and oxalyl chloride, has m. p. 320—322°. On oxidation, diphenyl 2:2':4:4':6:6'(?)-hexacarboxylic acid,  $C_{12}H_4(CO_2H)_6$ , is formed, m. p. above 300°; the *methyl* ester crystallises in needles, m. p. 202—204°. On oxidation of dimethylphenanthraquinone, 9:10-phenanthraquinone-2-carboxylic acid is obtained (compare Werner and Ney, Abstr., 1902, i, 441); this crystallises in red needles and sublimes also in red needles.

4:4'-Dimethoxydiphenylcarboxylic acid,  $C_{12}H_7(OMe)_2 \cdot CO_2H$ , crystallises in needles, m. p. 180°.

[With W. RAHTS.]—*p-Tolylphenylmethanedicarboxylic acid*,  $CO_2H \cdot C_6H_3Me \cdot CH_2 \cdot C_6H_4 \cdot CO_2H$ , crystallises in colourless plates, m. p. 337°; the *dimethyl* ester has m. p. 94°.

*Di-p-tolylmethanedicarboxylic acid* has m. p. above 300°.

2:2'-Dimethyldiphenyldicarboxylic acid forms colourless plates, m. p. 287°; the *dimethyl* ester separates in colourless needles, m. p. 124°.

The diphenyltetracarboxylic acid obtained on oxidation has m. p. 334°; the tetramethyl ester has m. p. 141°; the acid gives only very little fluorescein with resorcinol.

[With PROFULLA MITTER.]—*Dinitro-diphenylmethane-4:4'-dicarboxylic acid* crystallises in slender needles, m. p. 271° (decomp.).

*Methyl diphenylmethane-4:4'-dicarboxylate* forms slender needles, m. p. 81—82°.

Dibenzyl-*p*-carboxylic acid separates in slender needles, m. p. 173—174° (not 228—230° as stated previously, Abstr., 1911, i, 202). The *sodium* salt, glistening platelets, and *calcium* salt, slender needles, are described. On oxidation, benzoic and terephthalic acids are obtained.

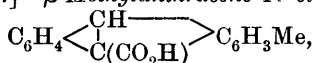
Dibenzyl-4:4'-dicarboxylic acid has m. p. 320°; the *dimethyl* ester crystallises in needles, m. p. 119° (compare Wolfenstein and Fischer, Abstr., 1904, i, 896).

Triphenylmethanetricarboxylic acid crystallises in prisms, m. p. 215° (decomp.).

Stilbenecarboxylic acid (?),  $CHPh \cdot CH \cdot C_6H_4 \cdot CO_2H$ , has m. p. 235—237°; the *methyl* ester is a yellow powder, m. p. 145°.

Stilbenedicarboxylic acid,  $C_2H_2(C_6H_4 \cdot CO_2H)_2$ , has m. p. 225° (decomp.). It could not be reduced. The above acids are regarded as derivatives of polymerised stilbene. With aluminium chloride, stilbene forms a polymeride, m. p. 220°.

[With D. BUTESCU.]—*β-Methylanthracene-10-carboxylic acid*,



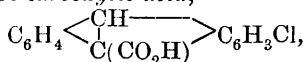
is colourless, m. p. 197°.

*β-Methylaceanthrenequinone* crystallises in well-formed, red needles, m. p. 251°.

*β-Chloroanthracene-10-carboxylic acid* separates in pale yellow needles, m. p. 228°.

*β-Chloraceanthrenequinone* forms red needles, m. p. 294—295°.

*α-Chloroanthracene-10-carboxylic acid*,



crystallises in bunches of pale yellow needles, m. p. 258° (decomp.).

*α-Chloroaceanthrenequinone* is more soluble in benzene than the *β*-isomeride; it forms red needles, m. p. 251° (decomp.).

*1:8-Dichloroanthracene-10-carboxylic acid* crystallises in fan-like aggregates of yellow platelets, m. p. above 270°.

*1:8-Dichloroaceanthrenequinone* forms pale brown plates, m. p. 268—270° (decomp.).

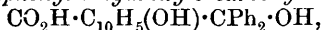
*1:5-Dichloroanthracene-10-carboxylic acid* separates in pale yellow needles, m. p. 205° (decomp.).

*1:5-Dichloroaceanthrenequinone* forms red needles, m. p. above 275°.

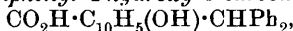
E. F. A.

**Synthesis of *ωω*-Diphenyl-1:4-naphthaquinomethane (*p*-Naphthafuchsone) and of Allied Compounds.** ZOFJA ZALESKA-MAZURKIEWICZ and AUGUSTIN BISTRZYCKI (*Ber.*, 1912, 45, 1429—1440. Compare Abstr., 1901, i, 701; 1904, i, 44).—Since benzilic acid condenses with *α*-naphthol to form, not the desired diphenyl-4-hydroxynaphthylacetic acid, but the lactone of diphenyl-1-hydroxy-*β*-naphthylacetic acid (Geipert, Abstr., 1904, i, 318), the following device has been employed in the synthesis of *p*-naphthafuchsone. A boiling benzene solution of benzilic acid and 1-hydroxy-2-naphthoic acid is treated with anhydrous tin tetrachloride (1 mol.), whereby *diphenyl-4-hydroxy-3-carboxynaphthylacetic acid*,  $\text{CO}_2\text{H} \cdot \text{C}_{10}\text{H}_5(\text{OH}) \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$ , m. p. 237—240° (decomp.), is obtained. *Diphenyl-4-hydroxy-3-carbomethoxynaphthylacetic acid*, m. p. 229° (decomp.), is prepared in a similar manner from methyl 1-hydroxy-2-naphthoate. The *dimethyl ester* has m. p. 211—212°.

A solution of diphenyl-4-hydroxy-3-carboxynaphthylacetic acid in concentrated sulphuric acid evolves carbon monoxide at 50—60°, whereby is formed *diphenyl-4-hydroxy-3-carboxynaphthylcarbinol*,



which crystallises in yellow prisms, darkens at about 135° and decomposes at 196—198°, and is converted by zinc dust and boiling 95% acetic acid into *diphenyl-4-hydroxy-3-carboxynaphthylmethane*,

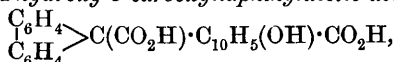


decomp. 207°. Diphenyl-4-hydroxy-3-carboxynaphthylcarbinol is converted by boiling *N*-potassium hydroxide or by *N*/2-potassium hydroxide at 140—145° into *ωω*-diphenyl-1:4-naphthaquinomethane,

(*p*-naphthafuchsone),  $\text{O}:\text{C}_{10}\text{H}_6:\text{CPh}_2$ , m. p.  $179^\circ$ , yellow needles, which develops a deep violet coloration with concentrated sulphuric acid, is remarkably stable to hot aqueous or alcoholic potassium hydroxide, and is reduced to diphenyl-4-hydroxynaphthylmethane by boiling 95% acetic acid and zinc dust.

Compounds analogous to the preceding have been obtained from *pp*'-tolilic acid and 1-hydroxy-2-naphthoic acid. *Di*-*p*-tolyl-4-hydroxy-3-carboxynaphthylacetic acid crystallises from diluted alcohol in colourless plates containing EtOH, decomp.  $205\text{--}216^\circ$ , and forms a dimethyl ester, m. p.  $233^\circ$  (decomp.). *Di*-*p*-tolyl-4-hydroxy-3-carboxynaphthylcarbinol,  $\text{C}_{26}\text{H}_{22}\text{O}_4\cdot\text{H}_2\text{O}$ , almost colourless needles, has m. p.  $116^\circ$  (decomp.).  $\omega\omega$ -*Di*-*p*-tolyl-1:4-naphthaquinomethane, yellow needles, has m. p.  $165^\circ$ .

The condensation of diphenyleneglycollic acid and 1-hydroxy-2-naphthoic acid in boiling benzene in the presence of tin tetrachloride yields diphenyl-4-hydroxy-3-carboxynaphthylacetic acid,



m. p.  $213\text{--}223^\circ$  (decomp.), which dissolves in warm concentrated sulphuric acid with a deep green colour, but does not thereby yield the expected carbinolcarboxylic acid  
C. S.

[Preparation of Anthraquinone Derivatives.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 243750. Compare Abstr., 1911, i, 980).—1-Arylthiolanthraquinone-2-carboxylic acids are readily prepared by the action of aryl mercaptans on 1-halogen- or 1-nitroanthraquinone-2-carboxylic acids in the presence of a condensing agent.

1-*p*-Tolylthiolanthraquinone-2-carboxylic acid, a yellow powder, is thus obtained from *p*-thiocresol and 1-chloroanthraquinone-2-carboxylic acid; when treated with phosphorus pentachloride, it furnishes a thioxanthone, dark red needles.

1-*p*-Chlorophenylthiolanthraquinone-2-carboxylic acid is yellow, and the corresponding thioxanthone an orange-yellow powder.

1- $\beta$ -Naphthylthiolanthraquinone-2-carboxylic acid, an orange-red powder, yields an orange-brown powder when treated with phosphorus pentachloride.

1- $\beta$ -Anthraquinonylthiolanthraquinone-2-carboxylic acid, an orange powder, is prepared from  $\beta$ -mercaptoanthraquinone and 1-chloroanthraquinone-2-carboxylic acid, it furnishes a brownish-yellow powder with phosphorus pentachloride.  
F. M. G. M.

Tannin. IX. MAXIMILIAN NIERENSTEIN (*Annalen*, 1912, 388, 223—258. Compare Abstr., 1911, i, 642).—The author has abandoned the use of the names "tannin" for digallic acid and "leucotannin" for leucodigallic acid; he now uses the name "tannin" to denote the polydigalloyl-leucodigallic anhydrides mentioned below.

Leucodigallic acid,  $\text{C}_6\text{H}_2(\text{OH})_3\cdot\text{CH}(\text{OH})\cdot\text{O}\cdot\text{C}_6\text{H}_2(\text{OH})_2\cdot\text{CO}_2\text{H}$ , previously only known in the form of its penta- and hexa-acetyl derivatives, has been obtained as a mixture of the *d*- and of the *dl*-forms by boiling an aqueous solution of tannin (*tanninum levissimum purissimum*, Schering) with zinc dust according to Iljin's method

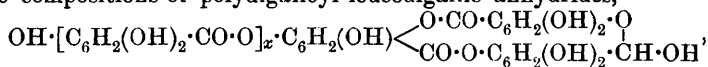
(Abstr., 1910, i, 331), gallic acid and gallaldehyde also being formed in the reaction. *dl*-Leucodigallic acid has also been obtained by the reduction of digallic acid by zinc dust and water, alcohol, or acetic acid, and by calcium hydride and moist ether; it has m. p. 278—280°, crystallises in fine needles, and does not exhibit tannoid properties (that is, is not absorbed by casein or precipitated by gelatin). The penta-acetyl derivative obtained directly from the acid and boiling acetic anhydride has m. p. 172—173°. *Hexaethylcarbonatoleucodigallic acid*,  $C_6H_2(O\cdot CO_2Et)_3\cdot CH(O\cdot CO_2Et)\cdot O\cdot C_6H_2(O\cdot CO_2Et)_2\cdot CO_2H$ , has m. p. 123° (decomp.).

The resolution of *dl*-leucodigallic acid itself cannot be effected. An alcoholic solution of *dl*-hexaethylcarbonatoleucodigallic acid, however, is readily resolved by strychnine. *l*-Hexaethylcarbonatoleucodigallic acid, small needles, has m. p. 127—128° (decomp.), and  $[\alpha]_D^{15} - 57\cdot35^\circ$  in alcohol. *d*-Hexaethylcarbonatoleucodigallic acid, small scales, has m. p. 132—134° (decomp.), and  $[\alpha]_D^{15} + 62\cdot50^\circ$ . These two derivatives are converted into their active parent acids by warming with 1% pyridine. *l*-Leucodigallic acid, m. p. 276—277° (decomp.), crystallises in needles, does not exhibit tannoid properties, and has  $[\alpha]_D^{15} - 70\cdot26^\circ$  in water, diminishing to  $-64\cdot58^\circ$  after ten days. *d*-Leucodigallic acid, m. p. 276—277°,  $[\alpha]_D^{15} + 104\cdot2^\circ$  in water,  $[\alpha]_D^{17} + 56\cdot4^\circ$  in alcohol, crystallises in stellate clusters of needles; *d*-penta-acetyl-leucodigallic acid, obtained by resolving the *dl*-form by strychnine, has m. p. 171° and  $[\alpha]_D^{15} + 76\cdot4^\circ$  in acetone.

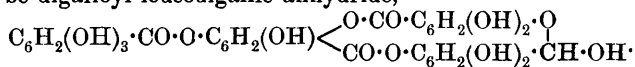
Leucodigallic acid yields gallaldehyde and gallic acid by hydrolysis with dilute sulphuric acid, is oxidised to ellagic acid and luteo-acid (pentahydroxydiphenylmethylolidecarboxylic acid) by 10% hydrogen peroxide in boiling aqueous solution, and is converted into purpurotannin by potassium persulphate and sulphuric acid in glacial acetic acid. Penta- and hexa-acetyl-leucodigallic acids are not attacked by benzoyl chloride and potassium cyanide in a similar manner to penta-acetyldigallic acid (Abstr., 1911, i, 642). As regards the nature of their condensation products with formaldehyde in the presence of hydrochloric acid, leucodigallic acid resembles tannin in yielding more than 90% of hydroxyaurincarboxylic acids soluble in water and very little diphenylmethane derivatives insoluble in water, whilst digallic acid resembles gallic acid in yielding 15 to 20% of the first type and about 80% of the second type of condensation products (compare Nierenstein and Webster, Abstr., 1908, i, 89).

From the results of his earlier researches, the author has previously regarded tannin as a mixture of digallic and leucodigallic acids containing a little gallic acid. The fact, however, that leucodigallic acid does not exhibit tannoid properties, whilst tannin is absorbed almost quantitatively by casein, prove that free leucodigallic acid cannot be a constituent of tannin. Further arguments against the view that tannin is a mixture of the three acids mentioned above are (1) the high molecular weight of tannin; (2) tannin scarcely conducts electrolytically, whereas digallic acid does so well (Herzig and Renner, Abstr., 1909, i, 713); (3) the methoxy value of methylotannin corresponds with four hydroxyl groups, not with five as in the case of digallic acid, or six as in the case of leucodigallic acids (Herzig, Abstr., 1905, i, 354).

Hence for these reasons, and from the fact that the acetylation of tannin by acetic anhydride yields a product containing 18.49 to 22.71% of penta-acetyl-leucodigallic acid, the author withdraws his former opinion of the constitution of tannin, and ascribes to tannin the compositions of polydigalloyl-leucodigallic anhydrides,



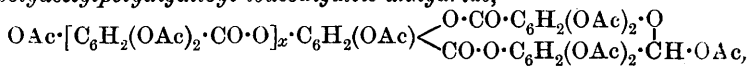
corresponding with those of Fischer and Freudenberg's depsides (Abstr., 1910, i, 265). According to this view, the simplest tannin would be digalloyl-leucodigallic anhydride,



Since, however, the tannin used by the author (*tanninum levissimum purissimum*, Schering) yields digallic and leucodigallic acids in the proportions 3:1 and 4:1, such tannin must be tri- or tetradigalloyl-leucodigallic anhydride. The author shows that this constitution of his tannin meets satisfactorily the above-mentioned objections to his former view of its constitution.

Tannin in pyridine cooled by a freezing mixture yields, by treatment with acetyl chloride, a little triacetyl gallic acid and a white, amorphous substance, m. p. 218—224° (decomp.), which does not give a coloration with ferric chloride, forms a sodium salt with 10% sodium carbonate in the cold, and from its analysis, basicity, and percentage of acetyl is *octadecylacetyltridigalloyl-leucodigallic acid*,  $\text{C}_{91}\text{H}_{71}\text{O}_{49} \cdot \text{CO}_2\text{H}$ . This constitution is supported by the fact that the reaction of the substance with ethyl chlorocarbonate and aqueous potassium cyanide in a freezing mixture yields triacetyl galloyl cyanide, ethylcarbonatodiacetyl galloyl cyanide (both identified, after hydrolysis, as galloylformic acid), and *d-ethylcarbonatopenta-acetyl-leucodigallic acid*,

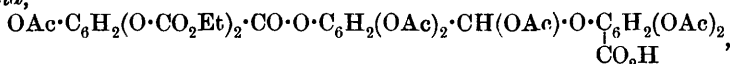
$\text{C}_6\text{H}_2(\text{OCO}_2\text{Et})(\text{OAc})_2 \cdot \text{CH}(\text{OAc}) \cdot \text{O} \cdot \text{C}_6\text{H}_2(\text{OAc})_2 \cdot \text{CO}_2\text{H}$ , m. p. 154—159° (decomp.),  $[\alpha]_D^{19} + 45.98^\circ$  in alcohol. The last-mentioned substance is converted by warm dilute pyridine into *d-penta-acetyl-leucodigallic acid*, the acetylation of which by acetic anhydride yields *d-hexa-acetyl-leucodigallic acid* (Abstr., 1910, i, 265). Quantitative experiments on the amount of ethylcarbonatopenta-acetyl-leucodigallic acid obtained from the acetylated tannin indicate that the ratio of digallic acid to leucodigallic acid in the tannin employed is 4:1, and therefore the tannin is tetradigalloyl-leucodigallic anhydride. The acetylation of tannin in strongly cooled acetone by keten yields a *polyacetyl polydigalloyl-leucodigallic anhydride*,



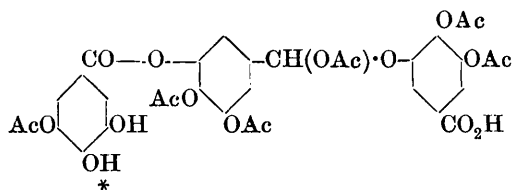
m. p. 287—299° (decomp.), and a trace of the corresponding acid. The anhydride is a white, amorphous powder, which is insoluble in cold aqueous sodium hydroxide. It is converted by warm 5% pyridine into *hydroxypolyacetyl polydigalloyl-leucodigallic acid*, which reacts with ethyl chlorocarbonate and *N*/10-potassium hydroxide to form, after acidifying with ice-cold sulphuric acid, *ethylcarbonatopolyacetyl polydigalloyl-leucodigallic acid*, a white, amorphous powder, m. p. 236—244°.

The products obtained by treating tannin, acetylated by keten, with

ethyl chlorocarbonate and aqueous potassium cyanide are triacetyl-galloyl cyanide, ethylcarbonatodiacetyl-galloyl cyanide (both identified as galloylformic acid), and *diethylcarbonatohexa-acetyl-galloyl-leucodigallic acid*,



m. p. 216—221° (decomp.). When warmed with dilute pyridine, the last substance yields *dihydroxyhexa-acetyl-galloyl-leucodigallic acid*, m. p. 257—259° (decomp.),  $[\alpha]_D^{25} + 33.33^\circ$ , microscopic needles. This acid, which readily yields the corresponding *dimethoxy-acid*,  $\text{C}_{35}\text{H}_{32}\text{O}_{19}$ , m. p. 219—221° (decomp.), with diazomethane, develops a pronounced green coloration with alcoholic ferric chloride. This indicates that the hydroxyl groups are in ortho-positions relative to one another. Assuming, therefore, that the polydigalloyl-leucodigallic acids are formed by the symmetrical condensation of digallic acid and leucodigallic



acid molecules, dihydroxyhexa-acetyl-galloyl-leucodigallic acid has the annexed constitution, and its anhydride (and probably, also, polydigalloyl-leucodigallic anhydrides in general) is formed by the elimination of water from the hydroxyl of the carboxyl group and that marked by the asterisk.

C. S.

**Tannin, and the Synthesis of Similar Substances.** EMIL FISCHER and KARL FREUDENBERG (*Ber.*, 1912, 45, 915—935).—Tannin, after careful purification, when hydrolysed with sulphuric acid yields from 7 to 8% of dextrose, an amount which is undoubtedly somewhat too small on account of the losses during isolation. It is considered that tannin is a compound of 1 mol. of dextrose with 5 mols. of digallic acid, analogous to dextrose penta-acetate and penta-benzoate. This formula is in agreement with the optical activity, molecular weight, weak acidity, and analytical results obtained with tannin.

In confirmation, compounds in every way similar to tannin have been obtained synthetically by combining dextrose with trimethylcarbonatogalloyl chloride in chloroform solution in presence of quinoline. On cautious hydrolysis of this compound with alkali hydroxide, pentagalloylglucose is obtained, which has all the properties of a tannin.

In like manner dextrose has been combined with *p*-hydroxybenzoic acid, also  $\alpha$ -methyl glucoside and glycerol with gallic acid.

The crystalline tannin, chebulic acid, also yields dextrose when hydrolysed.

Methods of purifying tannin by extraction with ether, with ethyl acetate, or by means of the potassium salt are described. The value of  $[\alpha]_D^{20}$  for different preparations varies around  $+70^\circ$ . The acidity is 1/10th that of gallic acid.

Trimethylcarbonatogalloyl chloride has been obtained in quantity in large, colourless crystals, m. p. 91—92° (corr.).

*Penta[trimethylcarbonatogalloyl]glucose* is a granular, colourless, amorphous powder; it was analysed after drying in a vacuum at 75° over phosphoric oxide. It sinters at about 90°, and begins to decompose at 130°,  $[\alpha]_D^{20} + 34.34^\circ (\pm 0.4^\circ)$ .

*Pentagalloylglucose* is a yellow, amorphous powder,  $[\alpha]_D + 31^\circ$  to  $+ 35^\circ$  in water or  $+ 44.4^\circ$  in alcohol. It softens at about 150°, and begins to decompose at 160°. It has an astringent and bitter, but not acid, taste. The aqueous solution precipitates gelatin, and has most of the properties of tannin.

*Penta[p-methylcarbonatohydroxybenzoyl]glucose*, prepared by interaction of *p-methylcarbonatohydroxybenzoyl chloride*, dextrose, and quinoline in chloroform solution, is a colourless, easily powdered, amorphous mass,  $[\alpha]_D^{20} + 100^\circ$ .

*Penta[p-hydroxybenzoyl]glucose* is obtained in hard, yellow-coloured, amorphous flakes,  $[\alpha]_D^{20} + 124.3^\circ$  to  $128.8^\circ$ , on hydrolysis with sodium hydroxide.

*Tetra[trimethylcarbonatogalloyl]- $\alpha$ -methyl glucoside* is a colourless, amorphous powder,  $[\alpha]_D^{20} + 48.7^\circ$ .

*Galloyl- $\alpha$ -methylglucoside* softens at 130°, decomp. 140°,  $[\alpha]_D^{20} + 26.4^\circ$ ; it is similar in properties to pentagalloyl glucose.

*Tri[trimethylcarbonatogalloyl]glycerol* is a colourless, spongy mass, very similar in properties to the dextrose derivatives. E. F. A.

**Gallocarboxylic [Pyrogalloldicarboxylic] Acid.** HUGO VOSWINCKEL and FRITZ DE WEERTH. (*Ber.*, 1912, 45, 1242—1246).—Previous methods for the preparation of pyrogalloldicarboxylic acid gave very unsatisfactory results (compare Sennhofer and Brunner, *Abstr.*, 1881, 267), but it is now found that almost theoretical yields are obtained by heating an intimate mixture of crystallised gallic acid and excess of either potassium or sodium hydrogen carbonate in sealed tubes at 150—160°. Assuming, as usual, that gallic acid is a 3 : 4 : 5-trihydroxybenzoic acid, Sennhofer and Brunner considered pyrogalloldicarboxylic acid to be 3 : 4 : 5-trihydroxy-*o*-phthalic acid, but the fact that acetyl chloride or acetic anhydride entirely fail to produce an anhydride has led the present authors to give it the constitution of a trihydroxyisophthalic acid. Their view is supported by the observation of Feist (*Abstr.*, 1908, i, 101), that a trihydroxyphthalic acid derived from Columba root differed from pyrogalloldicarboxylic acid, and also by the fact that the cotarnic acid of Roser (*Abstr.*, 1889, 418), which is undoubtedly a methoxy-methylenedioxy-*o*-phthalic acid, did readily form an anhydride. Analogous to the observation of Feist that it is extremely difficult to methylate the acid, the authors have found that it entirely resists complete acetylation, and they suggest that it has a ketonic or diketonic structure which might also explain the intense colours of the calcium and barium salts.

Heating the acid with acetyl chloride gave an *acetyl* derivative,  $C_8H_6O_7 \cdot C_2H_3O$ , which crystallised with  $\frac{1}{2}$  mol. acetic acid or with 1 mol. water when reprecipitated from its sodium hydroxide solution; with excess of acetic anhydride a *diacetyl* derivative,  $C_8H_4O_7(C_2H_3O)_2$ ,

was obtained which also separated with  $\frac{1}{2}$  mol. acetic acid, but which changed to a mono-acetylated compound in alkaline solution; on melting the acid with its own weight of acetic anhydride and potassium acetate, the carboxyl groups were eliminated, leaving pyrogallol triacetate. J. C. W.

**Humic Acids.** BRUNO TACKE and H. SÜCHTING (*Landw. Jahrb.*, 1911, 41, 717—754).—A study of the chemical and physical properties of peat carried out on the lines followed by A. Baumann and E. Gully (*Mitt. Bayr. Moorkulturanstalt.*, Nos. 3 and 4).

Fresh material, and samples dried at varying temperatures and for different periods, was treated with solutions of numerous acids and salts, also with organic solutions, such as gelatin and sugar. The amount of adsorption by the peat, and the chemical changes taking place in the unadsorbed liquid and in the solid were carefully studied, and experimental evidence brought forward to show that humic acids have a definite acid character independent of their colloidal properties.

F. M. G. M.

**Preparation of Pentachlorobenzaldehyde.** FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 243416).—*Pentachlorobenzaldehyde*, needles, m. p. 197—199°, is readily prepared by the action of concentrated or fuming sulphuric acid on pentachlorobenzylidene chloride, pentachlorobenzyl chloride, or the crude mixture obtained by chlorinating pentachlorotoluene at high temperatures. F. M. G. M.

**Molecular Compounds as Preliminary Products in Cases of Condensation.** II. JULIUS SCHMIDLIN and RUDOLF LANG (*Ber.*, 1912, 45, 899—912. Compare Abstr., 1910, i, 836).—In the case of organic condensations, by the study of the melting-point curves of mixtures of the two components, proof is afforded of the formation of molecular compounds in the same proportions as those in the condensation product.

Thus 1 mol. of *m*-nitrobenzaldehyde forms a molecular compound with two mols. of benzene, with which it condenses to a triphenylmethane derivative. It does not condense with phenol; in this instance the two branches of the melting-point curve cut in a single eutectic, excluding the formation of a molecular compound.

Two mols. of phenol condense abnormally with two mols. of *p*-hydroxybenzaldehyde, but a molecular compound of the same composition is formed.

The system benzhydrol-phenol shows two maxima corresponding with molecular compounds in the proportions 1 : 1 and 1 : 2. Systems containing dimethylaniline do not afford evidence of the formation of molecular compounds.

The Friedel Crafts' reaction is discussed from this point of view; in many cases aluminium chloride acts as a catalyst, in others it reacts in molecular proportions. In the case of the reaction between benzene and halogen alkyl, it is shown that there is no formation of a binary compound from either of the three components taken in pairs, and it remains only to assume the formation of a ternary compound between

all three components. Such appear to be fairly stable at low temperatures, but liberate hydrogen chloride when warmed.

E. F. A.

[Preparation of Triarylmethane Derivatives.] FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 243749).—It is found that halogenated benzene or diphenyl di- or poly-aldehydes condense readily with aromatic hydroxycarboxylic acids to form dyes. The following compounds are described in the original :

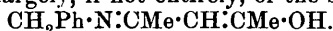
2 : 5-Dichloroterephthalaldehyde, m. p. 158°; tetrachloroterephthalaldehyde, m. p. 193°; 4 : 6-dichloroisophthalaldehyde, m. p. 163°; 4 : 4'-dichloro-3 : 3'-dialdehydodiphenyl, m. p. 204°; 4 : 4'-dibromo-3 : 3'-dialdehydodiphenyl, m. p. 192°, and 3 : 3'-dialdehydodiphenyl-4 : 4'-disulphonic acid.

F. M. G. M.

Angeli-Rimini Reaction of the Aldehydes. LUIGI BALBIANO (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 389—393).—The author has now repeated his previous work with the copper salts produced by means of Piloty's acid from anisyl methyl ketone (from anethole glycol) and benzyl methyl ketone (compare Angeli, this vol., i, 117), and finds that they do not give the Angeli-Rimini reaction when the stoichiometric quantity of alkali is employed. To account for the reaction which may be observed when an excess of alkali is used, he suggests an explanation differing from that of Angeli (*loc. cit.*).

R. V. S.

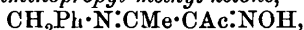
$\beta$ -Benzyliminopropyl Methyl Ketone. Keto-enol Isomerism. LEOPOLD RÜGHEIMER and G. RITTER (*Ber.*, 1912, 45, 1332—1340).—Acetylacetone and benzylamine interact according to the equation  $C_5H_8O_2 + C_7H_9N = C_{12}H_{15}ON + H_2O$ . From its behaviour with ferric chloride and the formation of a benzoate, the authors are of opinion that the product is largely, if not entirely, of the structure



The occurrence of two forms of the benzoyl derivative (no isomerism has yet been detected with the parent substance) is ascribed to *cis-trans*-isomerism due to the ethylenic linking. The C:N linking is indicated by the difficulty of reaction between acetylacetone and benzylmethylamine. These results render doubtful the earlier explanations of the isomerism observed with the condensation product of ethyl acetoacetate and benzylamine (Möhlau, *Abstr.*, 1895, i, 140; Hantzsch and von Hornbostel, *Abstr.*, 1898, i, 195).

$\beta$ -Benzyliminopropyl methyl ketone is obtained by the careful interaction of equimolecular quantities of acetylacetone and benzylamine; the product is a pale yellow oil, b. p. 183—183.5°/17 mm., which can be solidified to tablets, m. p. 24°. It is soluble in sodium hydroxide solution, and gives a coloration with ferric chloride. Attempts to condense the product with another molecule of benzylmethylamine by heating in a sealed tube were unsuccessful, the only isolated product being acetobenzylamide, m. p. 62—66°.

$\alpha$ -Oximino- $\beta$ -benzyliminopropyl methyl ketone,



was obtained by the action of sodium nitrite on the glacial acetic acid solution; it forms colourless crystals, m. p. 126—127°, soluble to a yellow solution in sodium hydroxide solution; it gives no coloration with ferric chloride. Treatment with boiling dilute sulphuric acid gave the  $\gamma$ -oxime of  $\beta$ , $\delta$ -triketopentane,  $\text{OH}\cdot\text{N}\cdot\text{C}(\text{COMe})_2$ .

Cautious benzylation of  $\beta$ -benzyliminopropyl methyl ketone yielded a mixture of benzobenzylamide (m. p. 106—107°), with a substance of doubtful nature, and two forms of the benzoyl derivative. The more easily fusible form (m. p. 119—121°) tends to change into the isomeric form, m. p. 132°. Neither form gives a coloration with ferric chloride, and both are easily hydrolysed by dilute potassium hydroxide solution, giving benzoic acid. D. F. T.

[Preparation of Nitromethylbenzanthrone.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 242621).—*Nitromethylbenzanthrone*, m. p. 243°, is prepared by nitrating methylbenzanthrone (m. p. 199°); when heated at 220—240° with sulphur, it furnishes a crystalline, glistening bronze paste, which forms a vat dye. F. M. G. M.

**Action of Iodides on Bromoanil.** Iodoanil and Some of Its Derivatives. HENRY A. TORREY and WILLIAM H. HUNTER (*J. Amer. Chem. Soc.*, 1912, **34**, 702—716).—In an earlier paper (Abstr., 1905, i, 217) it was shown that when bromoanil is heated with a solution of potassium iodide in acetone, dibromodi-iodo-*p*-benzoquinone is produced. A further study of this reaction has shown that in addition to dibromodi-iodo-*p*-benzoquinone, m. p. 258—259°, there are produced tetraiodo-*p*-benzoquinone, bromotri-iodo-*p*-benzoquinone, and iodoanil. Iodoanil can be obtained as the chief product by heating first with alcoholic potassium iodide, and subsequently with alcoholic sodium iodide solution.

*Bromotri-iodo-p-benzoquinone*, m. p. 253—254°, crystallises in short, broad, brown, prismatic crystals, and reacts with sodium phenoxide to form bromoiiododiphenoxy-*p*-benzoquinone. Iodoanil, m. p. 282—284° (decomp.), forms small, chocolate-coloured needles.

Dibromodi-iodoquinone unites with diphenylamine to form an additive compound,  $\text{C}_6\text{O}_2\text{Br}_2\text{I}_2\cdot\text{NHPh}_2$  (*loc. cit.*), which crystallises in purplish-black needles; its m. p. varies with the rate of heating. By the action of potassium phenoxide on dibromodi-iodo-*p*-benzoquinone, or on bromotri-iodo-*p*-benzoquinone, bromoiiododiphenoxy-*p*-benzoquinone, m. p. 282—283°, is produced, together with a small quantity of another substance, which is probably the tetraphenoxo-*p*-benzoquinone described by Jackson and Grindley (Abstr., 1896, i, 155). When a solution of dibromodi-iodo-*p*-benzoquinone in toluene is boiled with a large excess of aniline, there are formed dianilino-*p*-benzoquinone and another substance, which does not melt below 300°, and is probably bromodianilino-*p*-benzoquinone.

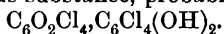
When iodoanil is heated with potassium phenoxide solution, it is converted into *di-iododiphenoxy-p-benzoquinone*, m. p. 290°. The following compounds were obtained by the action of cresoxides on bromo-, chloro-, and iodo-anil. *Dibromodi-m-tolylloxy-p-benzoquinone*, m. p. 193°; *dibromodi-p-tolylloxy-p-benzoquinone*, m. p. 254—263°

(decomp.); *dichlorodi-p-tolyloxy-p-benzoquinone*, m. p. 254—255°; and *di-iododi-p-tolyloxy-p-benzoquinone*, m. p. 272—274° (decomp.). When *di-iododiphenoxy-p-benzoquinone* is treated with sodium ethoxide, *di-iododiethoxy-p-benzoquinonedimethylhemiacetal*,  $C_6I_2(OEt)_2(OH \cdot OEt)_2$ , is produced, which forms minute, pale yellow crystals. *Di-iododimethoxy-p-benzoquinonedimethylhemiacetal* was obtained similarly as a white, amorphous powder.

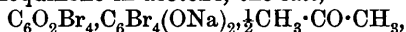
If iodoanil is treated with excess of sodium methoxide solution and the resulting hemiacetal is treated with *N*-sodium hydroxide, *iodoanilic acid* is produced, which forms yellowish-red, feathery crystals, and begins to decompose at about 205°.

By the action of aniline on *di-iododiphenoxy-p-benzoquinone*, *dianilino-p-benzoquinone* is formed, together with *iododianilino-p-benzoquinoneanil*,  $C_6HOI(NHPh)_2 \cdot NPh$ , which crystallises in deep yellowish-brown needles, and decomposes at about 225°.

When solid potassium iodide is added to a saturated solution of chloroanil in acetone, the salt,  $C_6O_2Cl_4 \cdot C_6Cl_4(OK)_2$ , is produced, which crystallises in green needles, and is hydrolysed by water with formation of a white, amorphous substance, probably the *hemioether*,



The *sodium salt*,  $C_6O_2Cl_4 \cdot C_6Cl_4(ONa)_2$ , has a bluish-green colour, and is converted by dilute sulphuric acid into a mixture of chloroanil and tetrachloroquinol. By the action of sodium iodide on a solution of tetrabromo-*o*-benzoquinone in acetone, the salt,



is produced, which forms bluish-green needles, and decomposes at 80°. Similar compounds were obtained from bromoanil and tetrachloro-*o*-benzoquinone. When a mixture of bromoanil, potassium iodide, and alcohol is left at the ordinary temperature, a green salt is not produced, but dibromodi-iodo-*p*-benzoquinone is gradually formed. E. G.

**Octaiodoquinhydrone.** C. LORING JACKSON and E. K. BOLTON (*Ber.*, 1912, 45, 871—873).—Iodoanil dissolved in benzene, saturated with sulphur dioxide and containing a drop or two of water, was set aside for four weeks, when large, lustrous, black crystals of *octaiodoquinhydrone*,  $C_6O_2I_4 \cdot C_6(OH)_2I_4$ , were deposited; these have decomp. 190°. When it is dissolved in benzene and a little alcohol and the solution is evaporated, a mixture of yellowish-brown iodoanil with colourless tetraiodoquinol is obtained. The latter is also formed when the black crystals are treated with sodium hydroxide and the solution is made acid. E. F. A.

**The Melting Point of Anthraquinone.** ERNST PHILIPPI (*Monatsh.*, 1912, 33, 373—374).—The m. p. (273°) generally assigned to anthraquinone is too low. Pure anthraquinone has m. p. 285—286° (corr.). This figure agrees with that recorded by Kempf (*Abstr.*, 1908, ii, 929). H. W.

**Preparation of  $\alpha$ -Hydroxyanthraquinone Alkyl Ethers.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 242379).— $\alpha$ -Hydroxyanthraquinone ethers are readily prepared from the sodium

derivative of the corresponding  $\alpha$ -hydroxyanthraquinone by the action of dialkyl sulphates in the presence of a condensing agent.

*Erythroxyanthraquinone methyl ether* was thus obtained from potassium erythroxyanthraquinone; the quinizarin dimethyl ether has m. p. 170—171° (Lagodzinski, Abstr., 1895, i, 232, recorded 143°).

F. M. G. M.

#### Preparation of Mercaptans in the Anthraquinone Series.

FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 241985).—When anthraquinonediazonium compounds are treated with salts of xanthic acid they yield the corresponding anthraquinonylxanthic esters; these are hydrolysed by alcoholic alkali hydroxides to the corresponding mercaptans.

*Anthraquinone 1-mercaptan*, prepared from 1-aminoanthraquinone, forms olive-brown flakes, m. p. 187°; the corresponding *anthraquinone 2-mercaptan* has an olive-green colour.

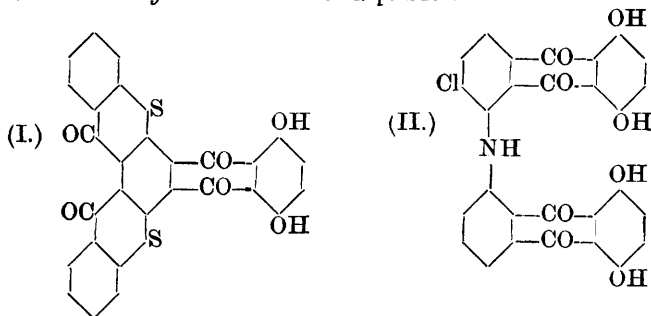
F. M. G. M.

**Dichloroquinizarins.** M. FREY (*Ber.*, 1912, 45, 1358—1364).—3:6-, 3:4-, and 4:5-Dichlorophthalic anhydrides react with quinol in the presence of boric acid with the formation of dichlorodihydroxybenzoylbenzoic acids, which, when heated with concentrated sulphuric acid, yield the corresponding dichloroquinizarins.

5:8-Dichloroquinizarin,  $C_6H_2Cl_2 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_2(OH)_2$ , crystallises in brownish-red needles, m. p. 266°. Its *diacetyl* derivative has m. p. 170°. When the *potassium* salt of 5:8-dichloroquinizarin is heated at 180° with potassium phenoxide and the product acidified, 8-chloro-5-phenoxyquinizarin is obtained in light red needles, m. p. 243°. Replacement of the second chlorine atom by the phenoxy-group was not observed. It could, however, be replaced by the *p*-toluidino-group by heating 8-chloro-5-phenoxyquinizarin with *p*-toluidine in the presence of potassium and copper acetates at 150°, whereby 8-*p*-toluidino-5-phenoxyquinizarin, m. p. 278°, is obtained. 5:8-Dianilinoquinizarin, m. p. 245°, is formed by heating 5:8-dichloroquinizarin and aniline with potassium carbonate and copper powder at 150—160°, whilst 1:4:5:8-tetrahydroxyanthraquinone, m. p. 246°, results when 5:8-dichloroquinizarin, slaked lime, water, and copper powder are heated at 250° during twenty hours. The *barium* salt,  $C_{14}H_4O_6Ba_2$ , of the latter was analysed. When 5:8-dichloroquinizarin and thiosalicylic acid are boiled in amyl alcoholic solution in the presence of copper and potassium acetates, *quinizarin-5:8-bis-o-thiolbenzoic acid*, m. p. 235°, is obtained, which, when dissolved in nitrobenzene and treated with phosphorus pentachloride and subsequently with aluminium chloride, yields *quinizarin-5:6:7:8-dithioxanthone* (I), m. p. 197—199°, the *barium* salt of which was analysed.

5:6-Dichloroquinizarin, m. p. 208°, is obtained in the same manner as 5:8-dichloroquinizarin. It yields a *diacetyl* derivative, m. p. 140°. When heated with  $\beta$ -aminoanthraquinone in boiling nitrobenzene solution in presence of copper and potassium acetates, it forms 5-anthraquinonyl- $\beta$ -amino-6-chloroquinizarin (II), m. p. above 300°.

6 : 7-Dichloroquinizarin, m. p. 288°, was similarly obtained in poor yield. Its *diacetyl* derivative has m. p. 125°.



H. W.

**Synthesis of Phenanthraquinones.** FRITZ MAYER (*Ber.*, 1912, 45, 1105—1113).—2 : 2'-Dialdehydodiphenyl and 2 : 2'-dialdehydo-6 : 6'-dimethyldiphenyl when warmed with an aqueous alcoholic solution of potassium cyanide are transformed into phenanthraquinone and 4 : 5-dimethylphenanthraquinone (compare Kenner and Turner, *Trans.*, 1911, 99, 2108). An attempt to apply the same reaction to 2 : 2'-dialdehydo-6 : 6'-dimethoxydiphenyl was unsuccessful.

*o*-Iodobenzylideneaniline, when heated with copper powder at 160—180°, is converted into 2 : 2'-*dibenzylideneaniline*, m. p. 98—99°, which is transformed by hydrochloric acid into 2 : 2'-dialdehydodiphenyl, m. p. 67° (Kenner and Turner, *loc. cit.*, give m. p. 62°). The latter compound, when heated with aqueous alcoholic potassium cyanide solution, yields phenanthraquinone, m. p. 204—205°, the identity of which was further established by transformation into its monoxime, m. p. 158°.

2-Nitro-3-methoxybenzaldehyde was converted into its oxime, and the latter reduced by ferrous hydroxide to 2-amino-3-methoxybenzaldehyde, m. p. 136—137°. This, when diazotised and treated with potassium iodide, yielded 2-iodo-3-methoxybenzaldehyde, m. p. 86—87°, which, when warmed with aniline, gave 2-iodo-3-methoxybenzylideneaniline, m. p. 107—108°, after previous softening. Treatment of the latter substance with copper powder at 200° led to the formation of 6 : 6'-dimethoxy-2 : 2'-dibenzylideneaniline, from which, by the action of hydrochloric acid, 2 : 2'-dialdehydo-6 : 6'-dimethoxydiphenyl, m. p. 120°, was obtained. No definite product was isolated from the action of aqueous alcoholic potassium cyanide solution on this substance.

A precisely similar series of reactions, with 2-nitro-3-methylbenzaldehyde as starting point, yielded the following compounds: 2-amino-3-methylbenzaldehyde, m. p. 127°; 2-iodo-3-methylbenzaldehyde, m. p. 83—84°; 2-iodo-3-methylbenzylideneaniline, m. p. 73°; 2 : 2'-dialdehydo-6 : 6'-dimethyldiphenyl, m. p. 111°. The latter substance, when heated with an aqueous alcoholic solution of potassium cyanide, formed 4 : 5-dimethylphenanthraquinone, m. p. 222—223°.

The action of potassium cyanide on *isophthalaldehyde* led to the formation of a *substance*, the analyses of which agreed with the formula  $C_{16}H_{12}O_4 \cdot H_2O$ , but in which the presence of water of crystallisation could not be confirmed. Oxidation with potassium permanganate in alkaline solution yielded *isophthalic acid*. H. W.

**Preparation of Santalol and Menthol Ethers.** CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 242421).—When santalol or menthol (or their sodium derivatives) in toluene solution or suspension is treated with chloromethyl ether in the presence of dimethylaniline (or other indifferent base), compounds of therapeutic value are produced.

*Methoxymethylsantalol*,  $C_{15}H_{23} \cdot O \cdot CH_2 \cdot OMe$ , a colourless liquid, b. p. 152—158°/4 mm., evolves formaldehyde when heated with dilute mineral acid.

*Methoxymethylmenthol*,  $C_{10}H_{19} \cdot O \cdot CH_2 \cdot OMe$ , has b. p. 100—102°/7 mm. F. M. G. M.

**Isomeric Tanacetyl Alcohols and Thujenes.** LEO A. TSCHUGAEFF and W. FOMIN (*Ber.*, 1912, 45, 1293—1298. Compare Tschugaeff, *Abstr.*, 1900, i, 129; 1901, i, 38; 1904, i, 515).—Tanacetyl alcohol, prepared from commercial tanacetone, has been resolved by the recrystallisation of the cinchonine salt of tanacetyl hydrogen phthalate. From the less soluble fraction was isolated a tanacetyl alcohol,  $D_4^{20}$  0.9187,  $[\alpha]_D + 116.93^\circ$  (compare Paolini, *Abstr.*, 1911, i, 730). The substance in the mother liquors was converted into a sparingly soluble strychnine salt, from which, after recrystallisation, a solid tanacetyl alcohol was obtained, m. p. 28°,  $[\alpha]_D - 9.12^\circ$  (in toluene).

The *d*-rotatory alcohol yielded an unstable and, to all appearances, homogeneous xanthate, which on decomposition gave apparently pure  $\alpha$ -thujene, b. p. 151°/759 mm.,  $D_4^{20}$  0.8301,  $n_D^{20}$  1.45150,  $\alpha_D - 37.20$ .

The *l*-rotatory alcohol gave a more stable xanthate, by the decomposition of which a thujene was obtained (presumably  $\beta$ -), b. p. 147°/739 mm.,  $D_4^{20}$  0.8208,  $n_D^{20}$  1.44708,  $[\alpha]_D + 110.78^\circ$ . D. F. T.

**The Constituents of Ethereal Oils.** I.  $\psi$ -Cedrol, a Physical Isomeride of Cedrol. II. Certain Sesquiterpene Alcohols. III. Tetrahydrocaryophyllene. FRIEDRICH W. SEMMLER and ERWIN W. MAYER (*Ber.*, 1912, 45, 1384—1394).—All specimens of cedar wood oil contain the primary alcohol cedrenol,  $C_{15}H_{24}O$ , and cedrene. Many specimens contain also the solid tertiary alcohol cedrol,  $C_{15}H_{26}O$ . In addition, the authors have isolated from the fractions of high b. p. a new, liquid, saturated, tertiary alcohol,  $C_{15}H_{26}O$ , which they name  $\psi$ -cedrol.

For the preparation of the latter, cedar wood oil was fractionated, the fraction of higher b. p. treated with phthalic anhydride and the unattacked portion again distilled. In this manner, a pale green oil, b. p. 147—152°/9 mm.,  $D^{20}$  0.9964,  $\alpha_D^{20} + 21.5^\circ$ ,  $n_D^{20}$  1.5131, was prepared, from which no solid substance could be obtained. Apparently, therefore, solid cedrol was not present in the oil employed.  $\psi$ -Cedrol reacts readily with sodium. With acetic

anhydride it yields an *acetate*. When oxidised, it does not yield a ketone. When heated with zinc dust, it gives a mixture of cedrene and *dihydrocedrene*, from which the latter substance was isolated after treatment of a solution of the mixture in chloroform with ozone. It has b. p. 106—115°/10 mm. (mainly 109—112°/10 mm.),  $D^{20}_D$  0.907,  $\alpha_D + 37^\circ$ ,  $n^{20}_D$  1.4882. A second *dihydrocedrene*, b. p. 122—123°/10 mm.,  $D^{20}_D$  0.9204,  $\alpha_D + 2^\circ$ ,  $n^{20}_D$  1.4929, was obtained by reduction of cedrene by means of hydrogen in the presence of platinum.

The alcoholic nature of  $\psi$ -cedrol was further proved by the action of formic acid on it, whereby cedrene was obtained, the physical constants of which agreed with those of the natural cedrene. The identity of the two compounds was confirmed by the oxidation of artificial cedrene to cedreneketonic acid and cedrenedicarboxylic acid, and transformation of the latter compound into its dimethyl ester. These compounds were identical with those prepared by Semmler and Risse (Abstr., 1912, i, 201) from natural cedrene.

II. According to Sandurin (Abstr., 1909, i, 98), guaiol is a tertiary alcohol. The authors, from the determination of its density and molecular refraction, draw the conclusion that it is a bicyclic alcohol with one double bond. Oxidation of it in aqueous acetone by means of potassium permanganate yielded the corresponding *glycerol*,  $C_{15}H_{28}O_3$ , m. p. 210—211°. Ozonisation in glacial acetic acid solution and subsequent decomposition of the ozonide yielded neutral and acidic products. From the former, a stable, light yellow *oil*,  $C_{14}H_{20}O_3$ , b. p. 138—144°/7 mm.,  $D^{20}_D$  0.9972,  $\alpha^{20}_D + 96^\circ$ ,  $n_D$  1.5276, which appears to be an oxide, and a *keto-lactone*,  $C_{15}H_{24}O_3$ , b. p. 200—208°/8 mm.,  $D^{20}_D$  1.067,  $n^{20}_D$  1.5005, were isolated.

From the fractions of higher b. p. prepared by distilling oil of carnations, a *sesquiterpene alcohol*,  $C_{15}H_{26}O$ , was obtained. It has b. p. 138—148°/8 mm.,  $D^{20}_D$  0.9681,  $\alpha_D - 17^\circ$ ,  $n_D$  1.5010, and is apparently a bicyclic alcohol with one double bond. Phosphorus pentachloride converts it into the *chloride*,  $C_{15}H_{25}Cl$ , b. p. 147—155°/12 mm.,  $D^{20}_D$  0.990, from which, by treatment with alcoholic potash, the *hydrocarbon*,  $C_{15}H_{24}$ , b. p. 123—126°/10 mm.,  $D^{20}_D$  0.9273,  $\alpha^{20}_D - 23^\circ$ ,  $n^{20}_D$  1.5024, was obtained.

III. In order to decide whether the same carbon skeleton is present in natural and "regenerated" caryophylline (Semmler and Mayer, Abstr., 1911, i, 73), both hydrocarbons were reduced by hydrogen in the presence of platinum. The tetrahydrocaryophyllene obtained in each case was identical. H. W.

**Bornylene.** LEO TSCHUGAEFF and W. BUDRICK (*Annalen*, 1912, 388, 280—293).—The researches of Jotsitsch (*J. Russ. Phys. Chem. Soc.*, 1909, 41, 542), Bredt (Abstr., 1909, i, 498), and Kondakoff (*ibid.*, 1910, i, 327), have raised the question of the individuality of bornylene. The present paper deals with the examination of the bornylene obtained from methyl *l*-bornyl xanthate. The purest *d*-bornylene, obtained by the decomposition of the xanthate at 176—177°, and sublimation and distillation over sodium of the product, followed by fractional distillation, purification by alcohol, and finally rectification over sodium, has b. p. 146.5°/750 mm., m. p. 109—109.5°,

$[\alpha]_C$  15·06°,  $[\alpha]_D$  19·29°,  $[\alpha]_E$  25·49°,  $[\alpha]_F$  31·06°, and  $[\alpha]_F/[\alpha]_C$  2·06 (compare Bredt, *loc. cit.*). Its oxidation in benzene by 1% aqueous potassium permanganate yields about 73% of *l*-camphoric acid; this is the only acidic product of the oxidation, camphenic and camphenilic acids (the formation of which would indicate the presence of some camphene) being specially, but unsuccessfully, sought for. The oxidation in a similar manner of a similarly prepared *l*-bornylene yields *d*-camphoric acid as the only acidic product. These camphoric acids are optically individual, indicating that the respective bornylenes do not contain *r*-bornylene.

When bornylene in benzene is exhaustively oxidised by 1% aqueous potassium permanganate, the products which are volatile with steam contain a small quantity of a hydrocarbon,  $C_{10}H_{16}$ , b. p. 153—153·5°, m. p. 64·5—65°, which is shown to be cyclene by direct comparison.

From the preceding experiments, therefore, it is seen that the active bornylene obtained by the decomposition of the methyl bornyl xanthate is a mixture of the active bornylene with a very little cyclene, and that racemisation does not occur during the decomposition.

C. S.

**Approximate Value of the Molecular Weight of Caoutchouc.** PAUL BARY (*Compt. rend.*, 1912, 154, 1159—1160).—A study of the equilibrium between sulphur and caoutchouc during vulcanisation (Abstr., 1911, i, 1003) gives  $(C_{10}H_{16})_nS_2$  as the formula for vulcanised rubber. Analysis shows that the minimum proportion of combined sulphur after vulcanisation is 2·5%, whence  $n = 18·4$ , a number in good agreement with Weber's formula,  $C_{200}H_{320}S_2$ . The molecular weight of the material at the temperature of vulcanisation is, therefore, approximately  $136 \times 20 = 2720$ .

W. O. W.

**The Colloidal Nature of Caoutchouc.** FELIX AHRENS (*Chem. Zeit.*, 1912, 36, 505—506).—Emulsions of rape oil and water may be prepared, in which either the oil or the water forms the closed phase. There must, therefore, be an intermediate point, at which the two liquids are in more intimate contact. It is in fact found that in emulsions of a certain concentration the oil globules become coated with a fine foam, and this very stable foam protects the globules against oxidation when a current of oxygen is passed in, provided that the temperature is not allowed to rise. In the latex, the caoutchouc globules are suspended in serum, and oxygen is always present, usually amounting to 2%. The globules take up this oxygen at the surface, and so form a protecting layer. If this layer is chemically or mechanically destroyed after coagulation, it is not re-formed, owing to the absence of the requisite constituents of the serum. The presence of this layer accounts for the reticulated structure of caoutchouc.

If two portions of dry washed Para rubber are taken, one is kneaded between close rollers, and two 8% solutions in benzene are prepared from them, the kneaded specimen becomes liquid in a few months, owing to the destruction of the protecting layer, whilst the untreated specimen is not altered.

C. H. D.

**Amygdalins and their Inter-reactions with Emulsin.** VERNON K. KRIEBLE (*J. Amer. Chem. Soc.*, 1912, 34, 716—735).—It was shown by Walker and Kriebie (*Trans.*, 1909, 95, 1437) that the rotation of a racemised amygdalin solution is independent of the nature and of the concentration of the alkali, and that the equilibrium point is independent of the temperature and of the concentration of the amygdalin. It was also found that racemic amygdalin could be partly resolved into its optical isomerides, and that when a racemised solution was evaporated to dryness on the water-bath the specific rotation was increased.

It is now shown that a minute trace of hydroxyl ions is capable of effecting the racemisation of amygdalin, and that the cyano-group is necessary for the change to take place. *r*-Amygdalin is composed of 56.25% of the *d*-form, and 43.75% of the *l*-form. The increase in rotation when racemic solutions are heated to dryness on the water-bath is due to a very small amount of hydroxyl ions produced by the hydrolysis of the barium salt of an unknown acid, minute quantities of which are always associated with amygdalin. The change giving rise to the increased rotation is a transformation of the cyano-group. The cause having been ascertained, it was easily removed, and it was then possible to isolate pure *d*-amygdalin, the properties of which closely resemble those of the *l*-form. *d*-Amygdalin, like the *l*-modification, is hydrolysed by emulsin into benzaldehyde, dextrose, and hydrogen cyanide, but at a slower rate. The *r*-form is hydrolysed more slowly than the *l*- and *d*-forms separately.

It has been shown by previous workers that emulsin, not only hydrolyses active benzaldehydecyanohydrin, but also synthesises it from hydrogen cyanide and benzaldehyde. Whilst Feist, Rosenthaler, and Auld found that *d*-benzaldehydecyanohydrin was always present in the hydrolytic solutions, the author has found that with certain specimens of emulsin, *l*-benzaldehydecyanohydrin was invariably obtained. With benzaldehyde and hydrogen cyanide, the *d*-form is obtained, which agrees with the results of the investigators mentioned.

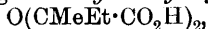
E. G.

**Strophanthus Glucosides from Various Sources.** ARTHUR HEFFTER and FRITZ SACHS (*Biochem. Zeitsch.*, 1912, 40, 83—124).—The authors give a detailed account of the literature of the various strophanthins (*Kombé*, *Hispidus*, and *Gratus*) which have been prepared, and call attention to the fact, that the botanical origin of many of the preparations which have been described is uncertain. For this reason they have confined their attention to the *Strophanthus hispidus* and *Strophanthus Kombé*, using materials of known origin, which had been submitted previously to botanical investigation. An amorphous product was obtained both from the hispidus and Kombé varieties in the following way: The residue from the alcoholic extract was taken up by water, the aqueous solution was clarified by the addition of lead acetate, the excess of lead separated from the filtrate of the lead salt, and the liquid was then evaporated down in the presence of excess of calcium carbonate. After evaporation to a syrup, the calcium carbonate was filtered off, and a large excess of

ammonium sulphate was added. The glucoside was precipitated, and was purified by repeated solution in alcohol and precipitation from the alcoholic solution by ether. From the hispidus plant, the glucoside had the rotation  $[\alpha]_D + 13.9^\circ$ , and from the Kombé plant  $[\alpha]_D$  was  $+11.87^\circ$ . Both yielded on hydrolysis a strophanthidin with  $[\alpha]_D$  about  $41^\circ$ . The pharmacological investigation, analyses, and methoxyl estimation of the glucosides from the two sources indicated that these substances were identical. In addition to these, the authors also succeeded in obtaining a crystalline glucoside from the Kombé plant. This was got by heating the calcium carbonate, after evaporation of the mixture (see above), with hot water. From the solution thus obtained, needles separated on cooling; it was recrystallised from hot water. The substance appears to be identical with that previously described by Arnaud. It contains 61.93% carbon, 7.64% hydrogen, and 4.73% methoxyl, and has  $[\alpha]_D + 28.72^\circ$ . It yields on hydrolysis strophanthidin, and differs from the amorphous products in that it has a slight hæmolytic action; otherwise the pharmacological action is very similar. All the products prepared give a green colour with concentrated sulphuric acid, which is in contrast with the pink colour obtained by some other authors with the strophanthin of different origins. S. B. S.

**Oxidation of Some Ketohydrofurans.** GEORGES DUPONT (*Compt. rend.*, 1912, 154, 987—989. Compare Abstr., 1911, i, 554, 804; this vol., i, 290).—Potassium permanganate oxidises ketotetramethyltetrahydrofuran, forming *tetramethyldiglycollic acid*,  $O(CMe_2 \cdot CO_2H)_2$ , m. p.  $153\text{--}155^\circ$ ; the *lead* salt crystallises with  $3.5H_2O$ ; the *diethyl* ester has b. p.  $114^\circ/13$  mm.,  $D^{16} 1.0173$ ,  $n_D 1.4292$  (compare Jungfleisch and Leroux, Abstr., 1908, i, 127).

Ketodimethyldiethyltetrahydrofuran undergoes oxidation by potassium permanganate, giving *dimethyldiethylglycollic acid*,



m. p.  $155^\circ$ ; the *lead* salt is anhydrous, and decomposes at about  $210^\circ$ . At the same time an *isomeride* of the acid is formed, having m. p.  $90\text{--}92^\circ$ ; the *lead* salt has m. p.  $252^\circ$  (decomp.). Ketodimethyltetrahydrofuran is oxidised in the same way, giving rise to a syrupy acid, b. p.  $132\text{--}133^\circ/12$  mm.,  $D^{18} 1.1316$ ,  $n_D 1.4282$ ; this is probably  *$\beta$ -hydroxyacetylbutyric acid*. W. O. W.

**The aci-Nitro-derivative of Ketotetramethyltetrahydrofuran.** GEORGES DUPONT (*Compt. rend.*, 1912, 154, 1176—1178).—Ketotetramethyltetrahydrofuran is added to the calculated amount of fuming nitric acid. After several days crystals are obtained, having m. p.  $71\text{--}72^\circ$  when crystallised from light petroleum, but which separate from benzene in large needles, m. p.  $78\text{--}79^\circ$ . The two varieties have the same chemical properties, but determinations of their refractive indices show the first modification to be *aci-nitrokotetramethyltetrahydrofuran*,  $O \begin{smallmatrix} \text{CMe}_2 \cdot \text{C} \cdot \text{NO}_2\text{H} \\ \text{CMe}_2 \cdot \text{CO} \end{smallmatrix}$ , whilst the second is the true *nitro*-derivative. The compound is strongly acid, and forms well-defined salts. The *potassium*, *sodium*, and *ammonium* salts crystallise in leaflets, and when added to aqueous solutions of salts of other metals give

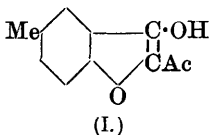
crystalline and often highly coloured precipitates. The salts of *calcium*, *barium* (with  $2\text{H}_2\text{O}$ ), *zinc*, *copper*, *mercurous* (yellow), *mercuric*, *lead* (yellow), *ferrous* (violet, with  $2\text{H}_2\text{O}$ ), *ferric* (brown), *nickel* (yellowish-green), *cobalt* (rose), *manganese* (golden-yellow, with  $3\text{H}_2\text{O}$ ), *chromium* (yellow), *tin*, *antimony*, *cadmium*, and *uranium* (golden-yellow) have been prepared.

Nitroketotetramethylhydrofuran distils in a vacuum, but decomposes when heated under ordinary pressure, in accordance with the equation :  $2\text{C}_8\text{H}_{13}\text{O}_4\text{N} = \text{C}_8\text{H}_{12}\text{O}_3 + 2\text{COMe}_2 + \text{H}_2\text{O} + 2\text{CO} + \text{N}_2$ . In addition to acetone and water, the liquid distillate contains *diketo-2 : 2 : 5 : 5-tetramethyltetrahydrofuran*,

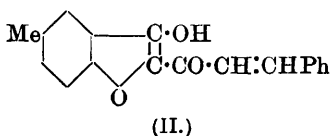
$\begin{array}{c} \text{CO} \cdot \text{CMe}_2 \\ \text{CO} \cdot \text{CMe}_2 \end{array} \text{>O}$ , a red liquid, b. p. about  $170^\circ$ .

When exposed to moist air this compound takes up  $2\text{H}_2\text{O}$ , forming colourless crystals, m. p. about  $80^\circ$ . The *dioxime* volatilises without melting at about  $240^\circ$ . W. O. W.

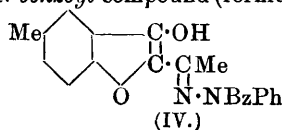
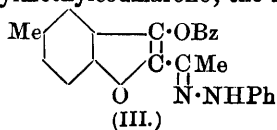
**The C-Acyl Derivatives of 2-Hydroxycoumarones.** KARL AUWERS (*Ber.*, 1912, 45, 976—994).—The 2-hydroxy-1-acylcoumarones (Auwers, *Abstr.*, 1910, i, 629) in their behaviour towards reagents for the carbonyl group resemble the aromatic *o*-hydroxyketones; they differ, however, in their greater tendency to form additive compounds. Methylation by methyl sulphate appears to be a direct substitution, producing stable O-ethers, whilst the action of methyl iodide and sodium methoxide is not so simple, giving C-methyl derivatives which immediately split into simpler molecules.



2-Hydroxy-1-acetyl-4-methylcoumarone (formula I annexed), recrystallised from light petroleum or precipitated by acid from alkaline solution, forms slender needles, m. p.  $87\text{—}89^\circ$ ; it separates from hot methyl alcohol, however, in compact crystals, m. p.  $104^\circ$ ; a mixture of the two modifications has the higher m. p., and even at the ordinary temperature the form of lower m. p. slowly isomerises. Treatment of this substance with acetyl chloride and pyridine forms the *acetyl* derivative; the acetyl group is less stably fixed than the benzoyl group in the corresponding benzoic ester, for the latter with semicarbazide yields a semicarbazone (m. p.  $220^\circ$ ), whilst the former yields only the semicarbazone of the original hydroxyacetyl-methylcoumarone. The *benzylidene* compound (formula II) forms yellow needles, m. p.  $119^\circ$ . The phenylhydrazone (described earlier) forms a *benzoyl* derivative (formula III), yellow needles, m. p.  $179\text{—}180^\circ$ , which is also obtained by the action of phenylhydrazine on the already described benzoate of the hydroxyacetylmethylcoumarone; the isomeric *N-benzoyl* compound (formula IV)

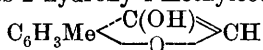


hydrazone (described earlier) forms a *benzoyl* derivative (formula III), yellow needles, m. p.  $179\text{—}180^\circ$ , which is also obtained by the action of phenylhydrazine on the already described benzoate of the hydroxyacetylmethylcoumarone; the isomeric *N-benzoyl* compound (formula IV)



is obtained by the interaction of the hydroxyacetylmethylcoumarone with *as*-benzoylphenylhydrazine hydrochloride; it is a yellow, crystalline powder, m. p. 186°.

Methylation by methyl sulphate in the presence of alkali yields 2-methoxy-1-acetyl-4-methylcoumarone, colourless needles, m. p. 98—99°; the semicarbazone of this ether forms yellow needles, m. p. 240°, the phenylhydrazone, needle crystals, m. p. 129°, and the benzylidene derivative, yellow needles, m. p. 131—133°; the semicarbazone is smoothly hydrolysed by oxalic acid solution to the original ether, but 30% sulphuric acid gives 2-hydroxy-4-methylcoumarone,



(m. p. 51—52°). Semicarbazones can be methylated by methyl sulphate, for example, the semicarbazone of 4-hydroxy-*m*-tolyl methyl ketone (needles, m. p. 221—225°) gives the methyl ether, colourless needles, m. p. 199°, b. p. 254°/760 mm., 132°/11 mm.; similarly, the semicarbazone of hydroxyacetylmethylcoumarone gives as main product the semicarbazone of the methyl ether (see above), together with an isomeride, yellow needles, m. p. 172—173°; the latter is converted into the former (m. p. 240°) on warming with glacial acetic acid.

2-Methoxy-1-benzoyl-4-methylcoumarone is obtained (like the corresponding acetyl compound) by the action of methyl sulphate; it forms slender needles, m. p. 77—78°.

The action of methyl iodide and sodium methoxide converts hydroxyacetylmethylcoumarone into 2-hydroxy-1:4-dimethylcoumarone,

$\text{C}_6\text{H}_3\text{Me} \begin{array}{c} \diagup \text{C(OH)} \diagdown \\ \text{O} \end{array} \text{CMe}$ , an oil, b. p. 125°/15 mm., which slowly crystallises in needles, m. p. 63°; it is very feebly acidic, and has a clinging odour.

The identity of this substance was confirmed by a synthesis from *p*-tolyl methyl ether and bromopropionyl bromide in the presence of aluminium chloride; the primary product, *o*-*α*-chloropropionyl-*p*-cresol,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO} \cdot \text{CHMeCl}$ , m. p. 84—85·5°, passes easily into the above hydroxydimethylcoumarone. The substance is very stable towards alkalis or acids, but is oxidised by permanganate to methylsalicylic acid. With an equimolecular quantity of semicarbazide, the substance gives the semicarbazone,  $\text{O} \begin{array}{c} \diagup \text{C}_6\text{H}_3\text{Me} \diagdown \\ \text{CHMe} \end{array} \text{C:N} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , m. p. 191°, which is hydrolysed to the parent substance by 30% sulphuric acid; excess of semicarbazide gives a substance, m. p. 225°, formed by the condensation of one molecule with two of semicarbazide.

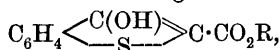
Methyl iodide and sodium methoxide act on the semicarbazone of 2-hydroxy-1-acetyl-4-methylcoumarone, giving some hydroxyacetyl 1:4-dimethylcoumarone (above), together with the O-methyl ether of the semicarbazone (above), and a colourless substance forming compact needles, m. p. 223°; the last-named with sulphuric acid gives dimethylcoumarone (m. p. 63°), and so must be a C-methyl derivative, but otherwise the structure is uncertain; methylation by methyl sulphate converts it into a substance, crystallising in needles, m. p. 192°.

Methylation of 2-hydroxy-1-benzoyl-4-methylcoumarone by methyl iodide and sodium methoxide gives the O-methyl ether (above),

together with methyl salicylate and hydroxy-1 : 4-dimethylcoumarone.  
D. F. T.

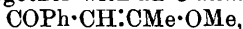
**Preparation of O-Alkyl and C-Alkyl Derivatives.** KARL AUWERS (*Ber.*, 1912, 45, 994—997. Compare preceding abstract).—Other substances have been investigated to discover how far the characteristic difference in behaviour towards methyl sulphate and methyl iodide extends.

Substances of the types  $C_6H_4 \begin{smallmatrix} \text{C(OH)} \\ \text{O} \end{smallmatrix} C \cdot CO_2R$ ,



and  $C_6H_4 \begin{smallmatrix} \text{C(OH)} \\ \text{NH} \end{smallmatrix} C \cdot CO_2R$  react with methyl sulphate, giving O-ethers, whilst with alkyl halides they primarily give products of the type  $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{O(S)} \end{smallmatrix} C \begin{smallmatrix} \text{R} \\ \text{CO}_2R \end{smallmatrix}$ , accompanied by some O-derivative. It is not yet certain whether the difference is to be ascribed to the alkylation agent or to the reaction conditions (for example, the medium, etc.).

$\beta$ -Diketones do not easily form O-ethers with methyl sulphate; for example, acetylacetone gave quite negative results, whilst benzoylacetone gave phenyl ethyl ketone (from the splitting of the primary  $COPh \cdot CHMe \cdot COMe$ ), together with an *O-methyl ether*, probably



b. p. 154—155°/16 mm.

D. F. T.

**Synthesis of *o*-Hydroxyflavone.** A. PISTERMANN and JOSEF TAMBOR (*Ber.*, 1912, 45, 1239—1242).—Of the eight possible monohydroxyflavones, Kostanecki and his pupils have already prepared six (compare Abstr., 1898, i, 369; 1899, i, 370; 1900, i, 669; 1901, i, 558; 1904, i, 764; 1907, i, 75), whilst *o*-hydroxyflavone is the subject of this paper and the remaining 8-hydroxyflavone is being studied.

Methyl *o*-methoxybenzoate and *o*-ethoxyacetophenone were condensed to 2-methoxy-2'-ethoxybenzoylacetophenone, an oily  $\beta$ -diketone which could not be crystallised, but which boiling concentrated hydriodic acid converted into 2'-hydroxyflavone,  $C_6H_4 \begin{smallmatrix} \text{O}-C \cdot C_6H_4 \cdot OH \\ \text{CO} \cdot C \end{smallmatrix}$ , crystallising from alcohol in light yellow, shining needles, m. p. 238.5°. This gave a pale yellow solution in strong sulphuric acid, but an intense yellow one in dilute alkalis, whilst the *acetyl* derivative,  $C_{17}H_{12}O_4$ , formed pale yellow needles, m. p. 90°, and the 2'-methoxyflavone,  $C_{16}H_{12}O_3$ , crystallised in colourless needles, m. p. 105°.

Similarly, *o*-ethoxyacetophenone has been coupled with ethyl acetate and with ethyl propionate, the crude 2-ethoxyacetylacetophenone,  $C_{12}H_{14}O_3$ , being an oil, which crystallised from dilute alcohol in colourless needles, m. p. 56—57°, and was converted by hot hydriodic acid into the 2-methylchromone of Bloch and Kostanecki (Abstr., 1900, i, 502); the *o*-ethoxypropionylacetophenone,  $C_{13}H_{16}O_3$ , also

formed colourless needles, m. p.  $46^{\circ}$ , but did not give a crystallisable product with hydriodic acid. J. C. W.

**Action of Hydrogen Peroxide on Bromothiophens.** MAURICE LANFRY (*Compt. rend.*, 1912, 154, 1090—1092. Compare Abstr., 1911, i, 740, 1009).—The bromothiophens are much more resistant to the action of hydrogen peroxide than thiophen itself, and in no case do they yield a sufficient amount of oxythiophens (*loc. cit.*) for identification. Monobromothiophen is decomposed by hydrogen peroxide with liberation of bromine and formation of dibromothiophen. The latter is less easily decomposed, whilst tri- and tetra-bromothiophen are unaltered by the reagent. W. O. W.

**Preparation of Derivatives and Substitution Products of 3-Keto-(1)-thionaphthens.** GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE IN BASEL (D.R.-P. 242461).—The action of carbonyl chloride on indoxyl has been described previously (Abstr., 1911, i, 675); it is now found that a similar condensation takes place when a cooled aqueous alkaline solution of 3-keto-(1)-thionaphthen (its homologues or substitution products) is treated with carbonyl chloride. The product forms glistening red, leaflets, m. p.  $123-125^{\circ}$ . F. M. G. M.

[Preparation of "Tetramethylthioindigo."] KALLE & Co. (D.R.-P. 242998).—When 4-carboxy-*m*-xylyl-5-thiolacetic acid (this vol., i, 126) is heated at above  $100^{\circ}$  with moist sulphuric acid, it yields "tetramethylthioindigo" without sulphonation; the same reaction also takes place when phosphoric or boric acids are employed.

F. M. G. M.

**Preparation of Berberine Derivatives.** MARTIN FREUND (D.R.-P. 242573. Compare Abstr., 1900, ii, 588; 1905, i, 657).—When  $\alpha$ -benzylidihydroberberine methiodide (Abstr., 1905, i, 151) is warmed in dilute alcoholic solution with excess of ammonium hydroxide, it furnishes a *base*, a crystalline powder, m. p.  $187-188^{\circ}$ ; this when reduced with a lead cathode in dilute sulphuric acid at  $20-25^{\circ}$  (or with tin and concentrated hydrochloric acid) is converted into a *base*, forming yellow, rhombic tablets, m. p.  $163^{\circ}$ , containing C=75% and H=6%, and yielding crystalline *salts*. *iso*Butylidihydroberberine, yellow leaflets or needles, m. p.  $112-113^{\circ}$ , was prepared from berberine hydrochloride and *isobutyl* bromide by Grignard's reaction; it furnishes a *methiodide*, yellow needles, m. p.  $200^{\circ}$  (decomp.), which, when treated with excess of ammonium hydroxide (or sodium carbonate), yields a *base*,  $C_{25}H_{29}O_4N$ , brownish-yellow prisms, m. p.  $146^{\circ}$ . This base when electrolytically reduced is converted into two *bases*, one consisting of yellow, rhombic tablets, m. p.  $155-157^{\circ}$ , which does not combine with methyl iodide; the other, colourless crystals, m. p.  $175-176^{\circ}$ , yields a *methiodide*, m. p.  $246^{\circ}$ . F. M. G. M.

**Preparation of Tetrahydroberberine Derivatives.** MARTIN FREUND (D.R.-P. 242217. Compare Abstr., 1907, i, 632; 1905, i, 657; this vol., i, 383).—Contains details of the preparation of compounds previously described.

*α-Ethyltetrahydroberberine methiodide* has m. p. 229°, and by the action of silver hydroxide, as previously described (*loc. cit.*), yields a base, m. p. 130—131°. F. M. G. M.

**Crystallisation of Quinine and Quinine Trihydrate.** JULES VILLE (*Bull. Soc. chim.*, 1912, [iv], 11, 398—400).—Anhydrous quinine has been obtained in the form of minute, colourless lamellæ by passing air containing ammonia into a solution of quinine hydrobromide maintained at 100°. The alkaloid sublimes slightly at 165—167°, and melts at 172—173°. Quinine trihydrate separates in long silky needles when enough dilute ammonia to produce faint opalescence is added to a solution of quinine hydrobromide in acetone and water, and the mixture is set aside. The trihydrate melts at 89—90° when projected on a heated mercury surface; it loses part of its water in the air, and is completely dehydrated over sulphuric acid, T. A. H.

**[Rearrangement of Cinchonine and Quinine into their Poisonous Isomerides, Cinchotoxine and Quinotoxine.]** PAUL RABE (*Ber.*, 1912, 45, 1447—1449).—This rearrangement (*Abstr.*, 1911, ii, 33) had been previously described by Biddle (compare this vol., i, 296). C. S.

**Dihydrohydrastinine: the Stereochemistry of Compounds Containing Nitrogen.** MARTIN FREUND and KEITA SHIBATA (*Ber.*, 1912, 45, 855—861).—By the action of ethylene bromide, magnesium, and ether on hydrastinine, two isomeric dihydrohydrastinines are obtained. The stable isomeride, m. p. 163°, crystallises in silky, lustrous, pointed prisms; the *hydrobromide* crystallises in slender needles, m. p. 238—239° (decomp.); the *hydriodide* separates in needles aggregated in rounded bunches, m. p. 238—239° (decomp.); the *hydrochloride* crystallises in platelets and prisms; the *sulphate* crystallises in platelets, m. p. 255—256°.

The stereoisomeric *isodihydrohydrastinine*, m. p. 175—176°, crystallises in rhombic plates or prisms. It is converted into the stable form when melted; the mixture of the two forms sinters at 144°, m. p. 155—156°. The *hydrobromide* crystallises in needles, m. p. 212—213°; the *hydriodide* forms bunches of needles, m. p. 207—208°; the *hydrochloride* crystallises in plates; the *sulphate* separates in needles, m. p. 250—251°.

Dihydrohydrastinine forms an *hydrogen tartrate* crystallising in needles, m. p. 158—159°; the isomeric acid tartrate could not be obtained in crystalline form. Neither isomeride could be resolved into optically active *d*- and *l*-forms, and they are regarded as internally compensated inactive meso-forms.

The monomethiodide of dihydrohydrastinine crystallises in prisms, m. p. 218°; it is basic and forms a hydriodide crystallising in rhombic plates, m. p. 205—206°; the methiodide of the *iso*-base separates in rhombic plates and prisms, m. p. 235—236°, and gives a hydriodide crystallising in rhombic plates, m. p. 228—229°.

*N-Methyldeisodihydrohydrastinine* crystallises in well-formed, mono-

clinic plates, m. p. 175—176°; the *hydriodide* has m. p. 151—152°. It forms an additive compound with methyl iodide with difficulty; the *methiodide* crystallises in needles, m. p. 189—190° (decomp.).

*N*-Methyldehidrohydrastinine was obtained as an oil readily reacting with methyl iodide to form a methiodide, which loses trimethylamine on treatment with alkali.

E. F. A.

**Morphine. XXIII. Preparation and Hydrolysis of an Iodocodeide.** LUDWIG KNORR and WALTER HARTMANN (*Ber.*, 1912, 45, 1350—1353).—The hydrolysis of the so-called  $\alpha$ -chlorocodeide yields  $\psi$ -codeine and smaller quantities of *allo*- $\psi$ -codeine and *iso*-codeine (Knorr and Hörlein, *Abstr.*, 1908, i, 361), complex atomic rearrangements taking place which obscure conclusions as to the composition of the halogen codeides.  $\alpha$ -Iodocodeide has therefore been prepared, in the hope that the iodine atom would be replaceable at a lower temperature than the chlorine atom, but even when hydrolysis took place at the ordinary temperature, the same complicated changes occurred as with the chloro- and bromo-compounds.

$\alpha$ -Iodocodeide was prepared by heating  $\alpha$ -chlorocodeide with potassium iodide in ethyl alcoholic solution. It forms light orange needles, which soften at about 167°, and have m. p. about 200°. In chloroform solution it has  $[\alpha]_D^{20} + 136.5^\circ$  ( $c = 3.95$ ). Its *hydriodide*, m. p. 180—182°, is very characteristic.

When hydrolysed by acetic acid, it yields  $\psi$ -codeine and *allo*- $\psi$ -codeine (isolated as hydriodides) and *isocodeine* (isolated as hydrogen oxalate). The same products were obtained when the hydrolysis was performed with silver acetate and acetic acid.

H. W.

**Morphine. XXIV. Methods of Preparation of Ethers of  $\psi$ -Codeine.** LUDWIG KNORR and WALTER HARTMANN (*Ber.*, 1912, 45, 1354—1358).—The codeine methyl ether obtained by Knorr and Roth (*Abstr.*, 1911, i, 1014) by the action of sodium methoxide on a methyl alcoholic solution of  $\alpha$ -chlorocodeide differs from that obtained by Pschorr and Dickhäuser (*Abstr.*, 1911, i, 908), and is to be considered as the methyl ether of  $\psi$ -codeine (compare previous abstract). Such ethers of  $\psi$ -codeine are readily obtained by heating  $\alpha$ -chlorocodeide with alcohols.

$\psi$ -Codeine methyl ether is obtained by heating  $\alpha$ -chlorocodeide with methyl alcohol at 100—110° during two days in yield of 40—50%.  $\psi$ -Codeine ethyl ether, prepared in a similar manner, has m. p. 76°. Its *hydrochloride*,  $C_{20}H_{25}O_3N, HCl, \frac{1}{2}EtOH$ , forms white needles, m. p. about 255° (decomp.). Its *hydriodide* decomposes at 267—270°.  $\psi$ -Codeine propyl ether yields a *hydriodide*, m. p. about 259° (decomp.), but could not be obtained in the crystalline state.  $\psi$ -Codeine phenyl ether (prepared by H. Hörlein) is obtained by boiling  $\alpha$ -chlorocodeide and sodium phenoxide with absolute alcohol, and has m. p. 187°.  $\psi$ -Codeine p-tolyl ether, obtained similarly, has m. p. 165°,  $[\alpha]_D^{20} - 13.7^\circ$  ( $c = 2.78$ ) in chloroform solution. Its *hydrochloride* has m. p. 231°, whilst its *nitrate* decomposes at 180—181°.  $\psi$ -Codeine m-tolyl ether and its *nitrate* have m. p. 144° and 192° respectively, whilst  $\psi$ -codeine o-tolyl ether melts at 189° after previous softening.  $\psi$ -Codeine guaiacyl

*ether*, prepared from sodium ethoxide, guaiacol, and  $\alpha$ -chlorocodeide, has m. p.  $214^{\circ}$ , and forms beautiful crystalline salts, such as the *hydrochloride*, *nitrate*, decomposing at about  $197^{\circ}$ , *hydrogen oxalate*,

$C_{25}H_{27}O_4N, H_2C_2O_4$ ,  
m. p.  $197^{\circ}$ , and *hydrogen tartrate*,  $C_{25}H_{27}O_4N, C_4H_6O_6$ , m. p.  $205^{\circ}$ . H. W.

**Constitution of *iso*Narcotine and the Synthesis of Narcotine Derivatives of High Molecular Weight.** MARTIN FREUND and KARL FLEISCHER (*Ber.*, 1912, 45, 1171—1182).—In cases where opianic acid reacts as a lactone, the authors suggest that the expression opian(lact) should be employed. The compounds now described are of this type.

Bromohydrocotarnine, in which the active hydrogen atom in position 5 is replaced by bromine, could not be condensed with opianic acid. Accordingly, *isonarcotine* is regarded as 5-opianyl hydrocotarnine. Narcotine also contains the hydrogen atom in position 5, and condenses with opianic acid to a mixture of stereoisomeric  $\alpha$ - and  $\beta$ -opianylnarcotines,  $C_{32}H_{31}O_{11}N$ .

The methiodide of the  $\alpha$ -isomeride is converted by silver oxide into an ammonium base, which concentrated alkali hydroxide splits to form an amino-acid,  $C_{33}H_{37}O_{13}N$ ,  $\alpha$ -(5)-opianylhydratenarceine.

Narcotine condenses with formaldehyde, forming methylenedinarcotine, a l  vrotatory, crystalline compound. On oxidation, methylenedicotarnine is formed, which, like cotarnine, forms crystalline salts which give yellow solutions.

*iso*Narcotine does not condense with formaldehyde. Cotarnine also could not be condensed with formaldehyde or with opianic acid, although hydrocotarnine reacts with both of these.

$\alpha$ -Opianylnarcotine crystallises in radially-grouped aggregates of very slender needles, m. p.  $199^{\circ}$ ,  $[\alpha]_D^{25} - 94.73^{\circ}$ . The salts with mineral acids are oily; with concentrated sulphuric acid a violet-red coloration is obtained.

$\beta$ -Opianylnarcotine forms slender, colourless needles, m. p.  $173-175^{\circ}$ ,  $[\alpha]_D^{25} - 103.6^{\circ}$ .

$\alpha$ -Opianylnarcotine forms a *methiodide*, crystallising in lustrous, colourless platelets, which begin to change at  $210^{\circ}$ , m. p.  $233^{\circ}$ .

The *picrate* separates in yellow, microscopic, rectangular plates, m. p.  $217^{\circ}$ .

The *methiodide* of the  $\beta$ -isomeride forms a pale yellow powder without lustre, which sinters at  $200^{\circ}$ , decomp.  $222^{\circ}$ .

By the action of dilute nitric acid on  $\alpha$ -opianylnarcotine, a *compound*, crystallising in slender, yellow needles, m. p.  $206^{\circ}$  (decomp.), is obtained.

$\alpha$ -(5)-Opianylhydratenarceine crystallises in colourless, matted needles, which change at  $180^{\circ}$ , decomp.  $193^{\circ}$ .

Methylenedinarcotine forms a colourless, dusty, crystalline powder, which colours at  $200^{\circ}$ , m. p.  $215-216^{\circ}$ ,  $[\alpha]_D - 93.4^{\circ}$ , and gives a faint yellow coloration with concentrated sulphuric acid, changing to a dirty red on the addition of a drop of dilute nitric acid, and then decolorising immediately. The *methiodide* was obtained as an oil

solidifying to an amorphous mass. The *picrate* forms a crystalline, yellow powder changing at 165°, decomp. 173°; in sunlight it turns a sealing-wax red.

*Methylenedicotarnine hydrobromide* crystallises in yellow, prismatic rods, m. p. 240° (decomp.); the *free base* is a yellowish-white powder, m. p. 132° (decomp.). The *hydriodide* crystallises in deep yellow rods, decomp. 235°. E. F. A.

**Methylenedihydrocotarnine.** MARTIN FREUND and ADOLF DAUBE (*Ber.*, 1912, 45, 1183—1186).—The compound described as hydrodicotarnine by Bandow (*Abstr.*, 1897, i, 581), and obtained by the action of sulphuric acid on hydrocotarnine, contains in reality a CH<sub>2</sub> group more than stated by Bandow. It is obtained quantitatively by the action of formaldehyde and sulphuric acid on hydrocotarnine, and is properly termed methylenedihydrocotarnine. No such condensation takes place with bromohydrocotarnine, in which bromine replaces the active hydrogen.

Methylenedihydrocotarnine, CH<sub>2</sub>:  $\left[ C_6(OMe)(CH_2O_2) \begin{array}{l} \text{CH}_2 \cdot NMe \\ \text{CH}_2 \cdot CH_2 \end{array} \right]_2$ ,

has m. p. 211—212°. The hydrobromide crystallises in platelets, m. p. 240—244° (Bandow, *loc. cit.*, gives 218—220°). The hydroiodide forms colourless needles, m. p. 242° (Bandow gives 227—229°); the *dichromate* separates in reddish-yellow plates. The *dimethiodide* crystallises in yellow needles, which soften at 267°. E. F. A.

**Action of Aldehydes on Pyrrole Substances.** Pyrogenetic Decomposition of Derivatives of Dipyrrolylmethane. U. COLACCICCHI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 410—415. Compare *Abstr.*, 1911, i, 1030).—The present paper deals chiefly with the decomposition by heat of the product from paracetaldehyde and 3-acetyl-2:4-dimethylpyrrole, previously described.

Both at the ordinary and at reduced pressure this substance yields on distillation the same two products, namely, 5-acetyl-2:4-dimethylpyrrole and a substance, C<sub>9</sub>H<sub>13</sub>ON, which forms small, lustrous needles, m. p. 160°, and is probably 5-acetyl-2:3:4-trimethylpyrrole. In addition 3-acetyl-2:4-dimethylpyrrole is also formed in smaller quantity. In the decomposition, therefore, not only is the ethylidene linking broken, but the position of the acetyl group is changed. When 3-acetyl-2:4-dimethylpyrrole is heated in a sealed tube it is transformed quantitatively into the isomeride with the acetyl group in position 5.

When oximinoacetylacetone is reduced by Knorr's method in the presence of methyl ethyl ketone, 5-acetyl-2:3:4-trimethylpyrrole is not formed, but instead diacetyldimethylpyrazine, m. p. 98°. By reducing methyl ethyl ketoxime in the same way in the presence of acetylacetone, however, 5-acetyl-2:4:5-trimethylpyrrole, m. p. 209—210°, is obtained, and since this substance is not identical with the acetyltrimethylpyrrole obtained in the above dry distillation, it is probable that that derivative has the constitution assigned above.

When 3-acetyl-2:4:5-trimethylpyrrole is treated with hydrazine hydrate, the corresponding ketazine is obtained, m. p. above 280°.

R. V. S.

**Detection of *l*-Proline as a Primary Product of Protein Hydrolysis.** EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1912, 78, 96—114).—Emphasis is laid on the difficulty of isolating and purifying proline, particularly on the unsatisfactory nature of the solubility in alcohol as a criterion of purity. The conclusion is drawn that at present there is no satisfactory method of estimating the amount of pure proline contained in the decomposition products of a protein.

The fact that proline is a primary product of protein hydrolysis is definitely proved by its direct isolation as hydantoin from the products of fermentative hydrolysis of casein or gelatin or from the contents of the intestine. 0.5 Gram of the recrystallised proline hydantoin, m. p. 140°, was obtained from the intestine of five dogs.

E. F. A.

**Esterification of the Monoamino-acids by means of Ethyl Iodide. Separation of Pyrrolidonecarboxylic Acid from Glutamic Acid.** EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1912, 78, 115—127).—The silver salt of pyrrolidonecarboxylic acid is readily esterified by ethyl iodide, whereas, under like conditions, glutamic acid, aspartic acid, asparagine, and proline remain unaltered. It is thus possible to separate pyrrolidonecarboxylic acid from admixture with glutamic or other amino-acids.

Attempts to prove by this method the presence of pyrrolidonecarboxylic acid in the products of digestion of casein led to the isolation of an ester, which could not be identified, but which formed glutamic acid hydrochloride when hydrolysed with hydrochloric acid.

Ethyl pyrrolidonecarboxylate (Fischer and Bochner, Abstr., 1911, i, 484; Abderhalden and Weil, Abstr., 1911, i, 1049) crystallises in needles or platelets, m. p. 60—61.5°.

Proline forms a very unstable silver salt, which soon becomes black, especially when warmed with water.

E. F. A.

**Glutamic and Pyrrolidonecarboxylic Acids. III. Mercury Salts, Pyrrolidonyl Chloride, and Pyrrolidonylamide.** EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1912, 78, 333—343).—Glutamic acid gives a bulky, white precipitate on the addition of mercuric acetate solution. Pyrrolidonecarboxylic acid gives no such precipitate, and it is hoped to separate the two acids in this way.

*Mercuric glutamate*,  $\text{CH}_2\left\langle\begin{array}{c} \text{CH}(\text{NH}_2)\cdot\text{CO}_2 \\ \text{CH}_2\text{---CO}_2 \end{array}\right\rangle\text{Hg}$ , forms a heavy, sandy, crystalline powder; heated in a capillary, it has decomp. 208—209°.

*Mercuric pyrrolidonecarboxylate*,  $4(\text{C}_5\text{H}_6\text{O}_2\text{N})_2\text{Hg}\cdot 3\text{HgO}$ , resembles gypsum, and has decomp. 207—208°.

*Pyrrolidonyl chloride*, prepared by the interaction of thionyl chloride

with the carboxylic acid, forms colourless crystals; it is decomposed by water, giving pyrrolidonecarboxylic acid. By the action of ammonia in chloroform, *dl*-pyrrolidonylamide is obtained, m. p. 220—221° (corr.). This is also formed in small quantities on heating the ammonium salt of glutamic acid. E. F. A.

**Preparation of Phonopyrrolecarboxylic Acid from Hæmin.** HANS FISCHER and ERICH BARTHOLOMÄUS (*Ber.*, 1912, 45, 1315—1316).—Phonopyrrolecarboxylic acid, which can be obtained from hæmatoporphyrin by reduction (Piloty, *Abstr.*, 1909, i, 858; 1911, i, 92), is also obtainable in good yield by the reduction of hæmin. The phonopyrrolecarboxylic acid is separated first as the picrate (decomp. 163°), from which the free substance (colourless needles, m. p. 125—126°) is liberated by dilute sulphuric acid. D. F. T.

**Complex Chromium Fluorides. III.** N. COSTĂCHESCU (*Ann. Sci. Univ. Jassy*, 1912, 7, 87—100).—*Trifluorotripyridinechromium*,  $\left[ \text{Cr} \begin{smallmatrix} \text{F}_3 \\ \text{Py}_3 \end{smallmatrix} \right]$ , is obtained by heating sixteen grams of violet hexaaquochromium fluoride with 200 grams of pyridine on the water-bath for two hours. After collecting the green precipitate which is formed, the filtrate is concentrated until slender, violet crystals of the desired compound begin to separate. These can be dried in an atmosphere of pyridine, after which they are stable in the air. The crystals are readily soluble in water, giving a violet, neutral, non-conducting solution which does not contain fluoridion. On prolonged boiling the aqueous solution becomes blue in colour, after which a grey product is deposited containing two molecules of pyridine; finally, the green, hydrated chromium fluoride separates.

*Trifluorotripyridinechromium hydrate*,  $\left[ \text{Cr} \begin{smallmatrix} \text{F}_3 \\ \text{Py}_3 \end{smallmatrix} \right], \text{H}_2\text{O}$ , is prepared by heating 25 grams of the violet compound,  $\left[ \text{Cr}(\text{H}_2\text{O})_6 \right] \text{F}_3 \cdot 3\text{H}_2\text{O}$ , with 180 grams of pyridine under reflux on a water-bath until the solid has almost dissolved. An intense blue solution is obtained, which, after separation from the green solid formed and further concentration, deposits dark blue crystals of the required hydrate. A further quantity of these crystals can be obtained by extracting the green solid with chloroform. They are readily soluble in water, the solution possessing properties similar to that of the anhydrous compound. When the solution in chloroform is evaporated on the water-bath at a temperature just below the boiling point of water, *trifluoroaquodipyridinechromium*,  $\left[ \text{Cr} \begin{smallmatrix} \text{Py}_2 \\ \text{H}_2\text{O} \\ \text{F}_3 \end{smallmatrix} \right], \text{H}_2\text{O}$ , is deposited as a greyish-violet powder, which is soluble in water to a neutral solution possessing a slight conductivity.

*Diffuorotetrapyridinechromium nitrate*,  $\left[ \text{Cr} \begin{smallmatrix} \text{Py}_4 \\ \text{F}_2 \end{smallmatrix} \right] \text{NO}_3$ , is obtained by the interaction of violet chromium fluoride, potassium nitrate, and pyridine. Prolonged heating on the water-bath is necessary, until the dark violet solution first formed changes to a lighter colour; after

filtering and concentrating the solution, the nitrate is deposited as violet crystals, which are soluble in water. The aqueous solution possesses a conductivity corresponding with that of a binary salt. By double decomposition with the appropriate potassium or sodium salts, the following compounds were obtained: The *thiocyanate*,  $\text{YSCN}$ , where  $\text{Y} = \left[ \text{Cr} \begin{smallmatrix} \text{Py}_4 \\ \text{F}_2 \end{smallmatrix} \right]$ , as violet needles; the *iodide*,  $\text{YI}$ , as a rosy-violet, crystalline powder; the *ferricyanide*,  $\text{Y}_3\text{FeC}_6\text{N}_6$ , in large, garnet-red crystals; the *nitroprusside*,  $\text{YNa} \left[ \text{Fe} \begin{smallmatrix} \text{NO} \\ (\text{CN})_5 \end{smallmatrix} \right], 4\text{H}_2\text{O}$ , as strawberry-red lamellæ; and the *platinichloride*,  $\text{Y}_2\text{PtCl}_6, 6\text{H}_2\text{O}$ , as brick-red, slender needles or leaflets.

Ammines corresponding with the above pyridine compounds could not be obtained. T. S. P.

**Complex Iron Salts.** N. COSTĂCHESCU and G. SPACU (*Ann. Sci. Univ. Jassy*, 1912, 7, 132—138).—The authors have succeeded in isolating the compound formed between ferrous chloride and pyridine in a pure condition (compare Reitzenstein, *Abstr.*, 1900, i, 162; Pfeiffer, *Abstr.*, 1902, i, 175) by the interaction of ferrous chloride and excess of pyridine at  $-15^\circ$  in an atmosphere of carbon dioxide. The reaction takes three to four days for completion, at the end of which time canary-yellow crystals of *tetrapyridineferrous chloride*,  $[\text{FePy}_4]\text{Cl}_2$ , are obtained. They change on exposure to the air, and on solution in water a greenish precipitate is produced, which changes to a red colour. With a concentrated solution of ammonium thiocyanate, the yellow tetrapyridineferrous thiocyanate is produced (compare Grossmann, *Abstr.*, 1906, i, 7). The solution in 1.19 hydrochloric acid, when saturated with hydrogen chloride at  $-18^\circ$ , gives crystals of the compound  $\text{FeCl}_3, \text{PyHCl}$  (compare Christensen, *Abstr.*, 1906, i, 875).

When exposed in a desiccator for two or three months to the action of concentrated sulphuric acid, tetrapyridineferrous chloride gives slender, acicular crystals of a *compound*,  $\text{FePyOCl}_2$ , to which it is difficult to assign a constitution, and which dissolves in water without decomposition, giving a strongly acid, red solution.

The *compound*,  $[\text{Fe}_23\text{PyHCl}]\text{Cl}_6$ , is formed by dissolving the tetrapyridine chloride in a small quantity of 1.19 hydrochloric acid and keeping the filtered solution in a desiccator over concentrated sulphuric acid. It forms monoclinic, yellow crystals, having m. p.  $125-128^\circ$ . The aqueous solution possesses a considerable conductivity. If the tetrapyridine chloride is dissolved in hydrobromic acid (D 1.38) and the solution allowed to evaporate spontaneously in the air, reddish, garnet-coloured, monoclinic crystals, showing violet in reflected light,

of the *compound*,  $[\text{Fe}_23\text{PyHBr}] \begin{smallmatrix} \text{Cl}_2 \\ \text{Br}_4 \end{smallmatrix}$ , are obtained. When these crystals are again dissolved in hydrobromic acid and the solution allowed to evaporate very slowly, large, reddish, garnet-coloured crystals of the *compound*,  $[\text{Fe}_23\text{PyHBr}]\text{Br}_6$ , are obtained. The corresponding iodides could not be prepared. T. S. P.

**Relation Between the Colour and Constitution the Pyridine Dyes from Secondary Aromatic Amines.** WALTER KÖNIG and G. A. BECKER (*J. pr. Chem.*, 1912, 85, [ii], 353—385. Compare this vol., i, 306).—In view of the many analogies existing between the dyes of the triphenylmethane and pyridine series, a systematic examination of the latter is being undertaken. The present communication deals with the dyes from aromatic secondary amines of the methylaniline type, and cyclic secondary amines, such as dihydroindole and tetrahydroquinoline.

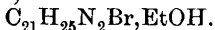
The absorption spectra of the dyes in alcoholic solution are recorded, and the colours, obtained by dyeing cotton mordanted with tannin, have been determined by means of Kallab's colour-analyser (*Zeitsch. angew. Chem.*, 1908, 21, 1637).

Dyes derived from amines of the methylaniline type are yellow or orange in colour, and show general absorption, whilst those derived from cyclic secondary amines are reddish-orange to violet in colour, and give well-marked absorption bands. In the case of dyes obtained from cyclic amines containing a five-membered ring, it is found that gradual diminution of the thickness of the solution causes the central absorption band to become divided, but this is not the case with those derived from amines containing a six-membered ring. In view of the ease with which the dyes may be prepared, it is suggested that these differences might be utilised to determine whether an amine contains a five or six-membered ring.

The influence of substitution on the colour of the dyes is discussed and interpreted from the point of view of Kaufmann's theory of the divisibility of the valency bond.

The majority of the dyes mentioned below were prepared by the addition of the amine (2 mols.) in alcoholic solution to a freshly prepared mixture of pyridine (1 mol.) and cyanogen bromide (1 mol.) in ether. In a few instances the preparation was effected by heating the amine with 2:4-dinitrophenylpyridinium chloride in alcohol solution. Many of the dyes crystallise with water or alcohol, which is often very firmly retained.

The *dye* from *N*-methyl-*o*-toluidine,  $C_{21}H_{25}N_2Br \cdot H_2O$ , forms a light yellow powder, m. p.  $218^\circ$ ; that from *N*-methyl-*m*-toluidine,



red needles, m. p.  $83^\circ$ ; the corresponding *para*-isomeride also crystallises with alcohol in red needles, m. p.  $140^\circ$ . The *dye* from *N*-methyl-*m*-xylylidine,  $C_{23}H_{29}N_2Br \cdot H_2O$ , is a dark yellow powder, m. p.  $125^\circ$ .

*N*-Methyl-*o*-anisidine, prepared from *o*-anisidine and methyl sulphate in nitrobenzene solution, and purified by means of the *nitroso*-derivative, has m. p.  $33.5^\circ$ , and yields a *dye* which could not be obtained in a pure condition.

*N*-Methyl-*p*-anisidine, prepared from *p*-anisidine and methyl sulphate in ethereal solution (compare Fröblich and Wedekind, *Abstr.*, 1907, i, 410), has b. p.  $130^\circ/15$  mm., m. p.  $33^\circ$ , forms a *zincichloride*, crystallising in lustrous leaflets, m. p.  $91^\circ$ , and yields a *dye*,  $C_{21}H_{25}O_2N_2Br$ , which crystallises in lustrous, brown leaflets, m. p.  $45^\circ$ .

The *dye* from *N*-methyl-*p*-phenetidine,  $C_{23}H_{29}O_2N_2Br$ , forms wooly masses of soft, red needles, m. p.  $137^\circ$ ; that from *N*-ethylaniline,

$C_{21}H_{25}N_2Br, H_2O$ , red needles, m. p.  $91^\circ$ ; that from N-ethyl-*p*-toluidine,  $C_{23}H_{29}N_2Br$ , red, microscopic leaflets, m. p.  $112^\circ$ ; that from N-ethyl- $\alpha$ -naphthylamine (b. p.  $168^\circ/14$  mm.),  $C_{29}H_{29}N_2Br$ , a green powder, m. p.  $98^\circ$ ; that from N-ethyl- $\beta$ -naphthylamine, dark red leaflets, m. p.  $64^\circ$ .

Propylaniline forms a *nitroso-derivative*, m. p.  $76^\circ$  (compare Wacker, Abstr., 1888, 466), and a *dye*,  $C_{23}H_{29}N_2Br$ , which crystallises in dark red needles, m. p.  $110^\circ$ . The *dyes* from isopropylaniline, isobutylaniline, and isoamylaniline could not be obtained in a pure condition. Allylaniline yields a *dye*,  $C_{23}H_{25}N_2Br, H_2O$ , crystallising in deep red leaflets, m. p.  $56^\circ$ .

N-Allyl-*p*-anisidine, prepared from *p*-anisidine and allyl bromide and purified by means of the *nitrosoamine*, has b. p.  $260^\circ$ , and yields a *dye*,  $C_{25}H_{29}O_2N_2Br$ , crystallising in small, flexible, red leaflets, m. p.  $98^\circ$ .

The *dye*,  $C_{21}H_{21}N_2Cl$ , obtained from dihydroindole and 2:4-dinitrophenylpyridinium chloride, forms a red powder, m. p.  $195^\circ$ .

2-Methyldihydroindole yields with cyanogen bromide a *dye*,  $C_{23}H_{25}N_2Br, 4H_2O$ , crystallising in violet leaflets, m. p.  $154^\circ$ ; with 2:4-dinitrophenylpyridinium chloride, the *dye*,  $C_{23}H_{25}N_2Cl$ , m. p.  $125^\circ$ .

2:5-Dimethyldihydroindole, prepared by reduction of 2:5-dimethylindole, is a yellow oil, b. p.  $235\text{--}237^\circ$ ; it forms a *platinichloride* (decomp.  $208^\circ$ ) and a bluish-red, crystalline *dye*,  $C_{25}H_{29}N_2Br$ , m. p.  $145^\circ$ .

2:6-Dimethylindole, obtained by condensing *m*-tolylhydrazine with acetone and fusing the resulting hydrazone with zinc chloride, crystallises in lustrous, silvery leaflets, m. p.  $52^\circ$ , b. p.  $153^\circ/11$  mm.,  $273^\circ$  under ordinary pressure, and is possibly identical with one of the dimethylindoles, described by Dennstedt (Abstr., 1889, 401); on reduction with zinc and hydrochloric acid it yields 2:6-dimethyldihydroindole, as a yellow oil, b. p.  $237\text{--}239^\circ$ , which forms a red crystalline *dye*,  $C_{25}H_{29}N_2Br$ , m. p.  $105^\circ$ , with previous sintering at  $95^\circ$ .

The *dye* from 3-methyldihydroindole,  $C_{23}H_{25}N_2Br, H_2O$ , forms reddish-violet, microscopic crystals, m. p.  $230^\circ$ ; that from 2:3-dimethyldihydroindole,  $C_{25}H_{29}N_2Br$ , a fiery-red, crystalline powder, m. p.  $188^\circ$ .

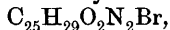
2-Methyl-3-ethyldihydroindole, prepared by reducing the corresponding indole with zinc and hydrochloric acid and purified by means of the *nitrosoamine*, is a yellow oil, b. p.  $251\text{--}252^\circ$ , and yields a *dye*, which forms glistening, green crystals, m. p.  $115^\circ$ .

The *dye*,  $C_{29}H_{33}N_2Br$ , from carbazoline forms dark red crystals, m. p.  $175^\circ$ .  $\alpha$ -Methyldihydro- $\beta$ -naphthindole yields a *dye*, m. p.  $194^\circ$  (not sharp), which was not obtained in a pure condition.

The *dye* from tetrahydroquinoline,  $C_{25}H_{25}N_2Br, H_2O$ , crystallises in light red leaflets, m. p.  $195^\circ$ ; that from 6-methyltetrahydroquinoline,  $C_{25}H_{29}N_2Br$ , in vivid red leaflets, m. p.  $206^\circ$ .

7-Methylquinoline is reduced by zinc and hydrochloric acid to 7-methyltetrahydroquinoline, a pale yellow oil, b. p.  $143^\circ/18$  mm., which yields a *dye*,  $C_{25}H_{29}N_2Br$ , crystallising in red leaflets, m. p.  $205^\circ$ . The *dye*

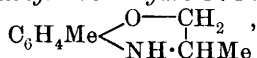
from 8-methyltetrahydroquinoline forms a green, crystalline powder, sintering at  $75^{\circ}$ ; that from 6-methoxytetrahydroquinoline,



violet leaflets, m. p.  $213^{\circ}$ ; that from 2-methyltetrahydroquinoline,  $\text{C}_{25}\text{H}_{29}\text{N}_2\text{Br}$ , vivid red crystals, m. p.  $135^{\circ}$ ; from 2:6-dimethyltetrahydroquinoline,  $\text{C}_{27}\text{H}_{33}\text{N}_2\text{Br}\cdot\text{H}_2\text{O}$ , red needles, m. p.  $126^{\circ}$ .

The *dye* from tetrahydro- $\alpha$ -naphthaquinoline, m. p.  $151^{\circ}$ , is green in colour, and could not be obtained pure. The *dye* from tetrahydro- $\beta$ -naphthaquinoline,  $\text{C}_{31}\text{H}_{29}\text{N}_2\text{Br}$ , crystallises in red leaflets, m. p.  $223^{\circ}$ ; that from  $\alpha$ -methylphenmorpholine (2-methyl-2:3-dihydro-1:4-benzoxazine) [Stoermer, Abstr., 1897, i, 473] in bluish-red crystals, m. p.  $205^{\circ}$ .

*o*-Nitro-*p*-tolylloxycetone,  $\text{C}_{10}\text{H}_{11}\text{O}_4\text{N}$ , prepared by condensing chloroacetone with *o*-nitro-*p*-cresol, crystallises in colourless prisms, m. p.  $75^{\circ}$ . It is reduced by zinc and hydrochloric acid to  $\alpha$ -*m*-dimethylphenmorpholine (2:7-dimethyl-2:3-dihydro-1:4-benzoxazine),



which has b. p.  $145^{\circ}/11\text{ mm.}$ ,  $162^{\circ}/21\text{ mm.}$ , and is accompanied by *p*-chloro- $\alpha$ -*m*-dimethylphenmorpholine (6-chloro-2:7-dimethyl-2:3-dihydro-1:4-benzoxazine). The last-mentioned compound crystallises in white leaflets, m. p.  $135^{\circ}$ , and yields a *dye*,  $\text{C}_{23}\text{H}_{23}\text{O}_2\text{N}_2\text{Cl}_2\text{Br}$ , crystallising in red prisms, m. p.  $241^{\circ}$ .

The *dye*,  $\text{C}_{25}\text{H}_{29}\text{O}_2\text{N}_2\text{Br}$ , from  $\alpha$ -*m*-dimethylphenmorpholine forms dark red crystals, m. p.  $195^{\circ}$ .

Tetrahydroquinoxaline yields a *dye*,  $\text{C}_{21}\text{H}_{23}\text{N}_4\text{Cl}\cdot\text{H}_2\text{O}$ , which sinters at  $135^{\circ}$ . F. B.

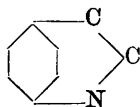
#### Betaines of Nipicotinic Acid and of Pipecolic Acid.

KIYOHISA YOSHIMURA (*Zeitsch. physiol. Chem.*, 1912, 78, 156—158).—The dimethylbetaine of nipicotinic acid,  $\text{C}_8\text{H}_{15}\text{O}_2\text{N}$ , consists of hygroscopic prisms, which have a sweet taste and react neutral to aqueous solution. The aurichloride,  $\text{C}_8\text{H}_{15}\text{O}_2\text{N}\cdot\text{HAuCl}_4$ , forms golden-yellow prisms or columns, m. p.  $240$ — $244^{\circ}$  (decomp.). The hydrochloride crystallises in colourless prisms, m. p.  $285$ — $287^{\circ}$  with frothing. The picrate consists of large prisms or columns, m. p.  $175$ — $176^{\circ}$  (decomp.  $240^{\circ}$ ).

The dimethylbetaine of pipecolic acid is a neutral, hygroscopic syrup, which does not taste sweet. The aurichloride,  $\text{C}_8\text{H}_{15}\text{O}_2\text{N}\cdot\text{HAuCl}_4$ , forms lustrous, golden-yellow, four-sided plates, m. p.  $238$ — $240^{\circ}$  (decomp.). The hydrochloride forms prismatic crystals, m. p.  $224$ — $225^{\circ}$ . The picrate crystallises in tiny platelets, m. p.  $181$ — $182^{\circ}$  (decomp.  $235^{\circ}$ ). E. F. A.

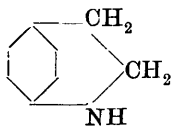
**Cyclic Imines. V. Dihydro-*p*-indole and *p*-Indole.** JULIUS VON BRAUN [with W. GAWRILOW] (*Ber.*, 1912, 45, 1274—1288).—The failure of Kipping (Trans., 1888, 21) and of Manoukian (Abstr., 1901, i, 528) to bridge over two carbon atoms other than in the ortho-position in the benzene ring has given rise to the view that one aromatic nucleus will only unite with a second in that position. The opinion of the author that the nature of the open chain which is to be linked up with the benzene nucleus is of supreme importance, and his

experience of the easy formation of a nitrogen seven-membered ring in homohydrocarbostyryl (Abstr., 1907, i, 524), and of the great ease with which open chain bases which contain chlorine form cyclic imines, have led him to try to build up a ring of the annexed type, with the result that he has succeeded in preparing dihydro-*p*-indole. For this purpose pure  $\beta$ -chloro-4-aminophenylethane,  $\text{CH}_2\text{Cl}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , was obtained by reducing Barger's nitro-derivative (Trans., 1909, 95, 2193) by means of stannous chloride, as a yellowish-brown oil with camphor-like odour. The hydrochloride,



$\text{C}_8\text{H}_{11}\text{NCl}_2$ , is almost identical in form with the hydrochloride of the  $\beta$ -chloro-2-aminophenylethane, obtained by hydrolysing  $\beta$ -chloro-*o*-benzylaminophenylethane (Abstr., 1911, i, 747); they both melt at  $205^\circ$ , but mixed together, at  $150$ – $160^\circ$ . The *platinichlorides* show a difference, that from the para-base crystallising from hot water in red needles, m. p.  $192^\circ$ , whilst the other decomposes in hot water and melts at  $195^\circ$ , a mixture melting below  $190^\circ$ ; similarly with the *benzoyl* derivatives; the para-compound melts at  $128^\circ$ , the ortho- at  $120^\circ$ , and a mixture at  $103$ – $105^\circ$ . The para-base is also characterised by a *picrate*,  $\text{C}_8\text{H}_{10}\text{NCl}\cdot\text{C}_6\text{H}_3\text{N}_3\text{O}_7$ , m. p.  $155^\circ$ , which is very sparingly soluble in cold alcohol. That the substances do really belong to the para-series is further evidenced by the formation of hordenine from the nitro-derivative (Barger, *loc. cit.*), and by the conversion of the base into *p*- $\beta$ -chloroethylphenol,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl}$ , which, like *p*-hydroxychloroacetophenone, and unlike *o*-chloropropylphenol or *o*-hydroxychloroacetophenone, is only slightly volatile in steam, but may be distilled without loss of hydrogen chloride, b. p.  $158$ – $163^\circ/10$  mm., and is readily transformed into tyrosol. Unlike *o*- $\beta$ -bromoethylphenol, which readily undergoes ring formation to hydrocoumarone in cold alkali (Störmer and Kahlert, Abstr., 1901, i, 536), the *p*- $\beta$ -chloroethylphenol is only altered on heating, and yields an impure product, which is not volatile in steam; similarly, *p*- $\gamma$ -chloropropylphenol (to be described later) does not give a chroman in the way that the ortho-compound does (compare Braun and Steindorff, Abstr., 1905, i, 294).

The failure to produce a para-ring containing oxygen is remarkable in view of the fact that the  $\beta$ -chloro-*p*-aminophenylethane when diluted with ether spontaneously changes into the desired dihydro-*p*-indole, but even here the influence of alkali is to prevent ring formation. The dihydro-*p*-indole (annexed formula) is a colourless liquid, which soon darkens when exposed to air, boils at  $228$ – $230^\circ$ , and is very similar to the ordinary ortho-compound, the physical constants being almost identical; and the various derivatives are so much alike that only depressions of the melting points of the mixed substances indicate any difference. The

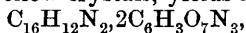


hydrochloride,  $\text{C}_8\text{H}_9\text{NH}_2\cdot\text{HCl}$ , melts at  $217^\circ$ , that of the ortho-base at  $219^\circ$ ; the yellow *platinichlorides*, m. p.  $211^\circ$ ; *picrates*, *o*-, m. p.  $174^\circ$ , *p*-, m. p.  $177^\circ$ ; *methiodides*, *o*-, m. p.  $192^\circ$ , *p*-,  $189^\circ$ ; the *p*-benzoyl derivative, m. p.  $118^\circ$ ; and also the *p*-benzenesulphonyl compound,  $\text{C}_8\text{H}_8\text{N}\cdot\text{SO}_2\text{Ph}$ , m. p.  $130^\circ$ , insoluble in alkali, have been prepared.

The benzoyl derivative yields with phosphorus pentachloride a chloro-benzoylaminophenylethane, m. p.  $128^{\circ}$ , which depresses the melting point of *o*-chloro- but not that of the para-isomeride. The dihydro-*p*-indole ring is very stable, resisting the action of concentrated hydrochloric acid in sealed tubes at  $180^{\circ}$ . When distilled with silver sulphate, it furnishes an indole which is so nearly like ordinary indole that it cannot be said with certainty that it is the para-compound; only a mixture of the picrates shows a depressed melting point,  $170$ — $174^{\circ}$  instead of  $175^{\circ}$ . J. C.W.

**New Method of Preparation of Substituted Indoles.** WALTER MADELUNG (*Ber.*, 1912, 45, 1128—1134).—A simple and apparently general method of preparing 2-substituted indoles consists in heating about equal quantities of an acyl-*o*-toluidide and sodium alkoxide for a few minutes at  $360$ — $380^{\circ}$  in a current of hydrogen, and decomposing the product (sodium derivative ?) with water. The yield is better the greater is the molecular weight of the sodium alkoxide; thus aceto-*o*-toluidide and sodium ethoxide yield 60% of 2-methylindole, and benzo-*o*-toluidide and sodium ethoxide yield 60% of 2-phenylindole. Indole itself cannot be thus prepared from form-*o*-toluidide.

2:2'-Di-indyl,  $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH} \\ \text{NH}\end{smallmatrix}\rangle\text{C}\cdot\text{C}\langle\begin{smallmatrix}\text{CH} \\ \text{NH}\end{smallmatrix}\rangle\text{C}_6\text{H}_4$ , m. p. about  $300^{\circ}$  (decomp.), is obtained in 15—20% yield by heating oxalo-*o*-toluidide and sodium amyloxide (rather more than 4 mols.), containing a little amyl alcohol, at  $360$ — $380^{\circ}$  in a current of hydrogen for about five minutes, distilling off the amyl alcohol, and decomposing the residue with water. It forms yellow crystals, yields a *picrate*,



decomp.  $178^{\circ}$ , brown needles with a violet shimmer, develops a bluish-black coloration in the pine shaving reaction and an orange coloration with concentrated sulphuric acid, and gives a red coloration with glacial acetic acid and hydrogen peroxide. C. S.

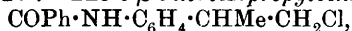
**Disruption of the Scatole Ring by means of Phosphorus Pentachloride.** JULIUS VON BRAUN and G. KIRSCHBAUM (*Ber.*, 1912, 45, 1263—1266).—In order to prepare alcohols and aldehydes with branched polymethylene chains and to compare them with those in which the side-chain is not substituted (compare *Abstr.*, 1912, i, 265), the applications of the Grignard reaction mentioned previously (this vol., i, 433) may be used. These give rise to fatty aromatic compounds which are methylated in the 4 or 5 position with regard to the benzene nucleus, but not such as contain the methyl group nearer the ring. The present paper describes a method for the production of  $\alpha$ -methyl derivatives.

Following the process for the transformation of quinoline into  $\gamma$ -phenylpropyl chloride (*Abstr.*, 1910, i, 843), 3-methylindole has been reduced (compare Wenzing, *Abstr.*, 1887, 957), the 3-methyl-dihydroindole converted into the *benzoyl* compound,



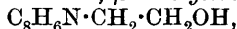
a well defined substance which crystallises from hot alcohol, m. p.

102°, and undergoes disruption when heated with phosphorus pentachloride at 115—120°. The *o*- $\beta$ -chloroisopropylbenzanilide,



thus obtained is almost insoluble in light petroleum, but dissolves freely in acetone, and crystallises from a mixture of these solvents in long, radiating needles, m. p. 133°. J. C. W.

**Tryptophol ( $\beta$ -Indolylethyl Alcohol), a New Product of the Fermentation of Amino-acids by Yeast.** FELIX EHRLICH (*Ber.*, 1912, 45, 883—889).—Tryptophan ( $\beta$ -indole  $\alpha$ -aminopropionic acid) is fermented by living yeast in a similar manner to other amino-acids (*Abstr.*, 1907, ii, 383; 1911, i, 127) with production of carbon dioxide, ammonia, and an alcohol,  *$\beta$ -indolylethyl alcohol*,



to which the name *tryptophol* is given.

The reaction is carried out either by growing yeast in a sterile solution of tryptophan containing sugar and nutrient salts, or by fermenting the solution directly with pressed yeast in presence of 10% sugar. The fermented solution is filtered through porcelain and evaporated in a vacuum at 40—50° to a syrup, which is extracted with alcohol, the extract evaporated, and the resulting syrup dissolved in water and warmed with sodium hydroxide. The oil which separates is then dissolved out with ether, and the ethereal solution on evaporation deposits an oil which soon becomes crystalline. After purification the substance separates in colourless, monosymmetric tablets melting at 59°, and subliming unchanged above this temperature. Tryptophol gives the characteristic reactions of an indole derivative. It differs from tryptophan in its reaction to bromine, a white turbidity being produced which on further treatment yields a white or grey, flocculent precipitate.

A delicate test for tryptophol consists in adding to the solution a crystal of dimethylaminobenzaldehyde and sufficient alcohol to dissolve it, and then one drop of 25% hydrochloric acid, when a violet-red coloration is produced, slowly in the cold, rapidly on warming, which is extracted when shaken with amyl alcohol, the alcoholic solution giving an absorption spectrum. One part in 10,000 may be detected in this way.

Tryptophol gives a *benzoate*,  $\text{C}_{19}\text{H}_{19}\text{N} \cdot \text{O}(\text{COPh})$ , pale yellow prisms, melting at 76°, and a *picrate*, brick-red needles, melting at 96°.

Tryptophol is also produced by the fermentation of tryptophan by means of *Willia anomala*. W. J. Y.

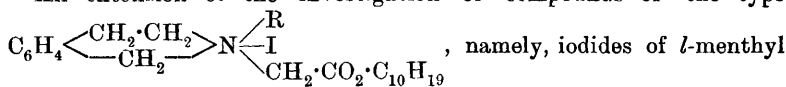
**Preparation of Isatin-naphthalides, their Homologues and Substitution Products.** FARBERKE VORM. MEISTER, LUCIUS &

BRÜNING (*D.R.-P.* 242614).—Isatin methyl ether,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C} \cdot \text{OMe}$  (or other oxygen isatin ethers), combines readily with  $\alpha$ - or  $\beta$ -naphthylamines to furnish compounds of the following general formula:  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \end{smallmatrix} \text{C} : \text{N} \cdot \text{C}_{10}\text{H}_7$  (the isatin nucleus substituted or otherwise).

*α-Isatin-α-naphthalide*, orange-yellow crystals, m. p. 246°, is prepared at the ordinary temperature in benzene solution; the isomeric *β-naphthalide* forms scarlet-red crystals, and has m. p. 208°.

*α-Dibromoisatin-α-naphthalide*, brownish-violet crystals, m. p. 223°, and the corresponding *β-naphthalide*, dark blue crystals, m. p. 226°, are also described. F. M. G. M.

**Stereoisomerism with Compounds Containing Asymmetric Nitrogen and Active Asymmetric Carbon.** II. EDGAR WEDEKIND and F. NEY (*Ber.*, 1912, 45, 1298—1315. Compare Abstr., 1909, i, 514; also E. and O. Wedekind, Abstr., 1908, i, 258).—An extension of the investigation of compounds of the type



esters of 2-alkyltetrahydroisoquinoliniumacetic acids. Several of these have now been resolved into pairs of stereoisomerides, one stereoisomeride being frequently much less stable than the other. The authors believe that the stable isomerides are those containing the *lævo*-configuration of the nitrogen atom. No definite case of such isomerism could be detected with compounds in which the tetrahydroisoquinoline is replaced by two different alkyl radicles.

2-Methyltetrahydroisoquinoline (*isokairoline*) reacts vigorously with *l*-menthyl iodacetate, forming the *l*-menthyl ester of 2-methyltetrahydroisoquinoliniumacetic acid iodide, a colourless, crystalline powder,  $[\alpha]_D - 32^\circ$  (approx.) in chloroform, decomp. 130—131°; it could not be resolved by fractional crystallisation. Treatment of the alcoholic solution with silver oxide produces menthol and an inactive *betaine*, colourless crystals, decomp. 137—138°.

*iso*Propylisoquinolinium iodide (yellow needles, decomp. 167—169°) is reduced by tin and hydrochloric acid to 2-isopropyltetrahydroisoquinoline, b. p. 256—258°/735 mm., which with *l*-menthyl iodacetate produces the *l*-menthyl ester of 2-isopropyltetrahydroisoquinoliniumacetic acid iodide; this can be separated by crystallisation into a less soluble form ( $[\alpha]_D - 12.54^\circ$  in alcohol, decomp. 146—148°) and a more soluble form ( $[\alpha]_D - 40.12^\circ$  in alcohol, decomp. 161—163°). The first form on evaporation of its alcoholic solution undergoes rearrangement, giving the latter isomeride.

2-Allyltetrahydroisoquinoline (b. p. 255—256°) was converted into the *l*-menthyl ester of 2-allyltetrahydroisoquinoliniumacetic acid iodide, a solid (decomp. 138—140°), which crystallises only with difficulty.

*n*-Butylisoquinolinium iodide forms yellow needles, decomp. 109—110°; by reduction it gives 2-*n*-butyltetrahydroisoquinoline, an almost colourless oil, b. p. 272—273°. This can be converted into the *l*-menthyl ester of 2-*n*-butyltetrahydroisoquinoliniumacetic acid iodide, which on recrystallisation gives pearly scales,  $[\alpha]_D$  (in alcohol)  $-29.2^\circ$ , decomp. 155—156°, whilst the mother liquor yields an isomeride,  $[\alpha]_D - 18.1^\circ$ , decomp. 140—141°. The latter isomeride in acetone solution is largely converted into the former. Treatment of an alcoholic solution of the more stable isomeride with silver oxide causes complete racemisation at the nitrogen atom.

2-isoButyltetrahydroisoquinoline is difficult to prepare, and the product with *l*-menthyl iodoacetate is a vitreous mass.

isoAmylisoquinolinium iodide, yellow needles, decomp. 118°, is reducible to 2-isoamyltetrahydroisoquinoline (a pale yellow liquid, b. p. 276—280°). The *l*-menthyl ester of 2-isoamyltetrahydroisoquinoliniumacetic acid iodide can be separated by recrystallisation into two fractions, one having  $[\alpha]_D + 6.4^\circ$  in alcohol, decomp. 164—165°, the other  $[\alpha]_D - 26.1^\circ$ , decomp. 156—158° (two other fractions decomposing at 184—185° and 152—154° respectively are ascribed to impurity in the isoamyl iodide originally taken). The *d*-rotatory specimen on keeping in alcoholic solution suffers rearrangement to the stereoisomeride. When the latter is treated in methyl-alcoholic solution with silver oxide, the resultant solution shows for a time a rapidly decreasing *lævo*-rotation, indicating auto-racemisation of the resultant betaine.

*n*-Octylisoquinolinium iodide (yellow needles, decomp. 83—85°) is reducible to 2-*n*-octyltetrahydroisoquinoline, b. p. 205—210°/25 mm.; the *l*-menthyl ester of 2-*n*-octyltetrahydroisoquinoliniumacetic acid iodide forms leaflets, decomp. 169—170°. Fractional recrystallisation gives products having the same temperature of decomposition, but with optical activity in alcoholic solution, varying from  $[\alpha]_D - 21.16^\circ$  to  $-14.96^\circ$ .

Benzylmethylethylamine (b. p. 194—196°) and benzylmethyl-*n*-propylamine (b. p. 215—217°) give no crystalline product with *l*-menthyl iodoacetate.

Benzylethyl-*n*-propylamine (b. p. 222—225°) gives the *l*-menthyl ester of benzylethyl-*n*-propylammoniumacetic acid iodide. Recrystallisation from various solvents only produced indefinite fractions with decomposition temperatures varying between 105° and 122°, and  $[\alpha]_D$  varying between  $-28^\circ$  and  $-45^\circ$ .

Benzylethyl-*n*-butylamine (b. p. 238—240°) gives the *l*-menthyl ester of benzylethyl-*n*-butylammoniumacetic acid iodide, an apparently single substance, decomp. 131°.

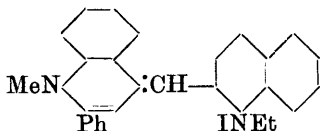
Benzylethylisopropylamine (b. p. 212—215°) and benzylethylisobutylamine (b. p. 232—234°) when treated with *l*-menthyl iodoacetate both give deposits of benzylethylamine hydriodide (decomp. 126°).

D. F. T.

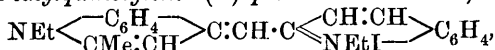
**Quinoline Dyes. II. Constitution, Synthesis, and Degradation of Cyanines.** ADOLF KAUFMANN and ERNST VONDERWAHL (*Ber.*, 1912, 45, 1404—1419. Compare Abstr., 1911, i, 328).—It has long been known that the cyanines and isocyanines are diquinolylmethane derivatives, and that the methane carbon atom is attached to one of the quinoline nuclei in position 4 in the cyanines and in position 2 in the isocyanines. The attachment of the methane carbon atom to the other quinoline nucleus has hitherto been undecided. However, since 1:2-dimethylquinolinium iodide reacts in the presence of alkali, not only with itself, but with the alkylidide of any 2-substituted quinoline to form isocyanines, it is certain that in the cyanines and the isocyanines the methane carbon atom is attached to the second quinoline nucleus in position 4. This is so even when the nucleus in question contains an easily mobile

substituent in position 4; thus, whilst 1:2-dimethylquinolinium iodide and 4-phenyl-2-methyl-1-ethylquinolinium iodide do not yield an *isocyanine*, 2-methyl-1-ethylquinolinium iodide reacts with 4-chloro-1-ethylquinolinium iodide to form ethyl-red, and with 4-chloro-2-phenyl-1-methylquinolinium iodide, m. p. 163—164°, to form the same dye as it does with 2-phenyl-1-methylquinolinium iodide (compare König, Abstr., 1906, i, 207).

The last-mentioned dye is 2-phenyl-1-methylquinolylene-4(2')-quinaldine ethiodide, m. p. 232—233°, green needles (the yellow normal iodide,  $C_{28}H_{26}N_2I_2 \cdot H_2O$ , has m. p. about 189°), and receives the annexed formula, because it loses ethyl iodide by heating and yields 2-phenyl-1-methylquinolylene-4(2')-quinaldine, m. p. 177°, brownish-yellow leaflets and needles, which in boiling alcoholic solution is oxidised by 1% potassium permanganate to 2-phenyl-1-methyl-4-quinolone, quinaldic acid, and another (unidentified) acid, m. p. about 198°.



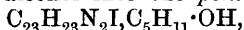
2-Methyl-1-ethylquinolylene-4(2')-quinaldine ethiodide,



m. p. 183°, dichroic, monoclinic crystals, prepared from 2-methyl-1-ethylquinolinium iodide and 10% potassium hydroxide in boiling methyl alcohol, forms a *periodide*, m. p. 160—162°, reddish-violet needles, which forms a normal *iodide*,  $C_{24}H_{26}N_2I_4$ , m. p. 196°.

Diethylethyroapocyanine (*loc. cit.*) is obtained as a by-product in the preparation of ethyl-red from the ethiodides of quinoline and quinaldine and 10% alcoholic potassium hydroxide at the ordinary temperature. When the preparation is effected at the b. p., more ethyl-red and less of the *apocyanine* dye are produced, whilst quinoline, 1-ethyl-tetrahydroquinoline, and unchanged quinaldine ethiodide have also been isolated from the products of the reaction.

Ethyl-red [1-ethylquinolylene-4(2')-quinaldine ethiodide] possesses the property of forming alcoholates, any one of which can be changed to another by long keeping or by short heating with an excess of the alcohol in question; thus the *methanol*,  $C_{23}H_{23}N_2I \cdot MeOH$ , dichroic prisms or plates, and the *ethanol*,  $C_{23}H_{23}N_2I \cdot EtOH$ , green, dichroic needles, obtained from ethyl-red and the respective alcohols, are converted by hot amyl alcohol into the *pentanol*,

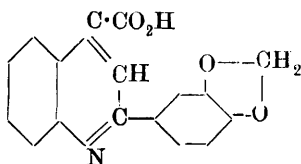


small, dichroic crystals.

The monoacidic salts of ethyl-red are intensely coloured; the di-acidic salts, for example, the *hydriodide*,  $C_{23}H_{23}N_2I \cdot HI \cdot H_2O$ , m. p. 233—234°, are yellow and unstable. C. S.

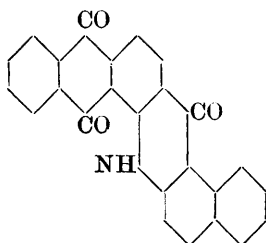
Preparation of 2-Piperonylquinoline-4-carboxylic Acid (Piperonylquinic Acid). CHEMISCHE FABRIK AUF ACTIEN VORM. E. SCHERING (D.R.-P. 244497).—2-Phenylquinoline-4-carb-

oxylic acid (phenylcinchoninic acid) is of therapeutic value but, possesses an unpleasant taste, a disadvantage from which the corresponding piperonyl derivative is free.



*2-Piperonylquinoline-4-carboxylic acid* (annexed formula), a green or grey, crystalline powder, m. p. 215°, is prepared by the condensation of aniline (93 parts), piperonal (150 parts), and pyruvic acid (88 parts) in hot alcoholic solution; the product separates on cooling.

F. M. G. M.



[Preparation of Naphthanthracridone.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 242063). — *Naphthanthracridone* (annexed formula), prepared by the condensation of 1-naphthylaminoanthraquinone-2-carboxylic acid, is readily halogenated, yielding orange-brown or red compounds these furnish valuable vat dyes.

F. M. G. M.

**Preparation of a Condensation Product from Dihydro-1:4-benzothiazone.** ACTIEN GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 243196. Compare Abstr., 1897, i, 302; 1898, i, 96).—When the colourless ketodihydro-1:4-benzothiazine is heated at 210—220° or boiled with nitrobenzene, naphthalene, or other indifferent solvents, it yields a red, crystalline condensation product, m. p. 358° (decomp.).

F. M. G. M.

**Conversion of Hydrazine Derivatives into Heterocyclic Compounds. XXVI. Action of Chlorine on Benzaldazine and Benzoylbenzylidenehydrazide.** ROBERT STOLLÉ (*J. pr. Chem.*, 1912, [ii], 85, 386—390. Compare Abstr., 1909, i, 123).—When dissolved in carbon tetrachloride and treated with chlorine at the ordinary temperature, benzaldazine is converted into dibenzoylhydrazide dichloride,  $\text{CPhCl:N:N:CPhCl}$  (Abstr., 1906, i, 461), which reacts with magnesium phenyl bromide in ethereal solution, yielding diphenylketazine; chlorination at the b. p. of carbon tetrachloride results in the formation of benzonitrile and *benzoylbenzylidenehydrazide chloride*,  $\text{CHPh:N:N:CPhCl}$ , which crystallises in colourless prisms, m. p. 56°, yields benzoylbenzylidenehydrazide with alcoholic silver nitrate or aqueous sodium carbonate, and on further treatment with chlorine is transformed into benzonitrile.

Chlorine reacts with benzoylbenzylidenehydrazide in ice-cold carbon tetrachloride solution, yielding 2:5-diphenyl-1:3:4-oxadiazole; in hot solution, benzoyl chloride and benzylidene dichloride, together with a small amount of the oxadiazole, are produced.

A solution of benzoylbenzylidenehydrazide and iodine in carbon tetrachloride, on treatment with chlorine at the ordinary temperature, deposits a yellow substance, m. p. 128°, which is converted by crystal-

lisation from the same solvent into 2:5-diphenyl-1:3:4-oxadiazole chloriodide,  $C_{14}H_{10}ON_2Cl$ . This crystallises in yellow leaflets or prisms, m. p.  $151^\circ$ , liberates iodine from potassium iodide, and has also been obtained by the action of chlorine on 2:5-diphenyl-1:3:4-oxadiazole in the presence of iodine.

The interaction of chlorine and benzyldeneaniline in carbon tetrachloride solution yields benzyldene-*p*-chloroaniline hydrochloride.

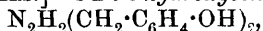
When kept for several months over potassium hydroxide, benzaldazine tetrabromide loses half its bromine, and yields a yellowish-red product, which is converted by sodium carbonate into benzaldazine and benzyldeneaminodiphenylpyrroldiazole (Abstr., 1905, i, 249).

*Benzaldazine hydrobromide*,  $C_{14}H_{12}N_2 \cdot HBr$ , prepared from its components in ethereal solution, forms small, pale yellow leaflets, m. p.  $165^\circ$ .

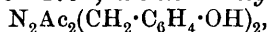
2:5-Diphenyl-1:3:4-oxadiazole hydrobromide,  $C_{14}H_{10}ON_2 \cdot HBr$ , is a white powder, m. p.  $200^\circ$ . F. B.

**Reduction of Aromatic Aldazines.** THEODOR CURTIUS (*J. pr. Chem.*, 1912, 85, [ii], 393—484).—A continuation of previous work (this vol., i, 137, 307).

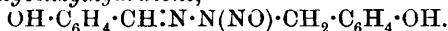
[With GUSTAV KÜPPERS.]—*s*-Di-*o*-hydroxybenzylhydrazine,



prepared by reducing di-*o*-hydroxybenzaldazine (salicaldazine) with sodium amalgam in alcoholic solution and decomposing the resulting disodium salt,  $N_2H_2(CH_2 \cdot C_6H_4 \cdot ONa)_2$ , with carbon dioxide, crystallises in white leaflets, m. p.  $117^\circ$ , is not hydrolysed by boiling with hydrochloric acid, and differs from the previously-described derivatives of *s*-dibenzylhydrazine, which form only monohydrochlorides, in yielding a dihydrochloride, crystallising in slender, white needles, m. p.  $143^\circ$ ; the diacetyl derivative,  $N_2Ac_2(CH_2 \cdot C_6H_4 \cdot OAc)_2$ , crystallises in white leaflets, m. p.  $178$ — $179^\circ$ ; the tetra-acetyl derivative,



has m. p.  $107^\circ$ . When treated with sodium nitrite, its solution in dilute acetic acid deposits a yellowish-brown, crystalline dinitroso-compound,  $N_2(NO)_2(CH_2 \cdot C_6H_4 \cdot OH)_2$ , which becomes brown at  $80^\circ$ , m. p.  $90^\circ$  (decomp.), gives off nitrous acid on exposure to air, and when boiled in alcoholic solution is converted into *o*-hydroxybenzaldehyde-nitroso-*o*-hydroxybenzylhydrazine,

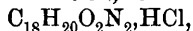


This crystallises in slender, pale bronze-yellow needles, m. p.  $145^\circ$ , and is hydrolysed by strong hydrochloric acid to salicylaldehyde.

*s*-Di-*m*-hydroxybenzylhydrazine, prepared by reducing di-*m*-hydroxybenzaldazine with sodium amalgam and alcohol, crystallises in pale yellow needles, m. p.  $183^\circ$ , and resembles the preceding ortho-compound in forming a diacetyl derivative, m. p.  $209^\circ$ , tetra-acetyl derivative, m. p.  $132^\circ$ , and dihydrochloride, m. p.  $154^\circ$ . Attempts to prepare a dihydrotetrazone by boiling an alcoholic solution of the hydrazine with mercuric oxide gave *m*-hydroxybenzaldehyde. On treatment with nitrous acid it yields *m*-hydroxybenzaldehydenitroso-*m*-hydroxybenzylhydrazine, which crystallises in slender, white needles, m. p.  $112$ — $114^\circ$  (decomp.).

[With RUDOLF GLASER.]—The *disodium* salt of di-*o*-hydroxybenzaldazine,  $N_2(CH \cdot C_6H_4 \cdot ONa)_2$ , prepared by the addition of alcoholic sodium ethoxide to a suspension of the aldazine in aqueous alcohol, forms greenish-yellow, rectangular, anisotropic plates, which become deep red at  $180^\circ$ , and char at a higher temperature without melting. It is decomposed by water with the separation of the original aldazine.

Di-*o*-ethoxybenzaldazine (Pascal and Normand, this vol., i, 147), obtained by heating di-*o*-hydroxybenzaldazine with sodium ethoxide and ethyl iodide in alcoholic solution, forms a *hydrochloride*,



m. p.  $146^\circ$ , which is resolved into its components by dissolving in alcohol.

Di-*o*-methoxybenzaldazine (Bouveault, Abstr., 1899, i, 287), prepared in a similar manner, yields a reddish-yellow, crystalline *hydrochloride*, m. p.  $160^\circ$ .

Di-*o*-benzyloxybenzaldazine, from salicaldazine and benzyl chloride, has m. p.  $150^\circ$  (Pascal and Normand, *loc. cit.*, give  $157.7^\circ$ ), and resembles the preceding methoxy- and ethoxy-compounds in being readily hydrolysed by sulphuric acid.

Di-*o*-ethoxybenzaldazine is reduced by zinc dust and acetic acid in alcoholic solution to di-*o*-ethoxybenzylamine,  $NH(CH_2 \cdot C_6H_4 \cdot OEt)_2$ . This is a pale yellow oil, b. p.  $180^\circ/20$  mm., and yields a *hydrochloride*, *nitrate*, *picrate*, and *platinichloride*, but only the last-mentioned salt could be obtained in the solid condition.

Di-*o*-methoxybenzylamine,  $C_{16}H_{19}O_2N$ , prepared from di-*o*-methoxybenzaldazine in a similar manner, has b. p.  $200^\circ/30$  mm.; of its salts only the *platinichloride* is solid.

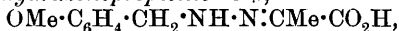
[With GEORG DETOROS.]—Di-*o*-methoxybenzaldazine is reduced by sodium amalgam and alcohol to *o*-methoxybenzaldehyde-*o*-methoxybenzylhydrazone,  $OMe \cdot C_6H_4 \cdot CH:N \cdot NH \cdot CH_2 \cdot C_6H_4 \cdot OMe$ , which forms white needles of a silky lustre, m. p.  $76^\circ$ , and yields an *acetyl* derivative, crystallising in lustrous prisms, m. p.  $101^\circ$ ; the *benzoyl* derivative has m. p.  $170^\circ$ .

The *nitroso*-derivative,  $OMe \cdot C_6H_4 \cdot CH:N \cdot N(NO) \cdot CH_2 \cdot C_6H_4 \cdot OMe$ , forms pale yellow needles, m. p.  $91^\circ$ .

*s*-Di-*o*-methoxybenzylhydrazone,  $N_2H_2(CH_2 \cdot C_6H_4 \cdot OMe)_2$ , obtained by reducing di-*o*-methoxybenzaldazine with alcohol and excess of sodium amalgam, and isolated in the form of its *hydrochloride* (long, yellow needles, m. p.  $154^\circ$ ), yields a *diacetyl* derivative, m. p.  $133$ — $134^\circ$ . Attempts to prepare the corresponding dibenzoyl and dinitroso-derivatives resulted in the formation of the above-mentioned benzoyl and nitroso-derivatives of *o*-methoxybenzaldehyde-*o*-methoxybenzylhydrazone.

*o*-Methoxybenzylhydrazone,  $OMe \cdot C_6H_4 \cdot CH_2 \cdot NH \cdot NH_2$ , obtained in the form of its *hydrochloride* (lustrous, white needles, m. p.  $123$ — $124^\circ$ ) by hydrolysing *o*-methoxybenzaldehyde-*o*-methoxybenzylhydrazone with dilute hydrochloric acid, is a colourless liquid, b. p.  $145$ — $149^\circ/14$  mm., and condenses with ethyl acetoacetate, forming 1-*o*-methoxybenzyl-3-methyl-5-pyrazolone,  $\begin{matrix} CH_2 \cdot CO \\ | \\ CMe=N \end{matrix} > N \cdot CH_2 \cdot C_6H_4 \cdot OMe$ , which crys-

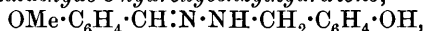
tallises in rosettes of red needles, m. p. 82—84°. Its hydrochloride reacts with pyruvic acid in concentrated aqueous solution, yielding *α*-*o*-methoxybenzylhydrazonopropionic acid,



lustrous prisms, m. p. 107·5°, and with potassium cyanate to form *o*-methoxybenzylsemicarbazide,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{N}(\text{NH}_2) \cdot \text{CO} \cdot \text{NH}_2$ , m. p. 214—215°.

The *nitroso*-derivative,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{N}(\text{NO}) \cdot \text{NH}_2$ , crystallises in lustrous, white needles, m. p. 65°, condenses with *o*-methoxybenzaldehyde, yielding the corresponding *nitroso*-*o*-methoxybenzylhydrazone, and when boiled with 10% sulphuric acid is converted into *o*-methoxybenzylazoimide,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{N}_3$ , a colourless liquid, b. p. 118°/14 mm., which is stable toward sodium hydroxide, but is hydrolysed by 30% sulphuric acid with the formation of hydrazoic acid.

*o*-Methoxybenzaldehyde-*o*-hydroxybenzylhydrazone,



is obtained as a by-product in the reduction of di-*o*-methoxybenzaldazine to *o*-methoxybenzaldehyde-*o*-methoxybenzylhydrazone by sodium amalgam in aqueous alcoholic solution. It forms a white, crystalline powder, which becomes yellow at 115°, has m. p. 153—157°, and is insoluble in the common solvents. The position of the methoxy-group has been established by the formation of *o*-methoxybenzaldehyde on hydrolysis with hydrochloric acid. It forms a *nitroso*-derivative, m. p. 148° (decomp.).

[With LEY FRANCIS POTTER.]—*m*-Methoxybenzaldehyde is most conveniently prepared by methylating *m*-hydroxybenzaldehyde with methyl sulphate and aqueous potassium hydroxide. With hydrazine sulphate it yields *di-m*-methoxybenzaldazine, which forms lustrous, yellow leaflets, m. p. 75°, and is different from the compound, m. p. 152°, described under the same name by Bouveault (*loc. cit.*).

5-*Di-m*-methoxybenzylhydrazine, prepared by reducing the preceding azine with sodium amalgam and alcohol, is a pale yellow oil; the *hydrochloride* forms slender, lustrous, white needles, m. p. 115°, and reacts with sodium nitrite, yielding *m*-methoxybenzaldehydenitroso-*m*-methoxybenzylhydrazone, yellow needles, m. p. 80° (decomp.), together with a *substance*, m. p. 164°, which crystallises in very light needles resembling down.

*m*-Methoxybenzylhydrazine is prepared by reducing *s*-*di-m*-methoxybenzaldazine with sodium amalgam and alcohol to *m*-methoxybenzaldehyde-*m*-methoxybenzylhydrazone, a brownish-yellow oil, and hydrolysing the latter with dilute hydrochloric acid. It forms a colourless oil, b. p. 158—160°/19 mm., which rapidly loses nitrogen when kept; the *hydrochloride* crystallises in stellar aggregates of needles, m. p. 123°, or in transparent plates of triclinic habit, and reacts with pyruvic acid, yielding *α*-*m*-methoxybenzylhydrazonopropionic acid, which forms fern-like aggregates of needles or rhombic plates, m. p. 99°. The *benzoyl* derivative,  $\text{N}_2\text{HBz} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , forms needles, m. p. 99°. The *nitroso*-compound,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{N}(\text{NO}) \cdot \text{NH}_2$ , crystallises in felted needles, m. p. 45—47°, condenses with *m*-methoxybenzaldehyde to form the previously-described *m*-methoxybenzaldehydenitroso-*m*-methoxybenzylhydrazone, and is converted by distillation with 10%

sulphuric acid into *m*-methoxybenzylazoimide, a colourless liquid, b. p. 134°/28 mm., which differs from the ortho- and para-isomerides in not being hydrolysed by sulphuric acid to hydrazoic acid.

*Di-m-methoxybenzylamine*,  $\text{NH}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_2$ , prepared by reducing di-*m*-methoxybenzalazine with zinc dust and acetic acid in alcoholic solution, is an almost colourless liquid, b. p. 225°/13 mm., and forms a *hydrochloride*, white leaflets, m. p. 141°, *nitrate*, needles, m. p. 128°, *picrate*, yellow platelets, m. p. 124°, and a stable *nitrite*, m. p. 104°. It is accompanied by *m*-methoxybenzylamine,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}_2$ , which forms a colourless oil, and yields a *hydrochloride*, crystallising in transparent plates or needles, m. p. 160°.

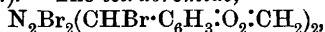
[With KARL TRAUMANN.]—Anisaldazine is reduced by sodium amalgam and alcohol to *p*-methoxybenzaldehyde-*p*-methoxybenzylhydrazone. This crystallises in white leaflets of a silvery lustre, m. p. 143° (decomp.), and yields an *acetyl* derivative, white needles, 87°, *benzoyl* derivative, lustrous, silky needles, m. p. 111—112°, a *nitroso*-compound,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{N}(\text{NO})\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , crystallising in light yellow leaflets, m. p. 106°, and a *picrate*, m. p. 90° (decomp.).

*p*-Methoxybenzylhydrazine *hydrochloride*, white needles, m. p. 194—195° (decomp.), is obtained by hydrolysing the preceding hydrazone with hydrochloric acid. On treatment with sodium hydroxide, it yields an oil, which after distillation under diminished pressure yields *p*-methoxybenzylhydrazine, together with the original hydrazone. With pyruvic acid it condenses to form  $\alpha$ -*p*-methoxybenzylhydrazonopropionic acid, white needles, m. p. 123—124°. The *dibenzoyl* derivative crystallises in stout, colourless prisms, m. p. 149°; the *nitroso*-derivative in large, lustrous, white plates, m. p. 91°, and is converted by distillation with 10% sulphuric acid into *p*-methoxybenzylazoimide, a colourless, oily liquid, b. p. 126°/14 mm.

*s*-Di-*p*-methoxybenzylhydrazine is obtained by reducing anisaldazine in alcoholic solution with excess of sodium amalgam. It crystallises in colourless leaflets of a silvery lustre, m. p. 71°, and yields a stable *nitrite*, white needles, m. p. 92° (decomp.), which on further treatment with nitrous acid is transformed into *p*-methoxybenzaldehyde-nitroso-*p*-methoxybenzylhydrazone; the *hydrochloride* forms leaflets, m. p. 236—237° (decomp.); the *acetyl* derivatives, lustrous, white, intergrown platelets, m. p. 113°.

When reduced with zinc and acetic acid in alcoholic solution, anisaldazine yields di-*p*-methoxybenzylamine (di-anisylamine), of which the *hydrochloride*, m. p. 245° (decomp.), *nitrate*, m. p. 171° (decomp.), and *nitrite*, m. p. 147° (decomp.), are described (compare Steinhart, Abstr., 1888, 51).

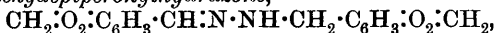
[With LEO FRANK GUTTMANN.]—*Piperonaldazine monohydrochloride* separates from a solution of the azine in concentrated hydrochloric acid in dark yellow leaflets, m. p. 207°; the *dihydrochloride*, prepared from its components in chloroform solution, has m. p. 213°, and readily loses hydrogen chloride; the *sulphate*,  $\text{C}_{16}\text{H}_{12}\text{O}_4\text{N}_2\cdot\text{H}_2\text{SO}_4$ , has m. p. 214 or 221° (decomp.). The *tetrabromide*,



forms a red powder, m. p. 185° (decomp.), which when shaken with pure dry acetone yields bromoacetone and *piperonaldazine dihydro*-

*bromide*, a yellow, crystalline powder. The *monohydrobromide* is obtained by incompletely brominating piperonaldehyde and shaking the product with ordinary acetone; it is a yellow, crystalline powder, m. p. 216°. The hydrochlorides and hydrobromides described above are resolved by water into their components.

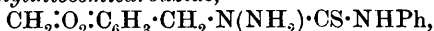
*Piperonaldehydepiperonylhydrazone*,



prepared by reducing the azine with sodium amalgam and alcohol, forms fan-like aggregates of white needles or leaflets, m. p. 116° (decomp.) with previous sintering at 109°; the *nitroso*-derivative crystallises in light yellow needles, m. p. 145° (decomp.), the *acetyl* derivative in small, flat plates, m. p. 146°, the *benzoyl* derivative in tufts of very slender needles, m. p. 125°. It is hydrolysed by dilute hydrochloric acid to *piperonylhydrazine*,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_5\text{:CH}_2\text{:NH}\cdot\text{NH}_2$ , which was isolated in the form of its *hydrochloride*, slender, white needles, m. p. 173·5°. The *acetyl* derivative of piperonylhydrazine is an oil; the *picrate*,  $\text{C}_{14}\text{H}_{18}\text{O}_9\text{N}_5$ , m. p. 140·5—141° (decomp.), is reddish-yellow, and crystallises from alcohol in clusters of yellow needles, m. p. 138·5°, containing one molecule of the solvent, which is lost at 98°. A mixture of the mono- and di-benzoyl derivatives is produced by shaking the hydrochloride with benzoyl chloride and aqueous sodium hydroxide.

*Piperonylsemicarbazide*,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_5\text{:CH}_2\text{:N}(\text{NH}_2)\cdot\text{CO}\cdot\text{NH}_2$ , obtained from piperonylhydrazine hydrochloride and potassium cyanate in aqueous solution, forms snow-white needles, m. p. 175°.

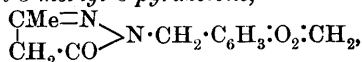
*Piperonylphenylthiosemicarbazide*,



from phenylthiocarbimide, crystallises in needles, m. p. 153·5°.

*α-Nitroso-α-piperonylhydrazine* forms long, slender needles, m. p. 91°, condenses with piperonaldehyde, yielding piperonaldehydenitroso-piperonylhydrazone, and when heated with dilute sulphuric acid is converted into *piperonylazoimide*,  $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_5\text{:CH}_2\text{:N}_3$ . The latter compound is a pale yellow oil, b. p. 142°/15 mm., which is decomposed by 30% sulphuric acid into nitrogen, formaldehyde, hydrazoic acid, piperonaldehyde, ammonia, and a solid base, consisting probably of 3 : 4-methylenedioxyaniline (Rupe and Majewski, Abstr., 1901, i, 103).

[With JOSEF SCHMITTMANN.]—*Piperonylhydrazine* is a pale yellow, viscid oil, b. p. 175—180°/14 mm. It reacts with ethyl acetoacetate, yielding 1-*piperonyl-3-methyl-5-pyrazolone*,

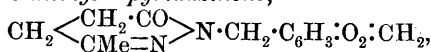


which crystallises in small needles, m. p. 155°, forms a white *silver* salt, and when dissolved in acetic acid and treated with sodium nitrite is converted into 4-*oximino-1-piperonyl-3-methyl-5-pyrazolone*,  $\text{C}_{12}\text{H}_{11}\text{O}_4\text{N}_3$ . This crystallises in light yellow, microcrystalline needles, m. p. 161°, and forms a greenish-yellow *silver* salt.

3-*Phenyl-1-piperonyl-5-pyrazolone*,  $\text{C}_{17}\text{H}_{14}\text{O}_3\text{N}_2$ , prepared from piperonylhydrazine and ethyl benzoylacetate, has m. p. 144·5°, and yields a white *silver* salt.

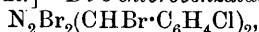
4-Oximino-3-phenyl-1-piperonyl-5-pyrazolone,  $C_{17}H_{13}O_4N_3$ , forms an intensely red powder, m. p.  $162^\circ$  (decomp.); the silver salt is yellow.

1-Piperonyl-3-methyl-6-pyridazinone,



prepared by heating piperonylhydrazine with ethyl lævulate, crystallises in long, colourless needles, m. p.  $101^\circ$ .  $\alpha$ -Piperonylhydrazonopropionic acid,  $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{N} \cdot \text{CMe} \cdot \text{CO}_2\text{H}$ , obtained from pyruvic acid, forms lustrous, colourless leaflets, m. p.  $143^\circ$ . When reduced with excess of sodium amalgam and alcohol, piperonaldazine yields *s*-dipiperonylhydrazine,  $\text{N}_2\text{H}_2(\text{CH}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{O}_2 \cdot \text{CH}_2)_2$ , which crystallises in yellow leaflets, m. p.  $88^\circ$ , and when heated in alcoholic solution with mercuric oxide is converted into piperonaldehydepiperonylhydrazone. The hydrazine forms a hydrochloride, m. p.  $223^\circ$ , a diacetyl derivative, m. p.  $138^\circ$ , dibenzoyl derivative, crystallising in yellow leaflets, m. p.  $98^\circ$ , and a dinitroso-derivative, which crystallises in white leaflets, m. p.  $95^\circ$  (decomp.), and when warmed in alcoholic solution yields piperonaldehydenitrosopiperonylhydrazone.

[With HERMANN PAULI.]—Di-*o*-chlorobenzaldazine tetrabromide,



prepared from its components in carbon tetrachloride solution, is an amorphous, red substance, m. p.  $172$ — $175^\circ$  (decomp.).

[With ERNST BOETZELEN.]— $\alpha$ -Naphthaldazine has m. p.  $156^\circ$ , and yields a tetrabromide, which crystallises in lustrous, golden-yellow, asbestos-like needles, m. p.  $170$ — $172^\circ$ , and is converted by acetone into  $\alpha$ -naphthaldazine dihydrobromide,  $\text{C}_{22}\text{H}_{16}\text{N}_2 \cdot 2\text{HBr}$ , bromoacetone being produced simultaneously.

[With ERNST HAAGER.]—It has been shown by Pascal and Normand (this vol., i, 147) that aromatic aldazines are decomposed by heat, giving stilbenes, and that the yield of the latter diminishes as the molecular weight of the azine increases.

This conclusion has been confirmed from the behaviour of di-2:4-dimethylbenzaldazine, which decomposes when heated at  $260$ — $370^\circ$ , yielding considerable quantities of  $\psi$ -cumene, 2:4-dimethylbenzonitrile, and ammonia, but only a very small amount of tetramethylstilbene.

F. B.

**Quinazolines. XXXI. Action of Methyl and Ethyl Iodides on Dihydro-4-quinazolones.** MARSTON T. BOGERT and GEORGE A. GEIGER (*J. Amer. Chem. Soc.*, 1912, 34, 683—693).—In continuation of work on the 4-dihydroquinazolones (this vol., i, 393, 395, and earlier abstracts), a study has been made of their behaviour towards methyl and ethyl iodides, and the following results have been obtained.

4-Dihydroquinazolones do not combine readily with alkyl iodides except under pressure and at temperatures of  $110^\circ$  or more. The iodide attaches itself to the nitrogen atom in the 1-position and not to that in the 3-position. The ethiodides usually have lower m. p.'s, and are more soluble in water or methyl alcohol than the corresponding methiodides. 6-Nitro-4-dihydroquinazolones cannot generally be made to unite with methyl or ethyl iodide. The alkyl iodide

additive products usually have high m. p.'s, and when heated further evolve the alkyl iodide.

By the action of methyl iodide on 4-dihydroquinazolone, 3-methyl-3 : 4-dihydroquinazolone, or 4-methoxyquinazoline, the same product, 3-methyl-3 : 4-dihydroquinazolone methiodide,  $C_6H_4 \begin{matrix} \text{NMeI} \cdot \text{CH} \\ \text{CO} \text{---} \text{NMe} \end{matrix}$ , m. p. 274° (corr.), is obtained in each case; this compound was first prepared by Knape (Abstr., 1891, 909). Ethyl iodide reacts with 4-methoxyquinazoline to form a substance, m. p. 249° (uncorr.), which has not yet been identified.

The following additive compounds are described: 2-Methyl-4-dihydroquinazolone methiodide, m. p. 220° (uncorr.); 3-methyl-4-dihydroquinazolone ethiodide, m. p. 230° (decomp.); 2 : 3-dimethyl-4-dihydroquinazolone methiodide, m. p. 245° (corr.), and ethiodide, m. p. 242° (corr.); 3-ethyl-4-dihydroquinazolone methiodide, m. p. 258° (decomp.), and ethiodide, m. p. 181° (corr.); 2-methyl-3-ethyl-4-dihydroquinazolone methiodide, m. p. 220° (decomp.), and ethiodide, m. p. 177° (corr.); 3-benzyl-4-dihydroquinazolone methiodide, m. p. 188° (corr.); 3-phenyl-2-methyl-4-dihydroquinazolone methiodide, m. p. 243° (decomp.), and ethiodide, m. p. 244° (corr.). 3-p-Tolyl-2-methyl-4-dihydroquinazolone methiodide has m. p. 234·5° (decomp.), and the methiodides of 3-p-anisyl-, 3-p-phenetyl-, 3- $\alpha$ - and 3- $\beta$ -naphthyl-2-methyl-4-dihydroquinazolone melt and decompose at 231·5°, 221°, 235°, and 238° respectively.

Attempts to methylate the amino-group of 3-amino-2-methyl-4-dihydroquinazolone with methyl iodide or sulphate in presence of alkali hydroxide were not successful, but by the action of methyl iodide alone, a methiodide, m. p. 201° (decomp.), was obtained.

2-Styryl-4-dihydroquinazolones add methyl iodide more easily than ethyl iodide. 3-Phenyl-, 3-p-anisyl-, 3-p-phenetyl-, and 3- $\alpha$ -naphthyl-2-styryl-4-dihydroquinazolones do not unite with methyl iodide when heated with it for ten hours at 150°. 2-Styryl-4-dihydroquinazolone methiodide has m. p. 235° (corr.), and when treated with silver nitrate is converted into the corresponding methyl nitrate compound, m. p. 177° (decomp.). 2-Styryl-4-dihydroquinazolone ethiodide has m. p. 217—218° (uncorr.); 2-styryl-3-methyl-4-dihydroquinazolone methiodide, m. p. 214° (decomp.); 2-styryl-3-ethyl-4-dihydroquinazolone methiodide, m. p. 207·5° (uncorr.); 3-p-tolyl-2-styryl-4-dihydroquinazolone, m. p. 219·5° (decomp.); 6-nitro-3-methyl-4-dihydroquinazolone methiodide, m. p. 228·5° (corr.); 2-phenylbutadienyl-4-dihydroquinazolone methiodide, m. p. 232·5° (corr.); and 2-p-hydroxy-m-methoxystyryl-4-dihydroquinazolone methiodide, m. p. 223—225° (uncorr.). E. G.

**Benzoylcyanamide and a Synthesis of Benzoylenecarbamide (Diketotetrahydroquinazoline) from o-Nitrobenzoylcyanamide.** OTTO DIELS and ALFRED WAGNER (*Ber*, 1912, 45, 874—883).—Benzoylcyanamide is easily prepared by shaking cyanamide with benzoyl chloride and sodium hydroxide; it has m. p. 141—142° (corr.). By the action of chlorine on it, chlorobenzoylcyanamide (Chattaway and Wünsch, *Trans*, 1909, 95, 129) is obtained. When this is treated in

the cold with dilute sodium hydroxide, hydrogen chloride is eliminated and a well characterised *compound*,  $C_8H_6O_2N_2$ , is obtained crystallising in platelets or needles, m. p.  $141^\circ$ , which perhaps has the constitution

$COPh \cdot N < \begin{smallmatrix} CO \\ NH \end{smallmatrix}$ . It unites with phenylcarbimide to form a *compound*,  $C_{15}H_{11}O_3N_3$ , m. p.  $150^\circ$ .

*as-Di-o-nitrodibenzoylcarbamide*,  $NH_2 \cdot CO \cdot N(CO \cdot C_6H_4 \cdot NO_2)_2$ , from cyanamide, pyridine, and *o*-nitrobenzoyl chloride, crystallises in rods and rectangular platelets, m. p.  $200^\circ$  (corr.). On oxidation with hydrogen peroxide in alkaline solution, one acyl group is eliminated and *o*-nitrobenzylcarbamide obtained. This is more conveniently prepared by the action of *o*-nitrobenzoyl chloride on carbamide; it crystallises in well formed yellow needles, m. p.  $237^\circ$  (corr., decomp.).

On reduction, *o*-aminobenzoylcarbamide,  $NH_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot CO \cdot NH_2$ , is obtained; it crystallises in small, brown needles, which on heating at  $200^\circ$  are converted quantitatively into *diketotetrahydroquinazoline*,

$C_6H_4 < \begin{smallmatrix} CO-NH \\ NH-CO \end{smallmatrix}$ . This separates in beautiful colourless crystals, m. p.  $356^\circ$  (corr.). Its solutions in concentrated sulphuric acid and in dilute alkalis fluoresce with a bluish-violet ground tone. E. F. A.

**Preparation of Nitrated Derivatives of Indigotin.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 242149).—Nitro-derivatives of indigotin are readily prepared by nitrating indigotin in the complete absence of water. Indigotin (13 parts) is added to a mixture of concentrated sulphuric acid (50 parts) with fuming acid (100 parts), and 6.3 parts of nitric acid (100%) mixed with concentrated sulphuric acid slowly dropped in at a temperature of  $-5^\circ$  to  $-10^\circ$ . The *nitroindigotin* prepared under these conditions forms a glistening, brown powder, and by increasing the proportion of nitric acid more highly nitrated indigotins are obtained.

The nitration of 2:1-naphthylindigotin, 5:5'-dibromoindigotin, dehydroindigotin acetate, and 5:5'-dibromodehydroindigotin acetate is also considered in the original, and the products are stated to reduce readily to the corresponding primary diazotisable amines.

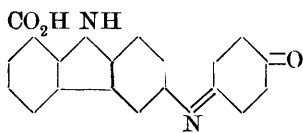
F. M. G. M.

**Preparation of Indophenol Condensation Products and their Leuco-derivatives from Carbazolecarboxylic Acids.**

LEOPOLD CASSELLA & Co. (D.R.-P. 241899. Compare Abstr., 1911, i, 488).—When carbazolecarboxylic acid is condensed with *p*-nitrosophenol in concentrated sulphuric acid solution, a *product* (annexed formula) is obtained in the form of a blue powder.

*Ethyl carbazolecarboxylate* crystallises from ether in glistening prisms, and forms a *product* with *p*-nitrosophenol. F. M. G. M.

**Preparation of Indophenol Condensation Products from Perimidine and its Derivatives.** ACTIEN GESELLSCHAFT FÜR ANILIN FABRIKATION (D.R.-P. 243545).—It is found that perimidine and its derivatives are readily converted into indophenols



by condensation with aminophenols in the presence of an oxidising agent, or by condensation with *p*-benzoquinonechloroimide.

When 2-methylperimidine (18.2 parts) and 2:6-dichloro-*p*-aminophenol hydrochloride (21 parts) are heated at 40° in dilute acetic acid with sodium dichromate, the *product* separates as a dark crystalline powder with a metallic lustre, whilst the *compound* from perimidine and *p*-benzoquinonechloroimide forms a reddish-violet mass. These compounds dissolve in alkali hydroxides with a blue coloration.

F. M. G. M.

“Thionylindigo.” M. CLAASZ (*Ber.*, 1912, 45, 1015—1032).—The suggestion is advanced that the colour of indigotin is due, not to the chromophore, CO·C:C·CO, but to an orthoquinonoid configuration,

indigotin containing, therefore, the group  $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{C} \end{array} \text{C}:$ . In order

to test the theory, it is necessary to prepare an “indigo” in which the carbonyl groups are replaced by groups which are not chromophores and yet are capable of tautomeric change. The thionyl group has been selected, because a comparison of the three yellow substances, benzil, anthraquinone, and acridone, with the three colourless substances, diphenyl disulphoxide, cyclic diphenyl disulphoxide, and diphenylamine sulphoxide respectively, shows that the thionyl group is devoid of chromophoric character. Were the colour of indigotin due to the chromophore CO·C:C·CO, it is to be expected, therefore, that “thionylindigo,”

$\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{SO} \end{array} \text{C}:\text{C} \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{SO} \end{array} \text{C}_6\text{H}_4$ , will be much less intensely coloured.

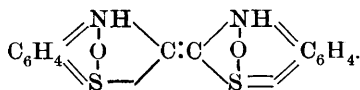
The substance, however, has a deep bluish-black colour. Consequently a quinonoid structure is claimed for indigotin and for “thionylindigo,” although it has not been decided whether one or two such groups are present in these molecules.

“Thionylindigo” has been obtained by the fusion of phenylglycine-*o*-sulphinic acid with potassium hydroxide, whilst its synthesis has been effected in the following way. *o*-Aminophenyl mercaptan hydrochloride, dissolved in water covered with ether, reacts with 40%

formaldehyde to form *benzothiazoline*,  $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{S} \end{array} \text{CH}_2$ , b. p. 270°, a yellow oil, an ethereal solution of which reacts with 1% iodine in aqueous potassium iodide in the presence of a concentrated solution of sodium hydrogen carbonate to yield “*benzothiazolinesulphine iodide*,”

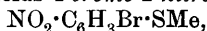
$\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{SI} \end{array} \text{CH}$ . The latter is a brown powder, which in glacial acetic acid reacts with hydrogen peroxide to form “*thionylindigo hydriodide*,”  $\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2\text{S}_2\cdot\text{HI}$ , from which alkalis liberate “thionyl-

indigo,”  $\text{C}_6\text{H}_4 \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{O} \quad \text{S} \end{array} \text{C}:\text{C} \begin{array}{c} \text{NH} \\ \diagup \quad \diagdown \\ \text{SO} \end{array} \text{C}_6\text{H}_4$  or



This substance yields with alkaline sodium hyposulphite a brown vat, which has very little affinity for the fibre, and is not re-oxidised by air, but is re-converted into "thionylindigo" by dilute hydrogen peroxide.

The following compounds have been obtained in the course of experiments to prepare "thionylindigo" by other methods. *o*-Nitrophenyl methyl sulphide yields 4-bromo-2-nitrophenyl methyl sulphide,

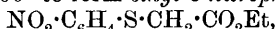


m. p. 130—131°, yellow needles, by bromination in hot acetic acid, and is converted into *o*-nitrophenylmethylsulphone,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{Me}$ , m. p. 106°, colourless plates, by oxidation in hot glacial acetic acid by hydrogen peroxide. The bromination of *o*-nitrophenylthiolacetic acid in hot glacial acetic acid yields *o*-nitrophenyldibromomethylsulphoxide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO} \cdot \text{CHBr}_2$ , m. p. 141°, colourless needles. The sulphoxide is not oxidised by hydrogen peroxide to the corresponding sulphone,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{CHBr}_2$ , m. p. 138°, colourless prisms, which is obtained, however, by the bromination of *o*-nitrophenylsulphoneacetic acid. *o*-Nitrophenylmethylsulphone is reduced to *o*-aminophenylmethylsulphone,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{Me}$ , m. p. 85—92°, to *o*-azoxyphenyl-

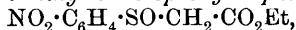
$$\begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{Me} \end{array}$$

methylsulphone,  $\text{SO}_2\text{Me} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \text{---} \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{Me}$ , m. p. 222°, yellow leaflets, by zinc dust and hot 90% acetic acid, and to *o*-hydroxylaminophenylmethylsulphone,  $\text{OH} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{Me}$ , by zinc dust and 40% acetic acid in the cold; the last substance yields the two preceding by autoreduction and autoxidation. When a boiling alcoholic solution of di-*o*-nitrophenyl disulphide is treated with sodium sulphide and sodium hydroxide and the clear filtrate reacts with ethylene dibromide, *o*-nitrophenylsulphuran,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , m. p. 206—208°, yellow crystals, is obtained, which is oxidised in hot glacial acetic acid by hydrogen peroxide to di-*o*-nitrophenylsulphonylethane,  $\text{C}_2\text{H}_4(\text{SO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$ , m. p. 258°, colourless needles. The latter is reduced to di-*o*-aminophenylsulphonylethane, m. p. 155—158°, by zinc dust and hot 50% acetic acid.

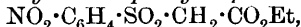
An alcoholic solution of sodium *o*-nitrophenyl mercaptide reacts with ethyl chloroacetate at 60° to form ethyl *o*-nitrophenylthiolacetate,



m. p. 46—48°, brown needles, which in glacial acetic acid is oxidised by hydrogen peroxide to ethyl *o*-nitrophenylsulphoxidoacetate,



m. p. 75—78°, or to ethyl *o*-nitrophenylsulphoneacetate,



m. p. 55—57°, according to the experimental conditions; the latter is converted into di-*o*-nitrophenyl disulphide by alcoholic ammonium sulphide.

C. S.

**Hydrazine Derivatives of Pyridinecarboxylic Acids.** HANS MEYER and JOSEF MALLY (*Monatsh.*, 1912, 33, 393—414).—The condensation products of hydrazine hydrate with the esters of the three pyridinemonomonocarboxylic acids, of dipicolinic, quinolinic and cinchomeronic acids have been investigated. In general, the compounds are readily prepared and are crystalline when pure materials are employed. The use of crude material leads to unsatisfactory results.

*Picolinic hydrazide* was obtained in colourless needles, m. p.  $100^{\circ}$ , by warming ethyl picolinate with hydrazine hydrate. It condenses readily with aldehydes; thus *benzylidenepicolinic hydrazide*, m. p.  $108^{\circ}$ , *vanillylidenepicolinic hydrazide*, m. p.  $208-209^{\circ}$ , and *o-chlorobenzylidenepicolinic hydrazide*, m. p.  $147^{\circ}$ , were isolated. When picolinic hydrazide is treated with hydrochloric acid and sodium nitrite, the very volatile *picolinazoimide* is obtained, which passes into the corresponding *urethane*, m. p.  $102-103^{\circ}$ , when its alcoholic solution is boiled. The latter substance is slowly hydrolysed by boiling fuming hydrochloric acid with the formation of the hydrochloride of 2-aminopyridine, which was identified by means of its platinichloride.

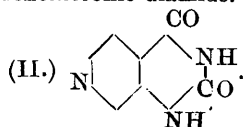
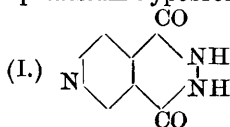
The hydrazide and benzylidenehydrazide of nicotinic acid have been described by Curtius and Mohr (Abstr., 1899, i, 73). *o-Chlorobenzylidenenicotinic hydrazide* has m. p.  $160-161^{\circ}$ . *Vanillylidenenicotinic hydrazide*, m. p.  $126-127^{\circ}$ , yields a yellow, crystalline *hydrochloride*, m. p.  $241-243^{\circ}$  (decomp.).

Ethyl isonicotinate, when similarly treated, yielded *isonicotinic hydrazide*, m. p.  $163^{\circ}$ , which combined with two molecules of hydrochloric acid, forming a *hydrochloride*, m. p. above  $300^{\circ}$ . Poor yields of the volatile *azoimide* were obtained when the hydrazide was acted on by sodium nitrite and hydrochloric acid. *Benzylideneisonicotinic hydrazide*, *vanillylidenisonicotinic hydrazide*, m. p.  $218^{\circ}$ , and *o-chlorobenzylideneisonicotinic hydrazide*, m. p.  $214^{\circ}$ , were prepared.

From dipicolinic acid (measurement of the rhombic crystals of which gave  $a:b:c = 0.7221 : 1 : 1.2866$ ), the following series of derivatives was obtained: *dipicolinic dihydrazide*, m. p.  $280^{\circ}$ ; *dibenzylidenedipicolinic dihydrazide*, m. p.  $297-298^{\circ}$ ; *divanillylidenedipicolinic dihydrazide*, m. p.  $269-270^{\circ}$ ; *di-o-chlorobenzylidenedipicolinic dihydrazide*, m. p.  $356-357^{\circ}$ . Treatment with sodium nitrite and cold hydrochloric acid transformed dipicolinic dihydrazide into the comparatively stable *dipicolinic diazoimide*, m. p.  $110-111^{\circ}$ , which yielded the corresponding *diurethane*, m. p.  $127^{\circ}$ , when its alcoholic solution was boiled. Mineral acids react very slowly with this compound; on the other hand, boiling alcoholic potash transforms it readily into 2:6-diaminopyridine, m. p.  $180^{\circ}$ .

The following derivatives of quinolinic acid were similarly prepared: *quinolinic dihydrazide*, m. p.  $224^{\circ}$ ; *dibenzylidenequinolinic dihydrazide*, m. p.  $160^{\circ}$ ; *di-o-chlorobenzylidenequinolinic dihydrazide*, m. p.  $210-211^{\circ}$ ; *divanillylidinequinolinic hydrazide*, m. p.  $252^{\circ}$  (decomp.).

Methyl cinchomerate under similar treatment yielded unexpectedly the *hydrazine* salt of hydrazidocinchomeronic acid, from which the free acid,  $C_7H_7O_3N_3$ , was readily isolated. Either of these substances, if heated at  $365-370^{\circ}$ , passes into the cyclic *hydrazide* of cinchomeronic acid (I), m. p.  $365^{\circ}$ . Blumenfeld (Abstr., 1896, i, 60) proposed the same formula for a substance which he obtained by the action of potassium hypobromite on cinchomeronic diamide. The two



substances are not identical. The one isolated by Blumenfeld has probably the isomeric composition (II).

The action of phenylhydrazine on the esters of the pyridine-carboxylic acids was also studied. Ethyl picolinate and methyl dipicolinate, when boiled with phenylhydrazine, yielded *picolinic phenylhydrazide*, m. p. 184—185°, and *dipicolinic diphenylhydrazide*, m. p. 244°, respectively. Esters of nicotinic and isonicotinic acids yielded only traces of phenylhydrazides. H. W.

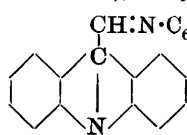
**Preparation of Readily Soluble Double Compounds from Di-alkylaminodimethylphenylpyrazolone, Caffeine, and Aromatic Acids.** CHEMISCHE WERKE VORM. HEINRICH BYK (D.R.-P. 243069).—The following compounds which are readily soluble in water and of therapeutic value are obtained by heating together molecular proportions of the components in aqueous or alcoholic solution (or by fusing them together in the absence of solvents), and subsequently evaporating to dryness at a low temperature, or in a vacuum. (1) The *compound* from dimethylaminodimethylphenylpyrazolone (235 parts), caffeine (212 parts), and salicylic acid (138 parts); also a *compound* (2) when the salicylic acid is replaced by benzoic acid, and a *compound* (3) when replaced by phthalic acid. F. M. G. M.

**Preparation of Derivatives of 4-Methylamino-1-phenyl 2:3-dimethyl-5-pyrazolone.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 243197. Compare Abstr., 1910, i, 78, 340).—The therapeutically active *isovaleryl* derivatives of 4-methylamino-1-phenyl-2:3-dimethyl-5-pyrazolone can be prepared by the action of either *isovaleryl* chloride, or *isovaleric* acid, or anhydride, on the foregoing compound, or by the methylation of 4-*isovaleryl*amino-1-phenyl-2:3-dimethyl-5-pyrazolone.

4-*isovaleryl*methylamino-1-phenyl-2:3-dimethyl-5-pyrazolone forms colourless crystals, m. p. 89—91°.

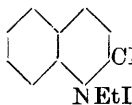
4-*Formyl*methylamino-1-phenyl-2:3-dimethyl-5-pyrazolone has m. p. 107—108°, and can be employed for the preparation of formylamino-antipyrine, m. p. 189° (Abstr., 1897, i, 112). F. M. G. M.

**Preparation of Condensation Products in the Pyridine, Quinoline, isoQuinoline, and Acridine Series.** A. KAUFMANN (D.R.-P. 243078).—When cyclic ammonium bases containing a methyl group in the  $\alpha$ - or  $\gamma$ -position to the ring nitrogen atom are heated with the *p*-nitroso-derivatives of tertiary aromatic amines in the presence of an alkaline condensing agent (such as piperidine, sodium, or potassium carbonate), they yield compounds which are readily hydrolysed to furnish an aldehyde and a primary amine.

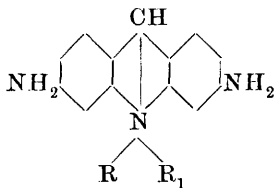


10-*p*-Dimethylaminophenylazomethinacridine (annexed formula), red crystals, m. p. 242—245°, was prepared by fusing *p*-nitrosodimethylaniline with 10-methylacridine at 100—120°; on hydrolysis it furnishes *p*-aminodimethylaniline and 10-acridylaldehyde.

**2-*p*-Dimethylaminophenylazomethinequinoline ethiodide** (annexed formula), green needles, m. p. 200° (approx. decomp.), was obtained in a similar manner from 2-methylquinoline ethiodide in alcoholic solution containing piperidine. F. M. G. M.



**Preparation of 3:6-Diamino-10-alkylacridinium Compounds.** LEOPOLD CASSELLA & Co. (D.R.-P. 243085).—It is found that



3:6-diaminoacridine (Abstr., 1911, i, 504) is readily acylated, and the ring nitrogen atom subsequently alkylated to yield (after hydrolysis) compounds of annexed general formula, where  $R = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $\text{C}_3\text{H}_7$ , or  $\text{C}_6\text{H}_5\text{CH}_2$ , and  $R_1 = \text{Cl}$ ,  $\text{SO}_4\text{H}$ , or  $\text{NO}_2$ .

3:6-Diamino-10-methylacridinium chloride, red needles, was prepared in nitrobenzene solution by the action of methyl *p*-toluenesulphonate on the acylated base, followed by hydrolysis. This compound has a marked trypanocidal reaction, 1 c.c. of a solution of one gram in 5000—5500 c.c. water being effective in the case of an infected mouse.

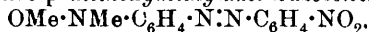
F. M. G. M.

**Derivatives of Azobenzene.** OTTO N. WITT and EDUARD KOPETSCHNI (*Ber.*, 1912, 46, 1134—1154).—The oxidation of *p*-nitroaniline in dilute sulphuric acid by ammonium persulphate at 40—45° yields a mixture of di-*p*-nitroazobenzene and di-*p*-nitroazoxybenzene, together with a little *p*-dinitrobenzene. (The last substance becomes the chief product, 75—77% of the reaction when *p*-nitroaniline in concentrated sulphuric acid is slowly added to warm aqueous ammonium persulphate. *o*-Dinitrobenzene can be obtained from *o*-nitroaniline by a similar process.) The reduction of the preceding mixture by 44% sodium hydrosulphide in warm aqueous alcoholic solution yields di-*p*-aminoazobenzene ("diphenine"), the *diacetyl* derivative, m. p. 295—296°, pale yellow crystals, of which crystallises from acetic acid in yellow prisms containing  $2\text{CH}_3 \cdot \text{CO}_2\text{H}$ , and does not experience the semidine transformation by treatment with alcoholic stannous chloride, but yields acetyl-*p*-phenylenediamine.

Di-*p*-nitrohydrazobenzene is formed as an intermediate product in the preceding preparation of di-*p*-aminoazobenzene. The paradoxical fact that the nitrated hydrazo-compound is converted into an aminoazo-compound in the presence of a mild reducing agent is the cause of the present investigation.

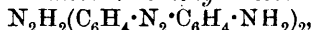
The authors confirm many of Green and Bearder's statements (*Trans.*, 1911, 99, 1960) regarding di-*p*-nitrohydrazobenzene. It is obtained best by reducing with aqueous ammonium hydrosulphide an acetone solution of dinitroazoxybenzene, or of the above-mentioned mixture of dinitroazoxybenzene and dinitroazobenzene. The substance is characterised by its extraordinarily labile nature, undergoing intra- and extra-molecular changes, whereby decomposition and condensation

products of very varied character are formed by the attack of different reagents. When heated in aqueous acetone on the water-bath with 50% potassium hydroxide and methyl sulphate, di-*p*-nitrohydrazobenzene yields *p*-nitro-*p*'-methoxymethylaminoazobenzene,

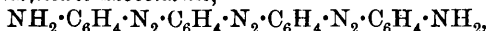


m. p. 186.5°, garnet-red needles with a bluish-violet shimmer, *p*-nitro-*p*'-methylaminoazobenzene,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NHMe}$ , m. p. 206—207° (acetyl derivative, m. p. 194—195°, orange-red needles), di-*p*-nitroazobenzene, and the dimethyl ether of di-*p*-nitrohydrazobenzene,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{NMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , m. p. 177°, citron-yellow crystals. The last substance, which is the chief product of the reaction, is converted into *p*-nitromethylaniline by sodium hydrosulphide, and yields, by treatment with 60—70% sulphuric acid, an emerald-green solution which rapidly decomposes, formaldehyde, di-*p*-nitroazobenzene, and *p*-nitromethylaniline sulphate being formed.

When heated in alcoholic solution for seven hours at 170° in the absence of air, di-*p*-nitrohydrazobenzene yields di-*p*-nitroazobenzene, *p*-nitroaniline, *p*'-nitroaminoazobenzene, and bisnitrobenzeneazo-azobenzene, m. p. 294° (Green and Bearder give m. p. 285—286° [*loc. cit.*]). The last substance is converted by boiling aqueous alcoholic sodium hydrosulphide into bisaminobenzeneazohydrazobenzene,

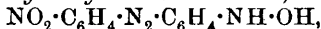


golden leaflets, which forms a sparingly soluble, violet hydrochloride, is converted into di-*p*-aminoazobenzene by boiling alcoholic ammonium hydrosulphide, and is oxidised in alcoholic solution by mercuric oxide to bisaminobenzeneazo-azobenzene,



garnet-red crystals, m. p. 294°, blackening at about 280°. This base, which is produced in quantity by the reaction of di-*p*-nitrohydrazobenzene and sodium sulphide in boiling 90% alcohol, forms a brown hydrochloride and an orange-red acetyl derivative, m. p. 361°, yields bisaminobenzeneazohydrazobenzene by reduction in sodium hydrosulphide, and can also be prepared by the reduction of *p*'-nitroaminoazobenzene by alcoholic sodium sulphide.

When warmed with concentrated sulphuric acid, di-*p*-nitrohydrazobenzene is converted, half into di-*p*-nitroazobenzene, and half into *p*-nitroaniline. When boiled, or heated at 105° under pressure, with alcohol and concentrated hydrochloric acid, di-*p*-nitrohydrazobenzene yields di-*p*-nitroazobenzene and an unstable, red substance, which is presumably *p*-nitro-*p*'-hydroxylaminoazobenzene,



since it yields the above-mentioned *p*-nitro-*p*'-methoxymethylaminoazobenzene by methylation.

It will be seen from the preceding transformations that di-*p*-nitrohydrazobenzene exhibits the typical behaviour of a hydrazo-compound. Its peculiar behaviour is due to the mobility of the hydrogen atoms of the hydrazo-group. These hydrogen atoms are easily removed (whereby dinitroazobenzene is produced), and are then available either for the reduction of one or both nitro-groups to hydroxylamino- or amino-groups, or for fission of the azo-linking, whereby primary amines are produced. The conversion of dinitrohydrazobenzene into

diaminoazobenzene in the presence of mild reducing agents is hereby explained. C. S.

**Heat Coagulation of Proteins.** HARRIETTE CHICK and CHARLES J. MARTIN (*Brit. Assoc. Report*, 1911, 281—286).—Compare Abstr., 1911, i, 822. C. H. D.

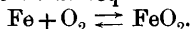
**The Refractive Indices of Solutions of Certain Proteins.** VII. **Salmine.** T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1912, 11, 307—312).—The value of  $\alpha$  (change in the refractive index of the solvent due to 1% of the protein) for salmine chloride and sulphate is identical within the experimental error, and  $= 0.00172 \pm 0.00009$ .

W. D. H.

**Direct Production of Carbamide from Proteins during Oxidation or Hydrolysis.** ROBERT FOSSE (*Compt. rend.*, 1912, 154, 1187—1188).—Béchamp (1856) stated that carbamide was formed during the oxidation of proteins by potassium permanganate, but his conclusions were controverted by Staedeler, Kolbe, and others. The following experiment, however, places the production of carbamide beyond doubt. Five grams of coagulated albumin are suspended in 100 c.c. of water, and treated gradually at 75—80° with 35 grams of potassium permanganate in portions of 5 grams. After filtration, the residue is washed with 150 c.c. of acetic acid, and the filtrate treated with 30 c.c. of a 5% solution of xanthhydrol, when dioxanthylcarbamide separates in brilliant crystals (Abstr., 1908, i, 41).

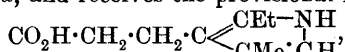
W. O. W.

**Chemical Nature of Specific Oxygen Capacity in Hæmoglobin.** RUDOLPH A. PETERS (*J. Physiol.*, 1912, 44, 131—149).—Hæmoglobin, at any rate as regards its iron-containing portion, is identical throughout vertebrates, and it is to this part of the molecule that the oxygen is attached. The ratio oxygen to iron agrees within experimental error with the value required for the reaction :



W. D. H.

**Constitution of the Coloured Constituent of the Pigment of Blood.** II. OSCAR PILOTY and EDMUND DORMANN (*Annalen*, 1912, 388, 313—329. Compare Abstr., 1911, i, 92).—Hitherto only basic substances have been isolated from the products of the reduction of hæmin by hydriodic acid and phosphonium iodide. Acidic products have now been isolated. The products of the reduction are basified and distilled with steam, and the residual liquor is filtered (the precipitate apparently contains hæmatopyrrolidinic acid) and extracted with ether after being acidified with dilute sulphuric acid. The ethereal extract contains phonopyrrolecarboxylic acid (the picrate of which has m. p. 157°, not 148°, as stated previously) and a new acid,  $\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}$ , m. p. 105°, stout prisms (picrate, m. p. 142.5°), which is called *xanthopyrrolecarboxylic acid*, and receives the provisional formula :

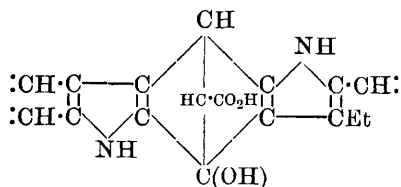


a very small quantity of a third acid is also present, which has not yet

*n n\**

been isolated. An aqueous solution of xanthopyrrolecarboxylic acid at 50° reacts with nitrous acid to form an *isomeride*, m. p. 201—202° (decomp.), of the oxime of hæmatic acid.

In consequence of the discovery of xanthopyrrolecarboxylic acid, it is suggested that the right-hand half of the formula previously



suggested for hæmatoporphyrin must be replaced by a complex such as the annexed; corresponding changes must be made in the suggested formulæ of mesoporphyrin and hæmin.

The presence of a complex such as, or similar to, this

would account, not only for the production of butyric acid which appears to be formed during the decomposition of hæmatoporphyrin and hæmin, but also for the presence of phyllopyrrole (2:3:5-trimethyl-4-ethylpyrrole) in the hæmopyrrole mixture (Willstätter and Asahina, this vol., i, 41).

The mean molecular weight of hæmatoporphyrin, determined in pyridine by the ebullioscopic method, is 1150; the value required by the formula suggested in this paper is 1168.

C. S.

**Echinochrome, a Red Substance in Sea Urchins.** J. F. McCLENDON (*J. Biol. Chem.*, 1912, 11, 435—441).—Just as hæmolytic agents cause hæmoglobin to leave red corpuscles, so do cytolytic agents cause echinochrome to leave the cells which contain the chromatophores which are coloured red by echinochrome. The pigment before extraction shows no absorption bands, but after extraction with ether, alcohol, or water two spectroscopic bands are seen, the positions of which vary with the solvent, but the measurements given are approximately the same as previously stated by McMunn. On the addition of iodine in potassium iodide, it is obtained in crystalline form, as A. P. Mathews found. The percentages of carbon, hydrogen, and nitrogen vary with the methods used. It is precipitated by alkalis in alcohol, also by phosphomolybdic and phosphotungstic acids, but not by tannin. It is probably amphoteric. No evidence that it acts as an oxygen carrier was found. Echinochrome is probably held in the same way as chlorophyll is held in the plant cell.

W. D. H.

**Keratin of Elephant Epidermis.** HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1912, 78, 55—61).—The purified air dry material contained 2·66% of ash comprising considerable quantities of iron. The total nitrogen was 14·26%, distributed as ammonia, 1·47%, melanin, 0·2%, monoamino-acids, 12·25%, diamino-acids, 0·32%.

On hydrolysis with hydrochloric acid the following results were obtained: glycine, 8·33%; alanine, 5·07%; valine, 2·43%; leucine, 3·6%; glutamic acid, 10·2%; phenylalanine, 2·33%; tyrosine, 5·2%; cystine, 4·70%.

About 10% of a residue remained on hydrolysis somewhat resembling asphalt, part of which consisted of fatty acids.

E. F. A.

**Action of Light and Hydrogen Peroxide on Proteins and Amino-acids.** JEAN EFFRONT (*Compt. rend.*, 1912, 154, 1111—1114).—When sterile solutions of peptone are exposed to sunlight, decomposition occurs, and hydrogen peroxide, nitrates, ammonia, and volatile acids appear in the liquid. The destruction of the peptone appears to be due to the hydrogen peroxide, since this substance brings about rapid and complete destruction of peptones and amino-acids, the transformation being analogous to that effected by proteolytic bacteria and amidases. W. O. W.

**Lipoids. XV. The Drying of Tissues and Blood for the Preparation of Lipoids.** SIGMUND FRÄNKEL and ALADAR ELFER (*Biochem. Zeitsch.*, 1912, 40, 138—144).—The authors have found that anhydrous sodium phosphate is preferable both to sodium and calcium sulphates for the drying of tissues. Less salt is used, and there is the further advantage that the hydrated salt is still liquid at 37°. The salt is, therefore, ground up with the tissue in warmed vessels, and then pressed in warm cloths. The material can be thus obtained in a dried form, which can be readily powdered without a great increase in bulk. S. B. S.

**Notes. [Tryptophan. Selective Absorption. Nomenclature.]** EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1912, 78, 159—163).—**I. Formation of a Brown Pigment from Tryptophan.**—Tryptophan mother liquors darken when kept for a long time, and finally a small quantity of a brown substance separates. This is soluble in both alkali and acid; it contains 38.3% C, 4.83% H, and 11.54% N. When burnt an odour of indole is perceptible. It is considered to be a condensation product derived from tryptophan or from a derivative of this. It no longer gives a coloration with glyoxylic acid and concentrated sulphuric acid.

**II.** The fluid obtained from the *spongiosa* of the head of the femur gave a precipitate of protein which contained a considerable proportion of tryptophan—above 3%. Tryptophan was also obtained from a compound present in the urine in a case of melanuria.

**III.** The behaviour of pieces of spinal nerve, sympathetic ganglion tissue, and of striped and smooth muscle fibre towards *l*-, *d*-, and *dl*-adrenaline has been studied with the object of detecting selective absorption by the tissue. No such absorption could be detected.

**IV. Nomenclature Simplification.**—Halliburton's suggestion to use the terms caseinogen and casein is supported.

It is proposed to use hæmatin instead of hæmochromogen. The general name sterol is proposed for all compounds of the cholesterol group. E. F. A.

**The Influence of Colloids on Ferments. II. The Action of Inorganic Colloids on Trypsin.** LUDWIG PINCUSOHN (*Biochem. Zeitsch.*, 1912, 40, 308—313).—Metallic colloids containing albumin as protective colloid, as well as oxides and peroxides, exert an inhibitory action on trypsin, and when in sufficiently high concentration, completely stop the ferment action. Metallic colloids prepared by the electrical dispersion method stimulate, on the other hand, tryptic

action, the concentration in which this action takes place being characteristic for each individual metal. S. B. S.

**The Action of Trypsin. I. Hydrolysis of Caseinogen by Trypsin.** E. H. WALTERS (*J. Biol. Chem.*, 1912, 11, 267—306).—The method of estimating the velocity with which caseinogen is hydrolysed by determining the nitrogen in the undigested portion after precipitation with acetic acid yields accurate results. Precipitation by acetic acid is hastened, and a clear filtrate assured by adding first a slight excess of alkali. The relation between the time of hydrolysis and the amount of "basic" sodium caseinogenate hydrolysed is what would be expected from the unimolecular formula. The velocity with which basic sodium caseinogenate is hydrolysed by trypsin is directly proportional to the concentration of the enzyme. The velocity constant decreases slightly as the concentration of the substrate increases. The nature of the base combined with caseinogen has no influence. There is no relation between the degree of dissociation and the rate with which basic caseinogenates are hydrolysed by trypsin. Rapid auto-hydrolysis occurs in solutions of neutral and basic caseinogenates of the alkalis and alkaline earths. W. D. H.

**Comparative Hydrolysis of Sucrose by Various Acids in Presence of the Invertase of *Aspergillus Niger*.** GABRIEL BERTRAND, M. ROSENBLATT, and (Mme.) M. ROSENBLATT (*Bull. Soc. chim.*, 1912, [iv], 11, 464—468. Compare this vol., i, 327).—The results obtained resemble generally those already recorded for yeast invertase (*loc. cit.*) *Aspergillus* invertase is, however, more susceptible to the influence of acid radicles than yeast invertase, and consequently the disturbing influences shown in the previous work are more accentuated in this. The optimum concentrations for most acids are higher for *Aspergillus* invertase than for yeast invertase, but they are identical for propionic acid, and less for nitric, formic, and phosphoric acids. These differences are not due to the salts present in the enzyme preparations used, and seem to be traceable to the influence of the acid on the enzyme itself. T. A. H.

**Action of Emulsin on Salicin in Alcoholic Solution.** ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1912, 154, 944—946; *J. Pharm. Chim.*, 1912, [vii], 5, 388—392. Compare Abstr., 1911, i, 1053).—An examination of another case in which, contrary to the usual view, alcohol does not inhibit the hydrolytic activity of an enzyme. Unlike gentiopicroin, salicin is not hydrolysed by emulsin in presence of 95° alcohol at the ordinary temperature. With alcohol of 90° strength, hydrolysis occurs, and equilibrium is attained after forty-eight days, when 37% of the glucoside has been decomposed. As the strength of the alcohol is diminished, equilibrium is more rapidly attained, and a greater proportion of the salicin undergoes hydrolysis. W. O. W.

**Studies on Enzyme Action. I. Some Experiments with the Castor Bean Lipase.** K. GEORGE FALK and JOHN M. NELSON (*J. Amer. Chem. Soc.*, 1912, 34, 735—745).—A comparative study has

been made of the hydrolysis of methyl acetate, ethyl butyrate, and olive oil by the lipase of castor seed. The addition of small quantities of alkali hydroxide at the beginning of the action does not affect the subsequent hydrolysis in the case of methyl acetate, but diminishes the rate of action in that of ethyl butyrate. The results obtained with olive oil do not lead to any definite conclusion. In ether, saturated with water, or acetone, containing a small quantity of water, methyl acetate is hydrolysed by lipase to a considerable extent both at the ordinary temperature and at the b. p. of the liquid. It has been found that small quantities of an active constituent can be extracted from the lipase by water and by ethyl acetate. By the electrolysis of an aqueous suspension of the lipase preparation, a substance was produced in the anode solution, probably by oxidation, which showed marked hydrolytic activity.

E. G.

**Preparation of Arsinic Acids of the Indole Series.** C. F. BOEHRINGER & SÖHNE (D.R.-P. 240793).—When indoles are heated with arsenic acid in either aqueous or organic solvents, substitution occurs in the para-position to the nitrogen atom in the indole ring; this new type of therapeutically active compounds crystallise readily, and form well characterised salts with either organic or inorganic bases.

**2-Methylindole-3-arsinic acid** (annexed formula), colourless needles, m. p. 180—182°, was obtained in 93% yield by gently warming anhydrous arsenic acid (28·4 parts) with 6 parts of water, and adding 2-methylindole (13·1 parts) with continual stirring, when the whole solidifies to a crystalline mass. The *sodium* salt,  $C_9H_9O_3NaAsNa, 2\frac{1}{2}H_2O$ , has m. p. 225—235° (decomp.); the *quinine* salt,  $C_{20}H_{24}O_2N_2, C_9H_9O_3NaAs, 2\frac{1}{2}H_2O$ , sinters at 155°, m. p. 170—172°.

*α-Naphthindolearsinic acid*,  $C_{12}H_{12}O_3NaAs$ , prepared in boiling absolute alcohol and toluene solution, is obtained in 56% yield.

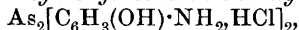
**5-Chloro-2-methylindole-3-arsinic acid**,  $C_9H_9O_3NClAs$ , m. p. 185—186° (decomp.), is similarly prepared from 5-chloro-2-methylindole.

F. M. G. M.

**3:3'-Diamino-4:4'-dihydroxyarsenobenzene Hydrochloride (Salvarsan) and Allied Substances.** PAUL EHRLICH and ALFRED BERTHEIM (*Ber.*, 1912, 45, 756—766).—3-Nitro-4-hydroxyphenyl-arsinic acid is reduced by methyl alcohol and 4% sodium amalgam to **3-amino-4-hydroxyphenylarsinic acid**,  $NH_2 \cdot C_6H_3(OH) \cdot AsO_3H_2$ , which crystallises in small prisms, is sparingly soluble, darkens above 170°, and decomposes without melting, possesses reducing properties, and forms a *sodium* salt,  $C_6H_7O_4NaAsNa, H_2O$  (or  $2H_2O$ ). By treating its solution in dilute hydrochloric acid and potassium iodide with sulphur dioxide, it is converted into (impure) **3-amino-4-hydroxyphenylarsenic oxide**,  $NH_2 \cdot C_6H_3(OH) \cdot AsO$ , which is soluble in acids and in alkali

hydroxides or carbonates, and forms an extremely soluble *hydrochloride*,  $C_6H_6O_2NaAs, HCl, \frac{1}{2}EtOH$ .

3 : 3'-*Diamino-4 : 4'-dihydroxyarsenobenzene hydrochloride*,



can be prepared by reducing the preceding compound with stannous chloride and hydrochloric acid, or by treating 3-nitro-4-hydroxyphenylarsinic acid in an aqueous solution of magnesium chloride with alkaline sodium hyposulphite at 55—60°, and acting on the isolated product with methyl-alcoholic hydrogen chloride. As thus prepared, the hydrochloride contains MeOH, and decomposes at 185—195°. It is easily soluble in water, but not in concentrated hydrochloric acid, and by treatment with sodium hydroxide yields 3 : 3'-*diamino-4 : 4'-dihydroxyarsenobenzene*, which is soluble in an excess of the alkali.

A delicate test for the hydrochloride is to treat it with *p*-dimethylaminobenzaldehyde in dilute hydrochloric acid, containing some mercuric chloride, whereby an orange coloration, and subsequently an orange precipitate, are produced.

Salvarsan is very readily oxidised in the air, yielding the amino-hydroxyphenylarsenic oxide. This fact is important from the physiological side, because the oxide is about twenty times as poisonous as salvarsan. By more energetic oxidation, for example, by hydrogen peroxide or iodine solution, salvarsan is converted into aminohydroxyphenylarsinic acid.

Solutions of salvarsan in water, methyl alcohol, or aqueous alkalis are very unstable. Even with the complete exclusion of oxygen, they become red and finally colourless, a complex, reddish-brown precipitate being formed.

C. S.

**Isomorphism in Organo-metallic Compounds. I. Derivatives of Quadrivalent Metals.** PAUL PASCAL (*Bull. Soc. chim.*, 1912, [iv], 11, 321—325).—Determinations of the fusion curves of binary mixtures of the tetraphenyl derivatives of silicon, tin, and lead show that these three compounds are isomorphous, and thus afford further evidence of the close relationship of lead to silicon and tin.

Tetraphenylsilicon, m. p. 233°, when mixed with varying quantities of tin tetraphenyl, begins to solidify at a slightly higher temperature than that at which solidification is complete, until the quantity of the silicon compound falls to 33%, when the mixture solidifies at a constant temperature of 221°. The corresponding figures for a mixture of tetraphenylsilicon and lead tetraphenyl are 34% and 218.8°. A mixture of tin tetraphenyl, m. p. 225.7°, and lead tetraphenyl, m. p. 227.7°, on the contrary, shows no eutectic point, and the crystals which separate are always richer in lead than the liquid. From these results the conclusion is drawn that these three compounds are similarly constituted and of very similar crystallographic form, and that they are able to form mixed crystals in all proportions.

T. A. H.

## Organic Chemistry.

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**The Formation of the Chief Constituents of Petroleum.** CARL ENGLER (*Petroleum*, 1912, 7, 399—403).—The author discusses the probable and possible origin of petroleum by means of polymerisation and depolymerisation of the decayed complex organic constituents of plant and animal remains.

The following distinct "phases" of bitumen are discussed: ana-bitumen, polybitumen, catabitumen, ecgonobitumen, and oxybitumen, and from these are traced the possible formation of the different constituents contained in petroleum. F. M. G. M.

**Preparation of Butadiene and its Homologues.** GEZA AUSTERWEIL (D.R.-P. 245180).—Isoprene, accompanied by varying quantities of butadiene and mono- and di-methylbutadienes, is obtained when vinyl bromide (107 parts) is slowly dropped into a mixture of magnesium (24 parts) and ether (400 c.c.), followed by the addition of  $\beta$ -chloropropylene (75 parts). After heating during a short period, the mixture is shaken with ice and dilute acetic acid, and the components are subsequently separated by distillation. The reaction takes place according to the equation:



where R is a halogen atom, and R', alkyl, aryl, or hydrogen.

F. M. G. M.

**Pyrogenic Acetylene Condensations.** RICHARD MEYER (*Ber.*, 1912, 45, 1609—1633).—The formation of benzene hydrocarbons by the dry distillation of coal is probably largely due to the aromatic nature of coal itself (compare Burgess and Wheeler, *Trans.*, 1911, 99, 649, and Pictet and Ramseier, *Abstr.*, 1911, i, 850), but the condensation of acetylene undoubtedly plays an important part. Berthelot expressed the opinion that coal-gas acetylene owes its origin to the decomposition of methane, but it has been shown that a much higher temperature is necessary for this change than for the production of tar, whilst the present author believes that the reverse action (conversion of acetylene into methane) takes place to a great extent. This, in conjunction with the ready condensation to aromatic hydrocarbons, would explain why acetylene occurs in only small quantities in coal gas.

The experiments of Berthelot have now been repeated on a large scale under carefully controlled conditions, and the resulting tar has been subjected to exact investigation. The apparatus consists in the main of two vertical tube furnaces heated electrically, each provided with an electric resistance thermometer and a number of receivers for the tar. The temperature of the first is maintained at 640—650°, and that of the second at 800°, very careful regulation being made possible by a number of electrical appliances. The acetylene is diluted with the same volume of hydrogen, since it otherwise inflames and deposits charcoal, but, nevertheless, a considerable proportion is decomposed

into methane. After passing through the furnaces, the gases are used to dilute further volumes of acetylene. The whole apparatus is placed in circuit with an exhaust, which, when once regulated, is made to work automatically, so that the gases circulate at a constant speed of about 40 litres per hour, a particle of acetylene spending about one minute in each furnace. In one experiment 1732 litres of mixed gases, containing 866 litres, or 952 grams, of acetylene, gave 601 grams of tar, that is, 63%. The loss is due to the formation of methane and hydrogen, and the excess of these gases must be removed from time to time.

The tar from the first furnace is richer in light oils, and that from the second in high-molecular hydrocarbons. They have been submitted to repeated fractionation and crystallisation, and any unsaturated hydrocarbons have been removed by bromine water. Benzene forms about one-fifth of the product. Electric heating was resorted to in order to thoroughly fractionate the portion boiling from 90° to 150°, and toluene, which Berthelot did not find, was definitely identified, whilst xylenes could not be characterised. The next higher fraction, up to 200°, was found to absorb bromine, the product on steam distillation giving bromohydroxyindene, m. p. 129°, from which indene was obtained by the method of Weissgerber and Dombrowsky (*Abstr.*, 1909, i, 219). Except in boiling point (179°) this has many of the properties of styrene, which could not be detected, and Berthelot was probably mistaken in assuming the formation of the latter.

The residue from the separation of indene, and the highest fractions, were redistilled, and the portion boiling between 200° and 300° was separated by steam distillation into naphthalene, diphenyl, and fluorene. Similarly, from the fraction 300—450° a small amount of anthracene together with pyrene and chrysene were obtained. These nine hydrocarbons have been most precisely characterised, and have all been found in coal-tar.

J. C. W.

**Hypoiodites in the Formation of Iodoform.** A. PIERONI (*Gazzetta*, 1912, 42, i, 534—536).—It is generally assumed that the formation of iodoform from acetone or compounds containing the group  $\text{CH}_3\cdot\text{CO}\cdot\text{C}$  or  $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{C}$  is brought about by the action of hypoiodites, just as chloroform is given by hypochlorites. If the iodoform produced by the interaction of an energetic base (for example, sodium hydroxide), iodine, and acetone really depends on the quantity of hypoiodite present, the amounts of iodoform which can be obtained must be proportional to the quantities of hypoiodite obtainable from the base and the iodine. Schwicker (*Abstr.*, 1895, ii, 213) showed that the reaction according to which hypoiodites are transformed in alkaline solution is of the third order; this author determined the quantity of hypoiodite formed in the reaction between a base and a solution of iodine in potassium iodide by titrimetric estimation of the iodine liberated by potassium hydrogen carbonate. The present author estimates the hypoiodite with acetone in alkaline solution, his results showing that the transformation of the hypoiodite is a reaction of the second order, and hence that the formation of iodoform is due to the action of the hypoiodite on the acetone.

The values of  $K$  for the formation of iodoform are of the same order of magnitude as those obtained by Schwicker. T. H. P.

**Condensation of the Sodium Derivatives of Primary Alcohols with Secondary Alcohols.** MARCEL GUERBET (*Compt. rend.*, 1912, 154, 1357—1359. Compare Abstr., 1910, i, 149, 454).—When secondary alcohols are heated with the sodium derivatives of primary alcohols, sodium hydroxide is formed together with a secondary alcohol in which the alkyl group of the primary alcohol is joined to the carbon atom next to that to which the hydroxyl group is attached.

*iso*Propyl alcohol when heated with sodium *iso*amyloxide at 220—230° forms  $\beta$ -methylheptane- $\zeta$ -ol, b. p. 172—173°,  $D^0$  0.8329, which under the action of potassium hydroxide at 230° yields hydrogen and an alcohol,  $C_{16}H_{34}O$ , b. p. 160—165°/15 mm., together with small quantities of formic acid and of an acid, the barium salt of which has the formula  $(C_7H_{13}O_2)_2Ba$ . It thus appears to be a secondary alcohol. This view is supported by its velocity of esterification, 18.8. When oxidised, it yields  $\beta$ -methylheptane- $\zeta$ -one, b. p. 170—171°, which gives a crystalline compound with sodium hydrogen sulphite, and was further identified by oxidising it to acetic acid and  $\delta$ -methylvaleric acid. Similarly,  $\gamma$ -propyloctane- $\beta$ -ol results from the interaction of propyl and octylic alcohols in the presence of sodium. It has b. p. 234—235°, m. p. +5°,  $D^{17}$  0.831, velocity of esterification, 16.4. Its acetic ester has b. p. 246—248°. When heated at 230° with an excess of potassium hydroxide, it yields hydrogen, an alcohol, b. p. above 300° (decomp.), and small quantities of formic and octoic acids. On oxidation, it yields  $\gamma$ -propyloctane- $\beta$ -one, b. p. 230—231°,  $D^0$  0.8405, which combines with sodium hydrogen sulphite, and can be further oxidised to acetic acid and propyl amyl ketone, b. p. 187—188°.

H. W.

**A Mode of Formation of Acraldehyde.** WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1912, 154, 1353—1354).—Acraldehyde is formed during the dry distillation of sodium formate. It was identified by transforming it into acraldehyde-ammonia, which yielded picoline when subjected to dry distillation. The platinichloride of the latter was analysed.

H. W.

**Condensation of Butyrone with Organo-magnesium Compounds.** MARCEL MURAT and GAËTAN AMOUREUX (*J. Pharm. Chim.*, 1912, [viii], 5, 473—478).—A number of tertiary alcohols obtained by treating dipropyl ketone with the Grignard reagent are described.

*Dipropylisoamylcarbinol*,  $C_5H_{11} \cdot CPr_2 \cdot OH$ ,  $D^0$  0.8548,  $D^{19}$  0.8388,  $n_D$  1.443, b. p. 114—116°/17 mm., obtained by condensing dipropyl ketone with magnesium *iso*amyl bromide, is a viscous, pleasant-smelling liquid. On catalytic dehydration with alumina, it yields a hydrocarbon,  $C_5H_{10} \cdot CPr_2$  or  $C_5H_{11} \cdot CPr_2 \cdot C_3H_7$ ,  $D^0$  0.7851,  $D^{21}$  0.7672,  $n_D$  1.434, b. p. 191—192°/760 mm., as a colourless, mobile liquid with a faintly alliaceous odour. On catalytic reduction over hot nickel this

olefinic hydrocarbon yields *dipropylisoamylmethane* [ $\delta$ -isoamylheptane],  $D^{14}$  0.7538,  $n_D$  1.425, b. p. 189—190°/760 mm.

*Dipropylisobutylcarbinol*,  $D^0$  0.8577,  $D^{14}$  0.8445,  $n_D$  1.439, b. p. 110—114°/20 mm., is a colourless, syrupy liquid. It is decomposed by hot alumina, giving a *hydrocarbon*,  $C_{11}H_{22}$ ,  $D^{15}$  0.7710,  $n_D$  1.433, b. p. 180—183°/760 mm., which is colourless and of disagreeable odour.

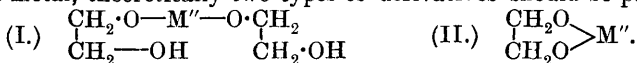
*Phenyldipropylcarbinol*,  $D^0$  0.9589,  $D^{15}$  0.9470,  $n_D$  1.516, b. p. 134°/26 mm. is a colourless, viscid liquid; the *acetyl* derivative has  $D^{15}$  0.8973 and b. p. 160°/19 mm. (decomp.). On dehydration,  $\delta$ -phenyl- $\Delta^7$ -heptene,  $CP^{ra}\cdot Ph\cdot C_3H_6$ ,  $D^{15}$  0.8855,  $n^{15}$  1.522, b. p. 228°/760 mm., is formed as a colourless liquid, which with nitrosyl chloride at  $-10^\circ$  gives a colourless *nitrosochloride*, m. p. 112° (decomp.).

*Benzylidipropylcarbinol*,  $D^0$  0.9506,  $D^{19}$  0.9386,  $n_D$  1.513, b. p. 161—164°/30 mm., is a viscous liquid with a pleasant odour. On dehydration by hot alumina, it yields a *hydrocarbon*,  $D^{19}$  0.902,  $n_D$  1.523, b. p. 246—248°/760 mm., which on catalytic reduction over nickel yields  $\delta$ -benzylheptane,  $CH_2Ph\cdot CHPr_2^a$ ,  $D^{14}$  0.854,  $n_D$  1.487, b. p. 241—244°/756 mm., and with nitrosyl chloride furnishes a *nitrosochloride*, m. p. 115°.

*cycloHexyldipropylcarbinol*,  $D^0$  0.9157,  $D^{19}$  0.9025,  $n_D$  1.469, b. p. 128—130°/11 mm., 256—260°/760 mm., is a colourless, syrupy liquid with a fruity odour, and gives an *acetyl* ester, b. p. 133—136°/5 mm. On dehydration, the alcohol furnishes an ethylenic *hydrocarbon*,  $D^{21}$  0.8441,  $n_D$  1.467, b. p. 226—228°/760 mm., which gives a *nitrosochloride*, m. p. 110° (decomp.). On reduction, this hydrocarbon furnishes  $\delta$ -cyclohexylheptane,  $D^{13}$  0.8468,  $n_D$  1.467, b. p. 228°/760 mm., a colourless, almost inodorous liquid. T. A. H.

**Metallic Glycoloxides.** E. CHABLAY (*Compt. rend.*, 1912, 154, 1507—1509).—Ethylene glycol dissolved in liquid ammonia reacts with a solution of sodium, potassium, or lithium in the same medium at  $-50^\circ$ , giving a monometallic glycoloxide,  $OM\cdot CH_2\cdot CH_2\cdot OH$ . The sodium and potassium derivatives are crystalline, whilst the *lithium* salt is a white, amorphous powder. These substances when heated in a current of hydrogen begin to lose glycol at  $165^\circ$ , and at  $200^\circ$  are rapidly converted into the corresponding dimetallic compounds,  $OM\cdot CH_2\cdot CH_2\cdot OM$ .

If, in the above reaction, a bivalent metal is substituted for the alkali metal, theoretically two types of derivatives should be possible.



Only the derivatives of type (II) can be obtained, and these have been prepared in the case of *calcium*, *strontium*, *barium*, and *lead*.

Monosodium ethyleneglycoloxide and thallium nitrate interact immediately in the cold, forming *dithallium ethyleneglycoloxide*,  $OTl\cdot CH_2\cdot CH_2\cdot OTl$ .

W. G.

**Decomposition of Glycerol by Ultra-violet Rays.** VICTOR HENRI and ALBERT RANC (*Compt. rend.*, 1912, 154, 1261—1263. Compare Abstr., 1910, i, 652; 1911, i, 255; ii, 833).—It is now

shown that when a solution of glycerol in water at a temperature of  $80^{\circ}$  is exposed to ultra-violet rays from a lamp of much higher intensity than that formerly used, formaldehyde is formed, together with other aldehydic substances giving the reactions of Legal and Lewin, and the liquid becomes acid. The action is accelerated by hydrogen peroxide.

T. A. H.

**$\beta$ -Aminoethyl Mercaptan.** SIEGMUND GABRIEL and JAMES COLMAN (*Ber.*, 1912, 45, 1643—1654).—The free base has been liberated from the hydrochloride (Abstr., 1891, 815), some derivatives have been studied, and in attempting to find a more convenient method for the production of the parent substance, ethyl mercaptophthalimide (Abstr., 1889, 870), a basic isomeride of this substance has been discovered.

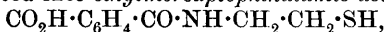
**$\beta$ -Aminoethyl mercaptan**,  $\text{HS}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ , sublimes in a vacuum in colourless, rhombic crystals, m. p.  $99-100^{\circ}$ ; it is strongly alkaline in water, undergoes oxidation in the air to diaminodiethyl disulphide, and forms a *picrate*, m. p.  $125-126^{\circ}$ . The hydrochloride condenses with ethylene chlorohydrin in presence of sodium methoxide, yielding an oily hydroxy base,  $\text{NH}_2\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{OH}$ , which saturated hydrochloric acid, in a sealed tube, converts into the *hydrochloride* of *chloroaminodiethyl sulphide*,  $\text{Cl}\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot\text{C}_2\text{H}_4\cdot\text{NH}_2\cdot\text{HCl}$ , which crystallises from acetone, m. p.  $77-78^{\circ}$ , and forms a readily soluble *picrate*, m. p.  $105^{\circ}$ . The chloro-base could not be condensed to form the ring compound thiomorpholine.

Instead of treating bromoethylphthalimide with potassium hydrosulphide, which complicates the preparation of ethyl mercaptophthalimide through the formation of diphthalylamidoethyl sulphide (*loc. cit.*), it has been heated with potassium ethyl xanthate. The *phthalimidoethyl xanthate*,  $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot\text{CS}\cdot\text{OEt}$ , was readily obtained in tufted needles, m. p.  $80^{\circ}$ , but could only be hydrolysed by boiling hydrobromic acid, yielding then a small amount of ethyl mercaptophthalimide, but chiefly the *hydrobromide* of an isomeric base,  $\text{C}_{10}\text{H}_9\text{O}_2\text{NS}\cdot\text{HBr}$ , m. p.  $218^{\circ}$ . The base itself, which proved to be the *anhydride* of *N- $\beta$ -ethyl mercaptophthalamic acid*,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}\cdot\text{NH}\cdot\text{CH}_2 \\ \text{CO}-\text{S}-\text{CH}_2 \end{smallmatrix}$ , is easily liberated by dilute alkali in short prisms, m. p.  $147^{\circ}$ , which dissolve in stronger alkali, the *potassium salt*,  $\text{C}_{10}\text{H}_8\text{NSO}_2\text{K}$ , forming shining flakes. The *hydrochloride*, m. p.  $207^{\circ}$ , the *platinichloride*, and the *picrate*, m. p.  $181^{\circ}$ , are described, and by the action of sodium nitrite the *nitrosoamine*,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}\cdot\text{N}(\text{NO})\cdot\text{CH}_2 \\ \text{CO}-\text{S}-\text{CH}_2 \end{smallmatrix}$ , has been obtained in needles, m. p.  $157-158^{\circ}$ , which revert to the imine when boiled with alcohol or hydrochloric acid, but decompose when warmed with dilute alkalis into phthalic acid, nitrogen, acetylene, hydrogen sulphide, and a trace of what is probably ethylene sulphide.

In certain respects this thio-base differs from its analogue, the *anhydride* of hydroxyethylphthalamic acid (Abstr., 1905, i, 650); it decomposes when heated; it is not hydrolysed by boiling water, but passed into the isomeric ethyl mercaptophthalimide; and when heated with hydrochloric acid it is not chlorinated, but is converted into the

isomeride with partial hydrolysis into phthalic acid and aminoethyl-mercaptan.

Conversely, when ethyl mercaptophthalimide is heated with dilute alkali it is converted into *ethylmercaptophthalamic acid*,



crystallising from ethyl acetate in leaflets which melt and change into the imide at 114—115°, but which are converted into the anhydride when heated with fuming hydrobromic acid. This agent has the same effect on thiocarbimidoethylphthalimide (Abstr., 1891, 1216) and on *phthaliminoethyl α-thiocarbamate*,  $\text{C}_8\text{H}_4\text{O}_2\cdot\text{N}\cdot\text{C}_2\text{H}_4\cdot\text{S}\cdot\text{CO}\cdot\text{NH}_2$ , which substance is obtained in colourless needles, m. p. 149°, from the thiocarbimido-compound by the action of sulphuric acid.

Methyl iodide converts the base,  $\text{C}_{10}\text{H}_9\text{NSO}_2$ , into the *hydriodide* of *ethylmercaptophthalmethylamic anhydride*,  $\text{C}_{11}\text{H}_{11}\text{O}_2\text{NS}\cdot\text{HI}$ , m. p. 221—222°, the *monohydrate* crystallising from hot water in long needles, and the *picrate* melting at 188°. The free base could not be obtained, alkali producing *ethylmercaptophthalmethylamic acid*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NMe}\cdot\text{C}_2\text{H}_4\cdot\text{SH}$ , in thin tablets, m. p. 167—168°; it is reconverted into the base by acetyl chloride, and on prolonged boiling with water, it changes into a syrup which probably contains methylaminoethyl mercaptan phthalate,  $\text{C}_8\text{H}_6\text{O}_4\cdot\text{NHMe}\cdot\text{C}_2\text{H}_4\cdot\text{SH}$ , since hydrochloric acid precipitates phthalic acid from its solution. The *β-methylaminoethyl mercaptan*,  $\text{NHMe}\cdot\text{C}_2\text{H}_4\cdot\text{SH}$ , is more readily obtained by the hydrolysis of the hydriodide of the methyl base by means of hydrochloric acid in a sealed tube. It forms a very hygroscopic, crystalline mass, giving a *picrate*, m. p. 90—91°, the mother liquor from which, after many days, deposits the *picrate*, m. p. 157°, of *di-β-methylaminoethyl disulphide*,  $\text{S}_2(\text{C}_2\text{H}_4\cdot\text{NHMe})_2$ , a base which is quickly obtained as a colourless oil by the oxidation of the mercaptan with iodine, and forms a *hydrochloride*,  $\text{C}_6\text{H}_{16}\text{N}_2\text{S}_2\cdot 2\text{HCl}$ , m. p. 204—205°. J. C. W.

**Green and Violet Complex Chromic Acetates.** RUDOLF F. WEINLAND and ERNST BÜTTNER (*Zeitsch. anorg. Chem.*, 1912, 75, 293—370. Compare Abstr., 1910, i, 503; Weinland and Dinkelacker, Abstr., 1909, i, 757; Werner, Abstr., 1908, i, 935).—Salts of the green hexa-acetatotriamminetrichromic base are prepared by passing dry ammonia into a solution of a salt of the hexa-acetato-base in absolute alcohol. The reaction is complete in a day, and one of the sparingly soluble salts may then be precipitated. The *iodide*,

$\left[ \begin{array}{c} (\text{OAc})_6 \\ \text{Cr}_3(\text{OH})_2 \\ (\text{NH}_3)_3 \end{array} \right] \text{I}$ , is best suited to the qualitative detection, and forms

hexagonal tablets. None of the salts contain less than six acetic residues. The bromide contains  $\text{H}_2\text{O}$ , and the chloride  $2\text{H}_2\text{O}$ . Salts with colourless acids are pale green in the solid state, and olive-green in solution. As with pyridine, the strength of the base is increased by the introduction of the ammonia, and the list of salts prepared includes a cyanide and a carbonate.

Werner's hexa-acetatomonamminetrichromic salts may be more readily prepared by heating hexa-acetatotrichromic diacetate with

ammonium acetate on a water-bath. The salts of the monoammine base are then separated by precipitation as iodide or as perchlorate,

and then have the formulæ:  $\left[ \text{Cr}_3 \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_2 \\ \text{NH}_3 \end{smallmatrix} \right] \text{I}, 2\text{H}_2\text{O}$  (or  $\text{ClO}_4, 3\text{H}_2\text{O}$ ),

whilst the thiocyanate and mercurichloride contain more ammonia.

When the attempt is made to prepare hexa-acetatotrichromic thiocyanate, a green, sparingly soluble salt is obtained, in which a thiocyanogroup has entered the complex. It dissolves in alcohol and also in

dilute alkalis, and may possibly be an acid,  $\left[ \text{Cr}_3 \begin{smallmatrix} (\text{OAc})_6 \\ (\text{OH})_3 \\ \text{CNS} \end{smallmatrix} \right] \text{H}, 2\text{H}_2\text{O}$ . It

dissolves in pyridine, yielding hexa-acetatotripyridine-trichromic thiocyanate.

Salts of a violet penta-acetatotrichromic base are obtained by repeated evaporation of the green salts on the water-bath. The

principal salt of the series is the *monoacetate*,  $\left[ \text{Cr}_3 \begin{smallmatrix} (\text{OAc})_5 \\ (\text{OH})_3 \\ \text{H}_2\text{O} \end{smallmatrix} \right] \text{OAc}, 11\text{H}_2\text{O}$ ,

which forms dark violet rhombohedra. It may be obtained directly from the green acetate, or by hydrolysis of any of the higher acetates of this series. At  $17.5^\circ$  it dissolves in 21.5 parts of water. Methyl alcohol removes  $6\text{H}_2\text{O}$ , leaving a crystalline residue of the same salt with  $5\text{H}_2\text{O}$ . The constitution is shown to be that given above, by means of the chemical reactions, molecular weight, and electrical conductivity. A double salt of the mono- and di-acetate, with  $10\text{H}_2\text{O}$ , is most easily prepared, and forms dark violet needles. The triacetate

crystallises in prisms,  $\left[ \text{Cr}_3 \begin{smallmatrix} (\text{OAc})_5 \\ (\text{OH})_2 \\ \text{H}_2\text{O} \end{smallmatrix} \right] (\text{OAc})_2, \text{H}_2\text{O}$ , and also with 3 more

mols.  $\text{H}_2\text{O}$ . The tetra-acetate forms thin tablets. The chloride-acetate, bromide-acetate, and sulphate-acetate have also been prepared, several different double salts being found to exist. The formate-acetate, from the mono-acetate and 85% formic acid, contains  $8\text{H}_2\text{O}$  outside the complex, and forms violet, readily soluble needles. A double salt of the mono-acetate of the violet penta-aceto-base and the mono-acetate of the green hexa-aceto-base crystallises in greyish-violet prisms.

Gussmann's triacetatotrichromic acetate (Abstr., 1911, i, 103) is more conveniently prepared by repeated evaporation of the green hexa-acetatodiacetate with water, and then forms long, tetragonal bipyramids,  $\left[ \text{Cr}_3 \begin{smallmatrix} (\text{OAc})_3 \\ (\text{OH})_4 \end{smallmatrix} \right] (\text{OAc})_2, \left[ \text{Cr}_3 \begin{smallmatrix} (\text{OAc})_3 \\ (\text{OH})_5 \end{smallmatrix} \right] \text{OAc}, 28\text{H}_2\text{O}$ , or by adding ammonium carbonate to the mother liquor from the penta-aceto-salt, and then removing ammonia by means of acetic acid. One part requires 1016 parts of cold water for solution. Methyl alcohol removes  $16\text{H}_2\text{O}$ , and a hydrate with  $16\text{H}_2\text{O}$  also exists. A tri-, tetra-, and hexa-acetate have been prepared, as well as a sulphate-acetate and an ammonia compound. The salts of this series are reddish-violet.

A table of the known chromiacetates is given, and attention is

drawn to the number of isomeric salts, isomerism not having been observed in the acetates of other metals. C. H. D.

**Carbohydrate Esters of the Higher Fatty Acids. III. Mannitol Esters of Lauric Acids.** W. R. BLOOR (*J. Biol. Chem.*, 1912, 11, 421—428).—*Mannitan dilaurate*,  $C_6H_{16}O_3(CO_2 \cdot C_{11}H_{23})_2$ , prepared by dissolving mannitol in warm concentrated sulphuric acid and adding lauric acid, forms microscopic needles, m. p.  $122^\circ$ . In chloroform solution,  $[\alpha]_D^{20} + 8.5^\circ$ .

*isoMannide dilaurate* was prepared by heating the preceding ester at  $200^\circ$  for a short time; it is colourless, has m. p.  $37.5^\circ$ ,  $n_D^{40} 1.4570$ ;  $[\alpha]_D + 125^\circ$  in ether or benzene solution.

The *isomannide* esters of lauric and closely related fatty acids are as well utilised by the animal organism as ordinary fats. W. D. H.

**Fatty Acids.** S. FACHINI and W. DORTA (*Chem. Rev. Fett. Harz-Ind.*, 1912, 19, 77—79. Compare *Ann. Soc. Chim. Ital. Sez. Roma*, 1910).—An account of further experiments based on an attempt qualitatively to separate mixtures of liquid and solid fatty acids by means of acetone.

The alkali salts of the higher fatty acids are practically insoluble in cold pure dry acetone; 100 c.c. of boiling 80% acetone dissolves about one gram each of sodium palmitate and sodium stearate, whilst sodium myristate is somewhat more soluble; the salts do not crystallise out, but the mixture solidifies to a clear transparent mass.

Potassium stearate is insoluble in cold 90% acetone; potassium palmitate is slightly soluble; when a mixture (1 gram) is boiled with 100 c.c. of 90% acetone, the potassium stearate crystallises out at  $46^\circ$ , the potassium palmitate at  $28$ — $30^\circ$ , whilst any potassium myristate remains in solution. F. M. G. M.

**Preparation of an Ester from Montana Wax.** ERNST SCHLIEHMANN'S EXPORT-CERESIN-FABRIK (D.R.-P. 244786. Compare Abstr., 1902, i, 72; 1909, i, 629; Trans., 1911, 99, 2302).—When refined Montana wax (100 parts) containing about 70% free montanic acid ( $C_{28}H_{57} \cdot CO_2H$ ) and glycerol (25 parts) are heated together (preferably under pressure), an *ester* containing two molecules of acid to one of glycerol is formed; it is a colourless wax, m. p.  $80$ — $81^\circ$ , and is soluble in the ordinary wax solvents. F. M. G. M.

**The Colouring Matters and Nitrogenous Substances in Fats.** GEORGES BOUCHARD (*Compt. rend.*, 1912, 154, 1620—1622).—The yellowish-brown aqueous layer obtained after removal of the upper layer of soap from the hydrolysis of any fatty matter by sodium hydroxide, on neutralisation gives a brown, gelatinous precipitate. This is purified by treatment with hydrochloric acid and then light petroleum; ether then extracts a soluble portion of composition approximating to  $C_{18}H_{28}O_4$ , the chemical behaviour of which indicates that it is a ketonic acid. The insoluble residue is a black, varnish-like mass which appears to be a mixture of acids richer in oxygen than the above mentioned, together with an acidic nitrogen

compound; the percentage of nitrogen in the latter varies from 0.5 to 3.8 with the different fats examined.

On examining more than one hundred purified fats, it was discovered that they all contained some hundredths of a % of nitrogen, the amount being as high as 0.05% for some animal fats, and as low as 0.01% for some vegetable oils.

D. F. T.

**Toxicity of Paints.** EDWARD C. C. BALY (*J. Soc. Chem. Ind.*, 1912, 31, 515—518).—Poisonous, volatile compounds are produced somewhat readily by the action of white lead, and more readily by the action of lead hydroxide, red lead, lead peroxide, and manganese dioxide on linseed oil. On the other hand, these compounds are formed only in minute quantities at the ordinary temperature by the interaction of linseed oil and zinc white or basic lead sulphate.

The vapour evolved by a mixture of linseed oil and white lead, as already stated, is very poisonous, producing certain specific symptoms, such as lassitude and severe localised headache, followed by diarrhoea, and it is this vapour which is undoubtedly responsible for the cases of supposed lead poisoning incurred by persons who have lived in rooms freshly painted with white lead. The vapour does not contain lead, however, but is probably a mixture of unsaturated aldehydes.

W. H. G.

**Synthesis of Closed Rings by means of Cyanamide.** 1. **Cyanamide and Ethyl Acetoacetate.** PERCI BRIGL (*Ber.*, 1912, 45, 1557—1563).—Ethyl acetoacetate and cyanamide condense in presence of sodium ethoxide to form the monosodium salt of *ethyl β-cyanoaminocrotonate*,  $\text{CN}\cdot\text{NH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ . This is readily broken down into its components by acids, and contains a hydrogen atom replaceable by metal. With hydrogen sulphide, an additive product, *ethyl β-thiocarbamidocrotonate*,  $\text{NH}_2\cdot\text{CS}\cdot\text{NH}\cdot\text{CMe}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , is obtained. This is stable and soluble in ether, and differs from the compound obtained by List (*Abstr.*, 1886, 443; 1887, 127) from thiocarbamide and ethyl acetoacetate, which probably contains a molecule of water more.

Sodium methoxide converts ethyl thiocarbamidocrotonate into thiomethyluracil,  $\text{CMe}\begin{smallmatrix} \text{CH}\cdot\text{CO} \\ \text{NH}\cdot\text{CS} \end{smallmatrix} \text{NH}$ , already described by List (*loc. cit.*).

*Ethyl β-cyanoaminocrotonate* forms long, asbestos-like, colourless needles, m. p. 70—72°; the *copper* salt is yellow; the *cobalt* salt is violet, subsequently becoming red; the other metallic salts are not characteristic.

*Ethyl β-thiocarbamidocrotonate* crystallises in yellow needles, m. p. 165—166° after previous sintering.

E. F. A.

**Dimorphism of Oleic Acid.** AAGE KIRSCHNER (*Zeitsch. physikal. Chem.*, 1912, 79, 759—761).—A second form of oleic acid was obtained in small, white crystals on setting aside a fairly pure specimen of the acid in a flat dish at 8—10°. The new form melts at a higher temperature than the ordinary modification, but the exact melting point cannot be given, as neither the new modification or oleic acid itself has been obtained pure.

G. S.

**New Isomerides of Oleic Acid:**  $\text{CH}_3 \cdot [\text{CH}_2]_4 \cdot \text{CH} : \text{CH} \cdot [\text{CH}_2]_{10} \cdot \text{CO}_2\text{H}$  and  $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH} : \text{CH} \cdot [\text{CH}_2]_9 \cdot \text{CO}_2\text{H}$ . Influence of Displacement of the Double Linking in the Molecule. SERGIUS FOKIN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 653—661).—Reduction of ricinoleic acid with hydrogen in presence of platinous hydroxide gave  $\lambda$ -hydroxystearic acid, which was then treated with hydrobromic acid, and the resulting bromostearic acid boiled with alcoholic potassium hydroxide, a solid and a liquid product being thus obtained.

The solid product contained stearic acid and a crystalline  $\Delta^1$ -oleic acid,  $\text{CH}_3 \cdot [\text{CH}_2]_4 \cdot \text{CH} : \text{CH} \cdot [\text{CH}_2]_{10} \cdot \text{CO}_2\text{H}$ , m. p. 34—36°, solidifying pt. 36—38°, iodine number 89.3 (theoretical 90), which on reduction by hydrogen in presence of platinous hydroxide gives stearic acid and, on oxidation with alkaline permanganate, (1) an acid,  $\text{C}_5\text{H}_{11} \cdot \text{CO}_2\text{H}$ ; (2) a decamethylenedicarboxylic acid,  $\text{C}_{12}\text{H}_{22}\text{O}_4$ , m. p. 104—105.5°, solidifying pt. 92—90°; (3)  $\lambda\mu$ -dihydroxystearic acid, m. p. 85—88°, solidifying pt. 84—82°, and (4) a waxy portion, m. p. 30—40°, which is probably a glycidic acid or a ketohydroxy-acid.

The liquid product has an iodine number of about 83.8, solidifies at about 6—8°, and gives stearic acid on reduction with hydrogen in presence of platinous hydroxide, whilst on oxidation it yields (1) *n*-heptic acid,  $\text{C}_7\text{H}_{14}\text{O}_2$ ; (2) a dibasic acid (? nonamethylenedicarboxylic acid),  $\text{C}_{11}\text{H}_{20}\text{O}_4$ , m. p. 100—101°, solidifying pt. 88—85°; (3)  $\kappa\lambda$ -dihydroxystearic acid; (4) a waxy product resembling that found in the solid portion. There is hence little doubt that the liquid product is  $\Delta^8$ -oleic acid.

From these results and those of other investigators, it seems that oleic acids with the double linking in an odd-even position ( $\eta\theta$ ,  $\iota\kappa$ ,  $\lambda\mu$ ) are solid, whilst those with this linking in an even-odd position ( $\theta\iota\kappa\lambda$ ) are liquid.

T. H. P.

**Preparation of Aluminium Glycollate.** HEINRICH BYK (D.R.-P. 245490).—*Aluminium glycollate*,  $\text{Al}(\text{OH})(\text{O} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{OH})_2$ , is readily prepared in crystalline form by treating an aqueous suspension of freshly precipitated aluminium hydroxide (1 mol.) with glycollic acid (2 mols.); the solution is filtered, and evaporated at 50—60° in a vacuum.

F. M. G. M.

**Action of Hydrogen Peroxide on Lactic Acid and on Dextrose.** JEAN EFFRONT (*Compt. rend.*, 1912, 154, 1296—1298).—Hydrogen peroxide acts on lactic acid at the boiling point of water with the formation of nearly the theoretical quantity of acetic acid. From 1—1.5% of ethyl alcohol are also obtained, and it is considered that the lactic acid has been broken down to carbon dioxide and alcohol, and the latter oxidised to acetic acid.

From dextrose under similar conditions, from 1—9% of alcohol, also acetaldehyde and acetic and formic acids are obtained in the proportion of two (acetic acid) to eight (formic acid). At the moment when the dextrose is half destroyed, 60% of volatile acids and 29% of oxalic acid are formed; when 90% of the sugar has been attacked, the proportion of oxalic acid is reduced to 7%, and when action is complete no oxalic acid is obtained. The proportion of volatile acid remains constant throughout.

E. F. A.

**Syntheses by means of Mixed Organic Derivatives of Zinc:  $\alpha$ -Alkoxyalkylacetic Acids.** EDMOND E. BLAISE and L. PICARD (*Bull. Soc. chim.*, 1912, [iv], 11, 537—546. Compare Abstr., 1911, i, 349; this vol., i, 232).—The production of ethyl chloroethoxyacetate and its reaction with mixed organic compounds of zinc, already dealt with (*loc. cit.*, compare Mylo, this vol., i, 4), are described in greater detail. The latter reaction is of special interest, since it is a general method for the synthesis of  $\alpha$ -alcohols by the direct attachment of the group  $-\text{CH}(\text{OH})-\text{CO}_2\text{H}$  to any radicle.

Ethyl  $\alpha$ -ethoxy-*n*-valerate, b. p.  $84^\circ/17$  mm. or  $76^\circ/12.5$  mm., obtained as already described (*loc. cit.*) or by treating  $\alpha$ -bromovaleryl chloride with ethyl alcohol, forms on hydrolysis  $\alpha$ -ethoxyvaleric acid, b. p.  $114^\circ/11$  mm.,  $124^\circ/17$  mm., as a slightly viscous liquid. The methyl ester, b. p.  $70^\circ/15$  mm., is a mobile liquid; the acid chloride, b. p.  $57$ — $58^\circ/12.5$  mm., is liquid; the amide, m. p.  $91^\circ$ , forms colourless needles. The anilide, m. p.  $68^\circ$ , crystallises from a mixture of benzene and light petroleum. The *p*-toluidide, b. p.  $184^\circ/11.5$  mm., is liquid.

T. A. H.

**Uranyl Oxalate.** WILLIAM OECHSNER DE CONINCK and ALBERT RAYNAUD (*Bull. Soc. chim.*, 1912, [iv], 11, 531—533).—Uranyl oxalate,  $\text{UO}_2\text{C}_2\text{O}_4$ , is moderately soluble in water, and sparingly soluble in alcohol ( $95^\circ$ ) or dry methyl alcohol, becomes anhydrous at  $100^\circ$ , and then on exposure to moist air, slowly absorbs  $3\text{H}_2\text{O}$ . On ignition in a closed vessel, it leaves a residue of uranous oxide,  $\text{UO}_2$ , in a condensed form, which is black, but shows green or brown tints by reflected light.

T. A. H.

**The Esters of Dichlorosuccinic Acid and Their Stereoisomerides.** GEORGES DARZENS and J. SÉJOURNÉ (*Compt. rend.*, 1912, 154, 1615—1617).—Two inactive dichlorosuccinic acids have already been described (Kirchhoff, Abstr., 1895, i, 20; Michael and Tissot, Abstr., 1893, i, 142; Riet, Abstr., 1895, i, 19).

On treating methyl *d*-tartrate in pyridine solution with thionyl chloride there is obtained an active methyl dichlorosuccinate, b. p.  $126^\circ/20$  mm.,  $106^\circ/4$  mm., m. p.  $62$ — $63^\circ$ ,  $[\alpha]^{20} - 66^\circ$  (in chloroform).

The corresponding ethyl dichlorosuccinate, obtained in a similar manner from ethyl *d*-tartrate, has b. p.  $116^\circ/3$  mm., and does not crystallise.

Methyl *dl*-tartrate under similar treatment yields an inactive product, presumably methyl *dl*-dichlorosuccinate, b. p.  $105^\circ/3$  mm., m. p.  $43^\circ$ ; this differs from both the inactive esters previously described (*loc. cit.*), and appears to offer a case of isomerism somewhat analogous to that of the malic acids.

Contrary to expectation, all the above esters on elimination of hydrogen chloride give ethyl chlorofumarate, b. p.  $117^\circ/7$  mm. This is explained by an assumption that the elimination of hydrogen chloride occurs at one carbon atom, and is followed by the movement of a hydrogen atom from the other carbon. The chlorofumaric esters resist the elimination of another molecule of hydrogen chloride.

D. F. T.

**The Decomposition of Some Higher Acids of the Oxalic Acid Group by Heat.** OSSIAN ASCHAN (*Ber.*, 1912, 45, 1603—1609).—Adipic, suberic, and sebacic acids, when submitted to dry distillation, are found to undergo changes in three directions: I, elimination of carbon dioxide and water, resulting in *cycloketones*; II, loss of carbon dioxide alone, giving saturated mono-basic acids; and III, the formation of unsaturated monobasic acids.

From adipic acid, *cyclopentanone* has been obtained in 60% yield, whilst valeric acid has been characterised in the form of its calcium salt, and potassium permanganate has revealed the presence of an unsaturated acid. Suberic and sebacic acids are more liable to complete decomposition, and the formation of ketones occurs to a much smaller extent, whilst larger yields of saturated and unsaturated acids are obtained. The formation of suberone and *n*-heptoic acid in the one case, and of *cyclononanone* and *n*-nonoic acid in the other, has been proved. J. C. W.

**Preparation of  $\alpha\beta$ -Diketonic Esters.** ANDRÉ WAHL and M. DOLL (*Compt. rend.*, 1912, 154, 1237—1240).—The preparation, properties, and certain reactions of homologues of ethyl acetylglyoxalate (ethyl diketobutyrate) are described (compare Bouveault and Wahl, *Abstr.*, 1904, i, 556; Wahl, *Abstr.*, 1907, i, 217; 1911, i, 108). The new esters were prepared by the general method already described.

*Ethyl propionylglyoxalate*,  $\text{CH}_2\text{Me}\cdot\text{CO}\cdot\text{CO}\cdot\text{CO}_2\text{Et}$ , b. p. 77—80°/10 mm.,  $D_0$  1.142, is sparingly soluble in water. *Ethyl butyryl-glyoxalate* has b. p. 83—86°/10 mm.,  $D_0$  1.104. *Ethyl heptylglyoxalate*, b. p. 124—128°/10 mm.,  $D_0$  1.021, is insoluble in water. All these esters are pleasant-smelling, mobile, yellow liquids, which are decolorised by water or alcohol; with aniline and hydroxylamine they yield uncrystallisable oils. With *o*-diamines they furnish quinoxaline derivatives; thus ethyl propionylglyoxalate gives with *o*-phenylenediamine, *ethyl 2-ethylquinoxaline-3-carboxylate*, colourless needles, m. p. 64°. With 1:2-naphthylenediamine, ethyl heptylglyoxalate yields *ethyl 2-hexylphenoquinoxaline-3-carboxylate*, m. p. 64—65°, whilst the corresponding compound given by ethyl butyrylglyoxalate has m. p. 83—84°.

The *disemicarbazones* derived from the three homologous diketonic esters in ascending order melt with decomposition at 235°, 247°, and 230° respectively, and are colourless, crystalline, sparingly soluble substances.

With phenylhydrazine, ethyl propionylglyoxalate yields 1-phenyl-3-ethyl-5-pyrazolone-4-phenylhydrazone,  $\text{C}_6\text{H}_5\cdot\text{N} \begin{smallmatrix} \text{N}=\text{CEt} \\ \text{CO}\cdot\text{C}\cdot\text{N}\cdot\text{NHPh} \end{smallmatrix}$ , orange crystals, m. p. 157°. The corresponding compounds formed from the other two esters in ascending order have m. p. 133—134° and m. p. 100—101° respectively (compare Bouveault and Wahl, *Abstr.*, 1904, i, 789).

With hydrazine hydrate the esters form the corresponding rubazonic acids of the type already described by Bouveault and Wahl (*loc. cit.*).

3 : 3'-*Diethylrubazonic acid*,  $\text{NH} \begin{array}{c} \text{CO} \cdot \text{CH} \cdot \text{N} \cdot \text{C} \cdot \text{CO} \\ \text{N} = \text{CEt} \quad \text{CEt} : \text{N} \end{array} \text{NH}$ , m. p. 235° (decomp.), and the corresponding *dipropylrubazonic acid*, m. p. 260° (approx.), both form red crystals and give violet tinted solutions with alkalis. T. A. H.

**Preparation of the Unconjugated Acids of Ox Bile.** SAMUEL B. SCHRYVER (*J. Physiol.*, 1912, 44, 265—274).—The crude acids are recrystallised from hot acetone, and over 80% are obtained in crystalline form. From the mixture the greater part of the cholic acid can be separated by heating a 1% solution of the sodium salts with one-fifth the volume of a 20% magnesium chloride solution on a water-bath. Most of the choleic and deoxycholeic acids separate as the magnesium salt, and the greater part of the cholate remains in solution. From the mixture of choleate and deoxycholeate, the former can be separated as an insoluble barium salt, and the deoxycholeic acid can be separated from the greater part of the still adhering cholic acid by reversion into the magnesium salt. No trace of Hans Fischer's lithocholic acid was found ; it is possibly a pathological product. W. D. H.

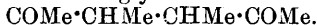
**Preparation of  $\alpha$ -Glucoheptonic Acid.** ARTHUR LIEBRECHT and GEORG ROSENFELD (D.R.-P. 245267).— $\alpha$ -Glucoheptonic acid is obtained in satisfactory yield when the product obtained from the treatment of dextrose during six days with hydrogen cyanide at 30° is boiled with barium hydroxide, the resulting precipitate decomposed with sulphuric acid, and the filtrate evaporated in a vacuum. F. M. G. M.

**Use of Carbonates in the Catalytic Preparation of Ketones.** JEAN B. SENDERENS (*Compt. rend.*, 1912, 154, 1518—1520).—A claim that his process for the preparation of ketones directly from acids, using thorium, zirconium, or uranium oxides as catalysts (compare Abstr., 1909, i, 286, 627 ; 1910, i, 11, 179, 318, 489 ; 1911, i, 134, 302) is independent of the work of Squibb and Conroy, who used carbonates. Further, the author points out that carbonates which, like many other compounds, furnish good yields of acetone from acetic acid, are almost inactive or produce irregular results with the homologues of this acid. W. G.

**Chemical Action of Light. XXIII. Behaviour of Methyl Ethyl Ketone.** GIACOMO L. CIAMICIAN and PAUL SILBER (*Ber.*, 1912, 45, 1540—1546\*).—It has been shown (Abstr., 1911, i, 513) that methyl ethyl ketone in methyl and ethyl alcoholic solution behaves very differently from acetone when exposed to light. In the case of acetone, *isobutylene glycol* and trimethylethylene glycol are formed ; with methyl ethyl ketone no glycol could be identified. It is now established that methyl ethyl ketone condenses with itself to form a diketone,  $\text{C}_8\text{H}_{14}\text{O}_2$ , the other product of the reaction being

\* and *Atti R. Accad. Lincei*, 1912, [v], 21, i, 547—553.

*sec.*-butyl alcohol. This diketone reacts with ammonia to form tetramethylpyrrole; it accordingly has the structure



The higher ketones behave similarly, whilst the products of the action of light on acetone when heated with ammonium acetate give a faint, but distinct, pine-splinter reaction for pyrrole, and also the Ehrlich reaction for acetylacetone.

The *diketone*,  $\text{C}_8\text{H}_{14}\text{O}_2$ , has b. p.  $82^\circ/11$  mm.; it forms a *dioxime*, crystallising in large, lustrous prisms, m. p.  $202^\circ$ .

The tetramethylpyrrole formed from it separates in nacreous platelets, m. p.  $114^\circ$ ; the *picrate* has yellow, prismatic crystals, m. p.  $130^\circ$ ; the *compound* with trinitroresorcinol forms reddish-brown needles, m. p.  $159^\circ$ .

The diketone reacts with phenylhydrazine to form a *pyrrole*,  $\text{C}_{14}\text{H}_{18}\text{N}_2$ , crystallising in colourless needles, m. p.  $130^\circ$ .

With *p*-phenylenediamine, a *compound* of the same composition, separating in faintly coloured, prismatic crystals, m. p.  $174$ — $175^\circ$ , is obtained.

E. F. A.

**The Preparation of Glucosone.** PAUL MEYER (*Biochem. Zeitsch.*, 1912, 40, 455—457).—In view of the fact that glucosazone is not soluble in water, the ordinary method of preparing glucosone from this by treatment with benzaldehyde has failed. The author shows, however, that glucosazone is soluble in benzaldehyde, and if 2 grams of the osazone are dissolved in 18 grams of the aldehyde and the mixture heated with 200 c.c. of water, glucosone is obtained in a yield up to 30% of the theoretical.

S. B. S.

**Action of Ultra-violet Rays on Starch.** JEAN BIELECKI and RENÉ WURMSER (*Compt. rend.*, 1912, 154, 1429—1432. Compare Abstr., 1910, i, 625; 1911, i, 255, 524).—Pure starch in aqueous solution when exposed to the ultra-violet rays from a quartz-mercury lamp undergoes hydrolysis and partial oxidation. The products formed are dextrans, reducing sugars (probably dextrose), pentoses, formaldehyde, and substances of an acid nature.

W. G.

**Action of Ultra-violet Rays on Starch.** LÉON MASSOL (*Compt. rend.*, 1912, 154, 1645—1646. Compare Massol, Abstr., 1911, i, 356; Bielecki and Wurmsier, preceding abstract).—A claim for priority.

D. F. T.

**Hydrolysis of Starch by Hydrogen Peroxide, alone or in the Presence of Animal and Vegetable Amylases.** C. GERBER (*Compt. rend.*, 1912, 154, 1543—1545).—Hydrogen peroxide even in dilute solutions (1 part perhydrol in 1000—3000 water) has a powerful hydrolysing effect on starch, the products being maltose and dextrans. In more concentrated solutions, oxidation of the maltose occurs. This hydrolysis is more closely allied to diastatic action than is the case with acids, maltose and not dextrose being the sugar formed. Rise in temperature increases the rate of the reaction very considerably.

A solution of perhydrol (1 : 8000) has a powerful retarding influence

on the amylase of *Ficus carica*, but has no effect on that of *Broussonetia papyrifera*, a strength of 1:25 being necessary to cause retardation with this amylase. With the amylase of trypsin, a solution 1:1000 has a slight accelerating effect, whilst a solution 1:25 has a marked retarding influence.

W. G.

**Acid of Oxalic Acid on Cellulose. Cellulose-oxalic Acid Ester.** JOHN F. BRIGGS (*J. Soc. Chem. Ind.*, 1912, 31, 520—522).—Cellulose is converted by oxalic acid, slowly at the ordinary temperature, more rapidly at higher temperatures, partly into a hydrocellulose and partly into a compound which is probably an acid oxalate of a hydrocellulose. The ester has not yet been isolated; it exhibits, even in the form of a sodium salt, a strong affinity for basic dyes.

W. H. G.

**Physical and Chemical Properties of Some Organic Amalgams.** HERBERT N. MCCOY and FRANKLIN L. WEST (*J. Physical Chem.*, 1912, 16, 261—286. Compare McCoy and Moore, *Abstr.*, 1911, i, 270).—The method of preparing tetramethylammonium amalgam previously described has been improved by carrying out the electrolysis of alcoholic tetramethylammonium chloride in a vessel cooled to  $-34^{\circ}$  by liquid ammonia. The electrolytic efficiency of the process was about 15% with ethyl alcohol and somewhat higher with propyl alcohol and acetonitrile as electrolytes.

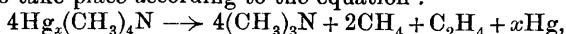
The amalgam was filtered by suction from the excess of liquid mercury, and the silver-white, granular, crystalline amalgam, having been washed with carbon tetrachloride, could be preserved under carbon tetrachloride at  $0^{\circ}$  for several hours. The crystals contained upwards of 5% of their mercury in combination, as estimated from the proportion of colloidal mercury obtained when water was added. The crystals float on liquid mercury, densities as low as 10.6 being recorded. The electrical conductivity falls off as the percentage of amalgam increases.

Tetramethylammonium amalgam spontaneously emits negative electricity as it decomposes, and the residual amalgam, if insulated, acquires a positive charge, attaining in one case 3.8 volts in a few minutes. A positively charged electroscope is discharged by the emission at a rate which is greater the higher the temperature of the amalgam and the nearer it is to the electroscope. The emission is without effect on a photographic plate, and is unable to pass through 0.044 mm. of aluminium, but may be carried by a current of air through a layer of glass wool or a long narrow tube. The conclusion is drawn that the phenomenon is not one of radioactivity, but consists of the emission of ionised molecules of the gaseous decomposition products.

Ammonium amalgam emits positive electricity as observed by Coehn, and also negative in about 1/50th to 1/20th the amount. Monomethylammonium amalgam also gives both kinds of ion, the proportions being similar. Tetramethylammonium amalgam is peculiar in that it emits no positive ions. The gas escaping from the mercury in minute bubbles is negatively electrified just as in the case

of air bubbled through mercury, as noticed by Lenard (1892). The phenomenon is distinct from that shown by potassium and sodium amalgams, in that ultra-violet light is not necessary, and, in fact, has no appreciable influence.

The decomposition of tetramethylammonium amalgam at 25° appears to take place according to the equation :



although the authors consider that this is not definitely established. The rate at which gas is evolved at 27° indicates that the action is unimolecular, so that it is necessary to assume that it takes place in stages. It is calculated that only one ion is produced per  $10^{10}$  molecules of trimethylamine evolved.

The preparation of monomethylammonium amalgam was also investigated. It was found that there is no better electrolyte than water in this case, and there is no advantage in working at -34° instead of 0°.

R. J. C.

**Precipitating Reagents for Amino-acids.** CARL NEUBERG and JOHANNES KERB (*Biochem. Zeitsch.*, 1912, 40, 498—512).—Mercuric acetate precipitates amino-acids in the presence of carbonates. The mercuric salts are not the normal salts of the acids, but appear to be the salts of the carbamic acids, formed by the action of the carbonate on the amino-acids; thus glycine, for example, appears to react as follows:  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}_2 + \text{Na}_2\text{CO}_3 = \text{CO}_2\text{Na}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Na}$ . Mercuric acetate acting on compounds of this description gives rise to basic mercuric salts of the corresponding acid; the reasons for these suppositions are the following: (1) The normal mercuric salts of amino-acids which are known have different properties to those obtained in the above reaction, some of them being easily soluble. (2) Glucosamine which contains no carboxyl group also gives a precipitate when treated with sodium carbonate and mercuric acetate. (3) Sodium carbonate is essential for the reaction, and cannot be replaced by sodium hydroxide. (4) On decomposition of the salts with hydrogen sulphide, carbon dioxide is evolved. (5) Similar precipitates could be obtained directly from the corresponding carbamic acids prepared by Siegfried's method. The authors give full details for carrying out the reaction.

S. B. S.

**Creatinine.** ERNST SCHMIDT (*Apoth. Zeit.*, 1912, Reprint 3 pp. Compare Abstr., 1911, i, 20).—The product obtained by the action of sodium nitrite on a nitric acid solution of creatinine is not a nitroso-compound, but an oxime; on treatment with hydrochloric acid, it gives hydroxylamine and an acidic substance, which proves to be methylparabanic acid, so that its constitution probably is  $\text{CO} \begin{smallmatrix} \text{NMe}\cdot\text{C}:\text{N}\cdot\text{OH} \\ | \\ \text{NH}-\text{CO} \end{smallmatrix}$ , that is, the *oxime of methylparabanic acid*.

The "nitrosocreatinine" of Kramm (Abstr., 1899, i, 85), obtained by the action of sodium nitroprusside on creatinine, is probably the guanidine analogue,  $\text{NH}:\text{C} \begin{smallmatrix} \text{NMe}\cdot\text{C}:\text{N}\cdot\text{OH} \\ | \\ \text{NH}-\text{CO} \end{smallmatrix}$ . Unlike the above

oxime, it possesses basic properties. On hydrolysis with hydrochloric acid, it yields, amongst other products, hydroxylamine and methyl-parabanic acid; on reduction with tin and hydrochloric acid, it gives a considerable quantity of methylguanidine. D. F. T.

**Oxidation of Potassium Cyanate by means of Hydrogen Peroxide.** ALEXANDER P. LIDOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 527—528. Compare Abstr., 1911, i, 429, 618).—In neutral solution the reaction between potassium cyanate and hydrogen peroxide seems to proceed according to the equation:  $2\text{KCNO} + \text{H}_2\text{O}_2 = \text{K}_2\text{CNO}_2 + \text{CNO} + \text{H}_2\text{O}$ . Not only the gas from the salt remaining in solution, but also that evolved, which is mainly soluble in alkali hydroxide and gives a precipitate with barium hydroxide solution, possesses a less weight than carbon dioxide. In presence of sodium hydroxide, which must be free from carbonate, the reaction is expressed by the equation:  $2\text{KCNO} + 2\text{NaOH} + 2\text{H}_2\text{O}_2 = \text{K}_2\text{CNO}_2 + \text{Na}_2\text{CNO}_2 + 2\text{H}_2\text{O}$ . Also, in presence of concentrated alcohol, which annuls the hydrolysing action of the water, the oxidation proceeds without generation of gas. T. H. P.

**Formation of Oxycyanates on Heating Potassium Cyanate with Copper Oxide or on Combustion of Potassium Cyanate in Oxygen.** ALEXANDER P. LIDOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 529—532. Compare preceding abstract).—When potassium cyanate is heated with a small quantity of an oxide or of a finely divided metal, for example, copper, it undergoes energetic oxidation according to the equations:  $2\text{KCNO} + \text{CuO} = \text{K}_2\text{CNO}_2 + \text{CNO} + \text{Cu}$  and  $2\text{KCNO} + \text{Cu} = \text{K}_2\text{CNO}_2 + \text{CN} + \text{Cu}$ . The quantities of gas evolved do not correspond exactly with these equations, owing to secondary reactions occurring to a slight extent. T. H. P.

**Synthesis of Carbamide by the Oxidation of Ammonia and Carbohydrates, Glycerol, or Formaldehyde.** ROBERT FOSSE (*Compt. Rend.*, 1912, 154, 1448—1450).—Contrary to the statement of Hofmeister (Abstr., 1897, ii, 335), carbamide is formed in considerable quantities when dextrose, lævulose, sucrose, dextrin, inulin, starch, glycerol or formaldehyde are oxidised in the presence of ammonium salts by means of potassium permanganate. The permanganate is added slowly to the ammoniacal sugar solution, and the mixture is then heated at 50—60° until the permanganate is all destroyed. After the addition of acetic acid, the liquid is filtered and the carbamide is precipitated by the addition of an alcoholic solution of xanth-hydrol. W. G.

**Preparation of Carbamic Esters of Tertiary Alcohols.** VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 245491).—The carbamic esters of tertiary alcohols are readily prepared by the action of a metal on a mixture of the alcohol and carbamyl chloride. *Amylene carbamate*,  $\text{NH}_2 \cdot \text{CO}_2 \cdot \text{C}_5\text{H}_{11}$ , colourless needles, m. p. 83—86°, with a camphor-like odour was prepared by treating a cooled mixture of amylen hydrate (88 parts), benzene (600 parts), and sodium (23 parts)

with carbamyl chloride (79.5 parts); the solution was acidified, filtered, the benzene removed by distillation, and the oily residue crystallised from alcohol. This reaction can also be carried out by Grignard's method.

*Methyldiethylcarbinylurethane*, colourless needles with a camphor-like odour, was obtained by adding methyl ethyl ketone (1 mol.) to magnesium ethyl chloride (prepared by Grignard's reaction), followed when the action moderated by carbamyl chloride to the well cooled solution.

F. M. G. M.

**Addition of Ethylidenebisurethane to Acetylacetone. II.** G. BIANCHI (*Gazzetta*, 1912, 42, i, 499—502).—Replacement of the aromatic aldehyde previously employed (*Abstr.*, 1911, i, 977) by acetaldehyde shows that alkylidene-urethanes, as well as arylalkylidene-urethanes give the additive reaction with  $\beta$ -carbonyl compounds.

*Urethanoethylideneacetylacetone*,  $\text{CHAc}_2 \cdot \text{CHMe} \cdot \text{NH} \cdot \text{CO}_2\text{Et}$ , prepared by the interaction of acetylacetone, urethane, and acetaldehyde (the last two compounds first reacting to give ethylidenebisurethane), forms radiating masses of white needles, m. p.  $77^\circ$ , gives the normal molecular weight in boiling benzene, exhibits neither acid nor basic reaction, and is highly stable towards mineral acids.

T. H. P.

**Chlorocamphornitrilic Acid.** JOHANN SCHEIBER and MAX KNOTHE (*Ber.*, 1912, 45, 1551—1553. Compare Bredt, this vol., i, 411).—Camphornitrilic acid is converted by aqueous sodium carbonate into camphanonitrile and camphanamide. Hydrogen cyanide is also produced, but camphonic acid could not be detected.

Chlorocamphornitrilic acid when placed in a bath at  $180$ — $190^\circ$  melts, becoming solid again on continued heating with the appearance of melting at  $240^\circ$ , followed by decomposition. When heated slowly, beginning at the ordinary temperature, it sinters at  $170^\circ$ . The product formed on heating at  $200^\circ$  is *chlorocamphorimide*,  $\text{CH}_2\text{—CCl—CO—CMe}_2\text{—CO—NH}$ , which crystallises in needles or platelets, decomp. above  $280^\circ$ . This is also obtained from chlorocamphornitrilic acid on treatment with concentrated hot hydrochloric acid.

E. F. A.

**Carbon Pernitride.** GEORGES DARZENS (*Compt. rend.*, 1912, 154, 1232—1234).—The formation and properties of carbon pernitride are described.

*Carbon pernitride*,  $\text{N}:\text{C}:\text{N} < \begin{smallmatrix} \text{N} \\ | \\ \text{N} \end{smallmatrix}$  or  $\text{N}:\text{C}:\text{N}:\text{N}:\text{N}$ , m. p.  $35.5$ — $36^\circ$ ,

formed by the action of cyanogen bromide on a well-cooled solution of sodium azoimide in water, forms colourless, odourless needles, soluble in water, alcohol, ether, or benzene, sparingly soluble in light petroleum. It sublimes slightly above its m. p. in a vacuum, but at  $70^\circ$  begins to decompose, and between  $170^\circ$  and  $180^\circ$  exploded with great violence. It is particularly sensitive to shock, and should only be prepared in small quantities. It is stable when pure, but in

presence of traces of bromine passes into a polymeride insoluble in ether; in aqueous solution it undergoes hydrolysis, furnishing eventually azoimide and carbon dioxide. Its heat of formation determined in a calorimetric bomb was  $-92.6$  cal., and that of the polymeride,  $-82.2$  cal.

T. A. H.

**The Composition of Potassium Ferrocyanide Gold-Baths.** ERNST BEUTEL (*Zeitsch. angew. Chem.*, 1912, 25, 995—998).—Potassium ferrocyanide gold-plating baths always contain alkali (sodium or potassium carbonate) to prevent the formation of Prussian-blue. Having previously studied the reaction between chlorauric acid and potassium ferrocyanide (Abstr., 1910, i, 723), the author has now investigated the effect of the addition of potassium carbonate in order to account for the phenomena observed with the above-mentioned bath. The action which takes place when the solution is boiled for a long time, oxygen being blown through the solution at intervals, is represented quantitatively by the equation:  $14\text{HAuCl}_4 + 10\text{K}_4\text{FeC}_6\text{N}_6 + 15\text{K}_2\text{CO}_3 + 5\text{O} + 10\text{H}_2\text{O} = 14\text{KAuCl}_4\text{N}_4 + 56\text{KCl} + 4\text{HCN} + 15\text{CO}_2 + 10\text{Fe}(\text{OH})_3$ . If the ferrocyanide is in excess, the following reaction takes place, some ferricyanide being formed:  $14\text{HAuCl}_4 + 14\text{K}_4\text{FeC}_6\text{N}_6 + 13\text{K}_2\text{CO}_3 + 7\text{O} + 10\text{H}_2\text{O} = 14\text{KAuCl}_4\text{N}_4 + 56\text{KCl} + 4\text{HCN} + 13\text{CO}_2 + 10\text{Fe}(\text{OH})_3 + 4\text{K}_3\text{FeC}_6\text{N}_6$ . In both these reactions the formation of the potassium auricyanide takes place slowly, and prolonged boiling is necessary.

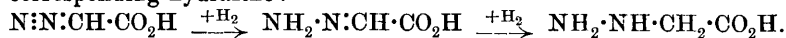
The above results show that the ferrocyanide plating-bath is really one of potassium auricyanide. The fiery, yellowish-green colour which it possesses is not due to the presence of gold, as has usually been supposed to be the case, but to the presence of potassium ferricyanide.

T. S. P.

**Reduction of Ethyl Diazoacetate.** AUGUST DARAPSKY and MORESHWAR PRABHAKAR (*Ber.*, 1912, 45, 1654—1665).—It was found previously that ethyl hydrazinophenylacetate is converted by nitrous acid into ethyl nitrosohydrazinophenylacetate, and this by sulphuric acid into ethyl triazophenylacetate (Darapsky, *Zeitsch. angew. Chem.*, 1910, 23, 2320), whereas Traube and Hoffa (Abstr., 1898, i, 235) found that ethyl hydrazinoacetate gave ethyl diazoacetate. The present paper describes better methods for the production of this ester, which forms a well-defined hydrochloride, and shows that the expected analogy with the phenylated compounds does also exist.

The hydrochloride of ethyl hydrazinoacetate is obtained in 40% yield by the interaction of hydrazine hydrate and monochloroacetic acid in alcohol, but a still better process, giving 90% yields, is the reduction of ethyl diazoacetate by means of sodium amalgam. Energetic reduction of this substance yields glycine, whilst ferrous sulphate produces the unstable ethyl hydrazacetate, the presence of this intermediate stage being also shown in the present process. The authors suggest that these reactions are best explained by adopting the open diazonium formula of Angeli and J. Thiele (Abstr., 1911, i, 845; 1912, i, 16) for fatty diazo-compounds. Hydraziacetic acid is therefore the

hydrazone of glyoxylic acid, which further reduction converts into the corresponding hydrazine:



An analogous case is the reduction of diazomethane to methylhydrazine (Pechmann, Abstr., 1895, i, 328). The free hydrazinoacetic acid (compare Traube and Hoffa, *loc. cit.*) may be obtained from the ester by means of baryta.

When the ester is treated with two molecules of nitrous acid, it breaks down into ethyl diazoacetate, a reaction which recalls the formation of a benzenediazonium salt by the action of nitrous acid on phenylhydrazine (Thiele, Abstr., 1908, i, 927). Curtius and Jay (Abstr., 1889, 340), by the reduction of ethyl diazoacetate with zinc and acetic acid, also obtained what are now regarded as indications of the formation of ethyl hydrazinoacetate, which shows another analogy between fatty and aromatic diazo-compounds, being comparable with E. Fischer's reduction of diazobenzene to phenylhydrazine.

When the hydrochloride of ethyl hydrazinoacetate is treated with one molecular proportion of sodium nitrite, the intermediate *ethyl nitrosohydrazinoacetate*,  $\text{NH}_2\cdot\text{N(NO)}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ , can be extracted with ether, which does not, however, effect complete extraction, as the substance is very soluble in water. It is a faint yellow oil producing a violet colour with ferric chloride. It partly decomposes on heating under reduced pressure, completely in the air, into nitrous oxide and ethyl aminoacetate; nitrous acid converts it into ethyl diazoacetate, and dilute sulphuric acid into ethyl triazoacetate.

J. C. W.

**Conversion of cycloHexane into Benzene.** RICHARD WILLSTÄTTER and DAVID HATT (*Ber.*, 1912, 45, 1464—1471).—The authors have applied the method of fission of ammonium bases at greatly reduced pressure (this vol., i, 17) to the introduction of three double bonds into cyclohexane.

For the preparation of cyclohexene, cyclohexanol was heated with oxalic acid (Zelinsky and Zelikoff, Abstr., 1902, i, 2). The yields were unsatisfactory, owing to the formation of considerable quantities of cyclohexyl oxalate, m. p. 42°. Better yields of cyclohexene were obtained from cyclohexanol and potassium hydrogen sulphate (compare Brunel, Abstr., 1905, i, 268), from which also small quantities of cyclohexyl ether, b. p. 239—240°/727 mm., 97—98·5°/8 mm., were isolated. For some unexplained reason, the latter compound is not identical with the cyclohexyl ether prepared by Ipatieff and Philipoff (Abstr., 1908, i, 342). cycloHexene was converted into its dibromide, from which, after heating with dimethylamine in benzene solution, dimethylamino- $\Delta^2$ -cyclohexene, b. p. 160·5—162·5°/725 mm., 89—91·5°/80 mm., was prepared. Its *platinichloride*, m. p. 185° (decomp.), and *methiodide*, m. p. 173—174°, were analysed. The corresponding ammonium base when heated under diminished pressure yielded trimethylamine and  $\Delta^{1,3}$ -cyclohexadiene, b. p. 78·3—78·8°/727 mm.,  $D_4^{20}$  0·8404,  $n_D^{20}$  1·47439,  $n_a^{20}$  1·47025,  $n_b^{20}$  1·48516,  $n_c^{20}$  1·49491. In the presence of platinum, it readily absorbed two molecules of hydrogen.

An examination of *cyclohexadiene* obtained from *cyclohexene*-dibromide and quinoline (Crossley, *Trans.*, 1904, **85**, 1403) showed it to be contaminated with *cyclohexene* (compare Harries and von Splawa-Neymann, *Abstr.*, 1909, i, 218), bromocyclohexene (compare Zelinsky and Gorsky, *Abstr.*, 1911, i, 847), and benzene.

From the product of the action of dibromocyclohexene on dimethylamine in cold benzene solution, *tetramethyldiamino- $\Delta^2$ -cyclohexene*, b. p. 90.5—92.5°/10 mm., 219.5—223.5°/725 mm.,  $D_4^{20}$  0.920, was isolated. Its *platinichloride*, darkening at about 240°, m. p. 259—260° (decomp.), and *methiodide*, m. p. 236° (decomp.), were examined. The corresponding quaternary base yielded trimethylamine and benzene on decomposition, this occurring at 98—104°/atmospheric pressure, 40—45°/20 mm., and -3 to +5°/0.008—0.02 mm. The benzene so obtained readily absorbed three molecules of hydrogen, and was in all respects identical with ordinary pure benzene. H. W.

**Hydrogenation of Aromatic Compounds by means of Platinum and Hydrogen.** RICHARD WILLSTÄTTER and DANIEL HART (*Ber.*, 1912, **45**, 1471—1481).—The quantitative hydrogenation of a variety of aromatic compounds has been studied. Full details of the method of preparing the platinum and of the arrangement of apparatus are given. In general, aromatic substances absorb hydrogen more slowly than do hydroaromatic or olefinic compounds, and hydrogenation appears to take place without the formation of intermediate compounds.

Chemically pure benzene is readily hydrogenated when dissolved in glacial acetic acid. In the absence of a solvent, it appears to possess a retarding influence on the activity of the platinum. The presence of a trace of thiophen completely inhibits absorption of hydrogen. Thiophen itself could not be hydrogenated. Commercial toluene and xylene are readily converted into methylcyclohexane and dimethylcyclohexane respectively. Durene is converted into 1 : 2 : 4 : 5-*tetramethylcyclohexane*, b. p. 169—170.5°/711 mm.,  $D_4^{20}$  0.825,  $D_4^{20}$  0.811,  $n_D^{20}$  1.44260,  $n_D^{20}$  1.44511,  $n_F^{20}$  1.45064,  $n_G^{20}$  1.45524. The purest commercial naphthalene could not be hydrogenated in glacial acetic acid solution, and was found to contain 0.25% sulphur. Pure naphthalene, on the other hand, readily absorbs hydrogen in ethereal, or more rapidly in glacial acetic acid, solution, with the formation of decahydronaphthalene, b. p. 188.5—190.5°/717 mm. (compare Leroux, *Abstr.*, 1904, i, 987). Phenol is converted into a mixture of cyclohexanol and cyclohexane. The reduction of aniline leads to the formation of ammonia, aminocyclohexane, and dicyclohexylamine, the *aurichloride* of which is described. Benzoic acid is readily reduced to cyclohexanecarboxylic acid. *m*-Chlorotoluene, dissolved in glacial acetic acid, readily reacts with hydrogen, but reaction ceases after the absorption of  $1\frac{1}{2}$  atoms, hydrogen chloride being simultaneously formed. The behaviour of allyl bromide is similar. Pure pyrrole is reduced to pyrrolidine in glacial acetic acid, but not in ethereal solution, whilst pyrrole which contains a trace of sulphur compounds is not so reducible. *iso*Hæmopyrrole can also be similarly hydrogenated. H. W.

**Bromination of Some Hydroaromatic Compounds.** FERNAND BODROUX and FELIX TABOURY (*Compt. rend.*, 1912, 154, 1514—1515. Compare Abstr., 1911, i, 533).—Bromine acting in the presence of aluminium bromide attacks 1-chloro-2-iodo-, 1-chloro-1:2-dibromo-, and 1:2-dichlorocyclohexane and various liquid di-, tri-, and tetrachlorocyclohexanes, forming in all cases hexabromobenzene. Chloro- $\Delta^1$ -cyclohexene behaves in the same way towards bromine. Tetrachlorocyclohexane, m. p. 173°, is, however, unacted on under the same conditions. A hydrocarbon, b. p. 80—81°, obtained by the action of quinoline on 1:2-dibromocyclohexane, yields hexabromobenzene when submitted to the above method of bromination. In cold chloroform solution, however, it yields a *tetrabromocyclohexane*, m. p. 85—86°, which is only slowly attacked by bromine containing 1% aluminium.

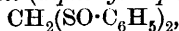
W. G.

**Sulphoxide and Sulphone Groups.** OSCAR HINSBERG (*J. pr. Chem.*, 1912, [ii], 85, 337—352).—Trimethylenetrisulphoxide and diphenylsulphoxidemethane possess acid properties and yield condensation products with diazonium salts; from this the conclusion is drawn that the sulphoxide group is an ionogen of the second order (compare Abstr., 1911, ii, 873).

*Trimethylenetrisulphoxide*,  $\text{SO} \begin{smallmatrix} \text{CH}_2 \cdot \text{SO} \\ \text{CH}_2 \cdot \text{SO} \end{smallmatrix} \text{CH}_2$ , prepared by oxidising trimethylene trisulphide with 30% hydrogen peroxide in glacial acetic acid solution, crystallises from water in colourless needles, which become brown at 235°, and have m. p. about 270° (decomp.). It decomposes explosively when rapidly heated, and is reduced by hydriodic acid or sodium hydrogen sulphite to the original trisulphide.

When warmed with alcoholic sodium ethoxide, it yields a *sodium salt*,  $\text{C}_3\text{H}_5\text{O}_3\text{S}_3\text{Na}$ , which forms a heavy, sandy powder and explodes at 120—130°. The sulphoxide dissolves in hydrochloric acid, forming an unstable *hydrochloride*, and condenses with benzaldehyde in the presence of sodium hydroxide, yielding an unstable, white, amorphous *substance*, m. p. 155—165° (decomp.). The *condensation products* with benzenediazonium chloride,  $\beta$ -naphthalenediazonium chloride, and diazotised  $\beta$ -naphthylamine-2:7-disulphonic acid are also described.

*Diphenylsulphoxidemethane (diphenylsulphinylmethane),*



prepared by oxidising diphenylthiolmethane with hydrogen peroxide in acetic acid solution at 0°, crystallises in prisms, m. p. 194°, and decomposes at a slightly higher temperature into diphenyl disulphide and formic acid. It dissolves in concentrated hydrochloric acid and also in alcoholic sodium ethoxide. It condenses with benzenediazonium chloride, yielding a brick-red *substance*,  $\text{C}(\text{SOPh})_2 \cdot \text{N} \cdot \text{NPh}$  or  $\text{CH}(\text{SOPh})_2 \cdot \text{N} \cdot \text{NPh}$ .

*Phenylsulphoxidephenylsulphonemethane*,  $\text{SO}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{SOPh}$ , is obtained by oxidising diphenylthiolmethane with 30% hydrogen peroxide and glacial acetic acid at the ordinary temperature. It forms thin, colourless prisms, m. p. 163° (decomp.).

With respect to the sulphone group,  $\cdot\text{SO}_2$ , it is pointed out that this differs from the other ionogenic groups of the second order in not

exerting a reactivating influence on adjacent methylene-hydrogen atoms; thus  $\beta$ -disulphones possess marked acid properties, but the methylene groups are not reactive. This difference is referred by the author to the difficulty with which the sulphones pass into the *aci*-form.

F. B.

**Preparation of Phenylcyclohexane and Dicyclohexyl; Direct Hydrogenation of Diphenyl.** PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1912, 154, 1390—1392).—Eykmán (Abstr., 1904, i, 26) obtained only phenylcyclohexane by direct hydrogenation of diphenyl in the presence of reduced nickel. The authors have repeated this experiment and find that this is the first step in the reduction, and that on submitting this product to further hydrogenation with a large excess of hydrogen at  $160^\circ$ , dicyclohexyl is obtained in a nearly pure state. Phenylcyclohexane and dicyclohexyl are best distinguished from one another by the action of a mixture of sulphuric and nitric acids in the cold. The former is violently attacked, giving solid nitro-compounds, whilst the latter is hardly acted on.

W. G.

**Passage of the Nitro-group from an Aliphatic Carbon Atom to the Benzene Nucleus.** GIACOMO PONZIO (*Gazzetta*, 1912, 42, i, 525—527).—The author has previously described two cases of intramolecular rearrangement in which the nitro-group passes from aliphatic carbon to the benzene nucleus; the  $\text{CH}\cdot\text{NO}_2$  group was originally united in one case to a phenyl and a nitro-group, and in the other to a phenyl group and a cyanogen group (Abstr., 1910, i, 192, 194).

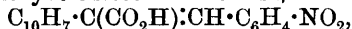
A similar rearrangement is now found to occur with  $\omega$ -nitrodiphenylmethane. On addition of a dilute aqueous solution of the potassium derivative of  $\omega$ -nitrodiphenylmethane (1 mol.) to a well-cooled dilute solution of benzenediazonium chloride (1 mol.) containing excess of sodium acetate, an amorphous, yellow precipitate immediately separates, which must be regarded as the azo-compound,  $\text{NO}_2\cdot\text{CPh}_2\cdot\text{N}_2\text{Ph}$ . But this is unstable and undergoes intramolecular transposition into benzophenone-*p*-nitrophenylhydrazone (compare Hyde, Abstr., 1899, i, 688). Such rearrangement favours the structure  $\text{:C}\cdot\text{NO}\cdot\text{OH}$  rather

than  $\text{:C}\begin{smallmatrix} \text{O} \\ \diagup \\ \text{N}\cdot\text{OH} \end{smallmatrix}$  for the *aci*-nitrohydrocarbons (compare Steinkopf and Jürgens, this vol., i, 152).

The tendency of the nitro-group to pass from the complex  $\text{:CH}\cdot\text{NO}_2$  to the benzene nucleus is shown also by the grouping  $\cdot\text{NH}\cdot\text{NO}_2$ , for example, nitroanilide,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{NO}_2$  or  $\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{NO}_2\text{H}$ , readily giving *p*-nitroaniline; here, too, the nitro-group passes preferably to the para-position.

T. H. P.

**New Synthesis of Chrysene.** RICHARD WEITZENBÖCK and HANS LIEB (*Monatsh.*, 1912, 33, 549—565).—On condensation of sodium 1-naphthylacetate with *o*-nitrobenzaldehyde in presence of acetic anhydride,  $\alpha$ -1-naphthyl-*o*-nitrocinnamic acid,



is obtained, which, when reduced, gives the corresponding amino-compound. When this is diazotised and the diazonium sulphate solu-

tion shaken with copper powder, a new six-carbon ring is formed, namely, chrysene-6-carboxylic acid. On distillation, carbon dioxide is eliminated and chrysene obtained.

From 2-naphthylacetic acid by a similar series of reactions a hydrocarbon, m. p. 158—160°, in all probability 3:4-benzphenanthrene, has been obtained. All five isomeric hydrocarbons,  $C_{18}H_{12}$ , composed of four benzene rings with not more than two carbon atoms in common, are now known.

*$\alpha$ -1-Naphthyl-o-nitrocinnamic acid* crystallises in yellow needles or granules, m. p. 173—174°.

*$\alpha$ -1-Naphthyl-o-aminocinnamic acid* forms almost colourless needles, m. p. 175—176°.

*Chrysene-6-carboxylic acid* separates in almost colourless needles, m. p. 222—223°.

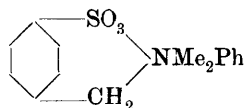
*$\alpha$ -2-Naphthyl-o-nitrocinnamic acid* crystallises in yellow needles, m. p. 177—178°.

*$\alpha$ -2-Naphthyl-o-aminocinnamic acid* also forms yellow needles, m. p. 191—192°.

3:4-Benzphenanthrene-1-carboxylic acid, purified by sublimation in a vacuum, crystallises in needles, m. p. 243°. When sublimed at the ordinary pressure, the hydrocarbon, m. p. 158—160°, is obtained; it forms colourless platelets after crystallisation from alcohol.

E. F. A.

#### Preparation of Phenylbenzyltrimethylammoniumsulphonic Acid.



FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 245535).—*Phenylbenzyltrimethylammoniumsulphonate* (annexed formula) is obtained by the methylation of calcium benzylmethylanilinesulphonate by the methods

previously described for the corresponding disulphonic acid (Abstr., 1911, i, 852).

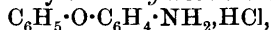
F. M. G. M.

**Some Physical Constants of cycloHexanol.** ROBERT DE FORCRAND (*Compt. rend.*, 1912, 154, 1327—1330).—The considerable variation in the m. p. ascribed to cyclohexanol is attributed to the facility with which this substance absorbs moisture. Dry cyclohexanol has b. p. 160.9° (corr.)/766 mm., m. p. 22.45°,  $D_4^{22.5}$  0.9471. It crystallises in well-defined, quadratic octahedra. At 11°, 100 parts of cyclohexanol dissolve 11.27 parts of water, whilst 100 parts of water dissolve 5.67 parts of cyclohexanol.

H. W.

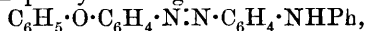
**New Colouring Matters Derived from *p*-Aminodiphenyl Ether.** ALPHONSE MAILHE (*Compt. rend.*, 1912, 154, 1240—1242).—The dyes obtained by diazotising the *p*-aminodiphenyl ether described already (this vol., i, 346) and treating the product with various amines, phenols, etc., are described.

*p*-Aminodiphenyl ether yields a *hydrochloride*,



m. p. 222°, and an *acetyl* derivative, m. p. 99°, crystallising in pearly leaflets. The diazotised product yields the following derivatives: with

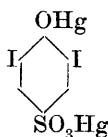
aniline, it gives the *azo*-compound,  $C_6H_5 \cdot O \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot NH_2$ , m. p.  $88^\circ$ , crystallising from alcohol in colourless needles, and giving red salts with acids. Diphenylamine gives the *azo*-derivative



m. p.  $38^\circ$ , crystallising in yellow leaflets and giving in alcohol an intensely bluish-violet solution with acids, which turns green with excess of acid, and then deposits *green crystals*, m. p.  $78^\circ$ . With dimethylaniline, the *product* obtained crystallises in green lamellæ, m. p.  $68^\circ$ , and forms a carmine-red solution with hydrochloric acid, a yellow solution with sulphuric acid, and dyes silk or wool a golden-yellow in acid solution.  $\alpha$ - and  $\beta$ -Naphthylamines yield a reddish-black *powder*, m. p.  $75^\circ$ , and a red *powder*, m. p.  $115^\circ$ , which in alcoholic solution are coloured violet and carmine-red respectively by sulphuric acid. With phenol the *compound*,  $C_6H_5 \cdot O \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot OH$ , m. p.  $118^\circ$ , yellow lamellæ, is formed; this gives a brown *mono-sulphonate*, which dyes silk or wool a dull brown. Resorcinol gives a *product*, m. p.  $75^\circ$ , crystallising in red needles.  $\beta$ -Naphthol yields a *substance* crystallising in yellow spangles. The naphtholsulphonic acids give *red dyes*, which dye cotton or wool directly carmine-red in acid baths.

In general, the *azo*-dyes derived from *p*-aminodiphenyl ether (phenoxyaniline) have a brighter tint than the corresponding aniline products, and melt at somewhat lower temperatures. T. A. H.

**Preparation of a Mercurous Salt of Di-iodophenol-*p*-sulphonic Acid.** H. TROMMSDORFF (D.R.-P. 245534).—*Mercurous di-iodophenol-p-sulphonate* (annexed formula) is obtained as a microcrystalline powder



when mercurous nitrate (524 parts) dissolved in cold nitric acid is treated with sodium di-iodophenol-*p*-sulphonate (484 parts); it has a neutral reaction, and differs in mercury content, therapeutic action, and in other respects from the previously prepared mercuric di-iodophenol-*p*-sulphonate. The temperature must not rise above  $30^\circ$  during the reaction. F. M. G. M.

**Separation of *m*- and *p*-Cresols.** F. HOFFMANN-LA ROCHE & Co. (D.R.-P. 245892).—Numerous methods for separating *p*- and *m*-cresols have previously been advocated. It is now found that if the crude sulphonated mixture (after suitable dilution) is extracted with benzene at about  $50^\circ$ , a separation is effected; the unsulphonated *p*-cresol is recovered from the benzene by evaporation, whilst any unsulphonated *m*-cresol is separated from the crystallised *m*-cresolsulphonic acid by treatment with steam. F. M. G. M.

**4-Amino-*o*-tolyl Mercaptan.** THEODOR ZINCKE and HEINRICH ROLLHAÜSER (*Ber.*, 1912, 45, 1495—1511).—The preparation and reactions of 4-amino-*o*-tolyl mercaptan have been investigated.

*Acetyl-p-toluidine-2-sulphonic acid*,  $NHAc \cdot C_6H_3Me \cdot SO_3H, H_2O$ , was prepared by the sulphonation of aceto-*p*-toluidide with fuming sulphuric acid. Its *potassium* salt,  $NHAc \cdot C_6H_3Me \cdot SO_3K, H_2O$ , was analysed. The latter, after being dehydrated, was transformed by means of

phosphorus pentachloride into *acetyl-p-toluidine-2-sulphonyl chloride*, m. p. 124°, from which the corresponding *anilide*, m. p. 220—221°, was obtained. By reduction with zinc dust, the chloride was converted into *4-acetyl-amino-o-tolyl mercaptan*, m. p. 95°. The acetyl group was eliminated from the latter by means of boiling hydrochloric acid, whereby the *hydrochloride* of 4-amino-o-tolyl mercaptan was obtained, which, when treated with sodium sulphide, yielded the free *base*, m. p. 47° (Hess, Abstr., 1881, 596, gives m. p. 42°), the *sulphate* and *diacetyl* derivative, m. p. 125°, of which were also examined.

4-Acetyl-amino-o-tolyl mercaptan was oxidised by ferric chloride to 4:4'-*diacetylaminoditolyl 2:2'-disulphide*, m. p. 220—221°, which, when boiled with aqueous-alcoholic hydrochloric acid, yielded the *hydrochloride* of 4:4'-*diaminoditolyl 2:2'-disulphide*, from which the free *base*, m. p. 94°, was liberated by means of ammonia.

4-Acetyl-amino-o-tolyl mercaptan was converted by methyl sulphate into 4-acetyl-amino-2-methylthioltoluene, m. p. 125—126°. The acetyl group was removed by hydrochloric acid, whereby 4-amino-2-methylthioltoluene, m. p. 47°, was obtained, the *hydrochloride* and *sulphate* of which were examined.

By the action of methyl iodide, 4-amino-2-methylthioltoluene was transformed into 2-methylthiol-p-tolyltrimethylammonium iodide, m. p. 200—202° (decomp.), which combined with bromine to yield a *perbromide*,  $C_{11}H_{18}NSIBr_2$ , m. p. 132° (decomp.), and with iodine to yield two *periodides*,  $C_{11}H_{18}NSI_2$  and  $C_{11}H_{18}NSI_4$ . When chlorinated in glacial acetic acid solution, it formed a *compound*, m. p. 168—170° (decomp.), the composition of which is approximately that required by the formula  $C_{11}H_{18}NSI_2Cl_4$ ; when boiled with water, this deposited yellow *needles*, m. p. 161° (decomp.), which corresponded approximately with the formula  $C_{11}H_{18}NSI_2Cl_2$ . 2-Methylthiol-p-tolyltrimethylammonium chloride, m. p. 134—137° (decomp.), was obtained when an aqueous solution of the corresponding iodide was heated with silver chloride. When the iodide was heated above its m. p., it decomposed with the formation of 4-dimethylamino-2-methylthioltoluene, b. p. 159°/17 mm., the *hydrochloride* of which was also analysed.

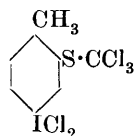
4-Amino-2-methylthioltoluene, when acted on by bromine in chloroform solution, yields a red bromine addition product, which, when dried and recrystallised from glacial acetic acid, was transformed into the *hydrobromide* of 5-bromo-4-amino-2-methylthioltoluene, from which the free *base*, m. p. 72—73°, was liberated by alkali. Its *acetyl* derivative, m. p. 122—123°, was prepared by the action of bromine in glacial acetic acid solution on 4-acetyl-amino-2-methylthioltoluene, and when hydrolysed by hydrochloric acid yielded the *hydrochloride* of the above bromo-compound.

4-Acetyl-amino-2-methylthioltoluene was converted by nitric acid (D 1.4) in glacial acetic acid solution into 5-nitro-4-acetyl-amino-2-methylthioltoluene, m. p. 163—164°, from which 5-nitro-4-amino-2-methylthioltoluene, m. p. 163°, was readily obtained. Stannous chloride reduced the latter to a *diamine*, which condensed with benzil to a *quinoxaline* derivative, m. p. 211—212°.

Hydrogen peroxide oxidised a solution of 4-acetyl-amino-2-methylthioltoluene in glacial acetic acid to *acetyl-p-toluidine-2-methylsulphoxide*, which separated from water +  $1\text{H}_2\text{O}$ , m. p. about  $150^\circ$ . The anhydrous substance has m. p.  $150-151^\circ$ . Potassium hydroxide transformed it into *p-toluidine-2-methylsulphoxide*, which crystallised from water +  $1\text{H}_2\text{O}$ , m. p.  $90-95^\circ$ , and from benzene in needles, m. p.  $120-121^\circ$ . Fuming hydrobromic acid converted each of the above-mentioned substances into an unstable *perbromide*, which readily passed into the hydrobromide of 5-bromo-4-amino-2-methylthioltoluene.

*Acetyl-p-toluidine-2-methylsulphone*, m. p.  $171^\circ$ , was obtained by the oxidation of 4-acetyl-amino-2-methylthioltoluene by excess of hydrogen peroxide or potassium permanganate. Hydrochloric acid hydrolysed it to *p-toluidine-2-methylsulphone*, m. p.  $91^\circ$ . When the above oxidation was accomplished by means of potassium permanganate, 4-acetyl-amino-2-methylsulphonebenzoic acid,  $\text{C}_{10}\text{H}_{11}\text{O}_5\text{NS}\cdot\text{H}_2\text{O}$ , m. p.  $260-261^\circ$ , was also formed. Oxidation of 4-amino-2-methylthioltoluene in glacial acetic acid solution by means of hydrogen peroxide yielded 2 : 2'-methylsulphone-4 : 4'-azoxytoluene, m. p.  $213-215^\circ$ .

4-Amino-2-methylthioltoluene was readily diazotised. Its *diazonium chloride* had m. p.  $70-72^\circ$ ; its *diazonium dichromate* was orange coloured. The former was readily transformed into 4-cyano-2-methylthioltoluene, m. p.  $57-58^\circ$ , which yielded the corresponding acid, m. p.  $169^\circ$ , on saponification. 4-Iodo-2-methylthioltoluene, b. p.  $176^\circ/16\text{ mm.}$ , D 1.53, was obtained from the diazonium chloride and potassium iodide. When treated with bromine in chloroform solution it yielded hydrobromic acid, together with a *perbromide* crystallising in red needles, which, on exposure to moist air, was converted into a mixture of 5-bromo-4-iodotolyl-2-methylsulphoxide, m. p.  $184^\circ$ , and 5-bromo-4-iodo-2-methylthioltoluene, m. p.  $72^\circ$ . The latter was more readily prepared by the action of chloroform and bisulphite on the *perbromide*.



4-Iodo-2-methylthioltoluene, when dissolved in chloroform and treated with dry chlorine, yielded 2-trichloromethylthioltolyl 4-iodochloride (annexed formula), which, when shaken with chloroform and potassium iodide, yielded 4-iodo-2-trichloromethylthioltoluene, m. p.  $44-45^\circ$ . Aniline transformed the latter into triphenylguanidine and 4-iodo-o-tolyl mercaptan, m. p.  $33-34^\circ$ .

**Syntheses in the Fatty Aromatic Series. IV. Mercaptans.** JULIUS VON BRAUN (*Ber.*, 1912, 45, 1563-1567. Compare Abstr. 1911, i, 968)—Homologues of benzyl mercaptan were prepared in order to study the influence of the fatty-aromatic group on the odour of the compound; the results prove that the sulphydryl group has by far the larger influence, even when the relatively small effect of the hydrocarbon residue,  $\text{C}_6\text{H}_5\cdot\text{CH}_2$ , is reinforced by increasing the number of methylene groups.

$\beta$ -Phenylethyl dithiourethane,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{S}\cdot\text{CS}\cdot\text{NH}_2$ , prepared by interaction of  $\beta$ -phenylethyl bromide with ammonium dithiocarbamate, crystallises in large, odourless platelets with silvery lustre, m. p.  $66^\circ$ . On heating under reduced pressure,  $\beta$ -phenylethyl mercaptan is formed.

This is better prepared by warming the dithiourethane with sodium hydroxide. It forms a colourless liquid, b. p.  $105^{\circ}/23$  mm., with a more disagreeable odour than benzyl mercaptan. The benzoyl derivative and disulphide are both oily.

$\gamma$ -Phenylpropyldithiourethane,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{S}\cdot\text{CS}\cdot\text{NH}_2$ , crystallises in colourless, odourless platelets, m. p.  $71^{\circ}$ .

$\gamma$ -Phenylpropyl mercaptan is a transparent liquid, b. p.  $109^{\circ}/10$  mm., very similar to the lower homologue.

$\epsilon$ -Phenylamylthiourethane forms a colourless, solid mass, m. p.  $75^{\circ}$ .

$\epsilon$ -Phenylamyl mercaptan has b. p.  $132$ — $134^{\circ}/10$  mm. The odour is exceptionally disagreeable.

E. F. A.

### Preparation of Acylarylaminonaphtholsulphonic Acids.

FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 245608).—6-Formylanilino-1-naphthol-3-sulphonic acid is readily prepared by the action of formic acid on 6-anilino-1-naphthol-3-sulphonic acid; it is isolated as a greyish-white mass; the sodium salt can be crystallised from dilute alcohol.

7-Formylanilino-1-naphthol-3-sulphonic acid is prepared in a similar manner from the isomeric aminonaphthol acid as a grey, resinous mass; these compounds combine readily with diazonium salts, but do not react with nitrous acid.

F. M. G. M.

Some cyclopentane Glycols. MARCEL GODCHOT and FÉLIX TABOURY (*Compt. rend.*, 1912, 154, 1625—1627. Compare Abstr., 1911, i, 385; this vol., i, 34).—cyclopentan-1:2-diol, already obtained by Meiser (Abstr., 1899, i, 741), can be obtained by converting the dibromide into the diacetate and hydrolysing this by alcoholic potash. It can also be obtained from the iodohydrin, which is prepared by the action of iodine and mercuric oxide on cyclopentene, by hydrolysis in the cold with potassium hydroxide, which produces the internal ether; this can be hydrated to the alcohol by heating with water for several hours at  $125^{\circ}$ . The latter method of preparation indicates a *cis*-configuration.

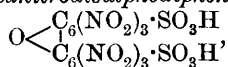
The *trans*-stereoisomeride can be obtained by the oxidation of cyclopentene with potassium permanganate; it has b. p.  $130^{\circ}/20$  mm., m. p.  $10^{\circ}$ ; diphénylurethane, m. p.  $195^{\circ}$ .

The dehydration of cyclopentanylcyclopentanol,  $\text{C}_5\text{H}_9\cdot\text{C}_5\text{H}_8\cdot\text{OH}$  (Godchot and Taboury, Abstr., 1911, i, 385), by distillation with zinc chloride yields a cyclopentanylcyclopentene, b. p.  $190^{\circ}$ ,  $D^{18}$  0.9183,  $n_D^{18}$  1.4953. Treatment with bromine in the presence of aluminium bromide converts this substance into a derivative,  $\text{C}_{10}\text{H}_8\text{Br}_6$ , m. p.  $308$ — $309^{\circ}$ . The hydrocarbon with bromine in carbon disulphide solution gives the dibromide, m. p.  $160^{\circ}$ , which can be hydrolysed by potassium carbonate to cyclopentanylcyclopentan-1:2-diol, b. p.  $189$ — $190^{\circ}$ , m. p.  $87$ — $88^{\circ}$ . As this is also obtainable from the cyclopentanylcyclopentene by the action of iodine and mercuric oxide with subsequent hydrolysis of the resultant iodohydrin by potassium carbonate, it is probably of *cis*-configuration.

D. F. T.

**Nitro-derivatives of Diphenylene Oxide.** ALPHONSE MAILHE (*Compt. rend.*, 1912, 154, 1515—1517).—Diphenylene oxide is attacked by fuming nitric acid, giving a viscous, brown mass; this on treatment with ether goes to a yellow powder, which by treatment with benzene and then with alcohol can be separated into three nitro-compounds: *Dinitrodiphenylene oxide*,  $\text{O} \begin{smallmatrix} \text{C}_6\text{H}_3\cdot\text{NO}_2 \\ | \\ \text{C}_6\text{H}_3\cdot\text{NO}_2 \end{smallmatrix}$ , m. p. 245°, in which the nitro-groups are probably *para* to the oxygen, *tetranitrodiphenylene oxide*,  $\text{O} \begin{smallmatrix} \text{C}_6\text{H}_2(\text{NO}_2)_2 \\ | \\ \text{C}_6\text{H}_2(\text{NO}_2)_2 \end{smallmatrix}$ , m. p. 168°, and *pentanitrodiphenylene oxide*,  $\text{O} \begin{smallmatrix} \text{C}_6\text{H}(\text{NO}_2)_3 \\ | \\ \text{C}_6\text{H}_2(\text{NO}_2)_2 \end{smallmatrix}$ , m. p. 122°, the first being the principal product. The dinitro-derivative on reduction with iron and acetic acid yields a *diamine*, m. p. 125°, which gives a red coloration with ferric chloride.

Further nitration of the polynitro-derivatives by means of a mixture of sulphuric and fuming nitric acids gives *hexanitrodiphenylene oxide*,  $\text{O} \begin{smallmatrix} \text{C}_6\text{H}(\text{NO}_2)_3 \\ | \\ \text{C}_6\text{H}(\text{NO}_2)_3 \end{smallmatrix}$ , m. p. 135°. No higher nitro-compound could be obtained, but the hexanitro-compound on warming with fuming sulphuric acid yields *hexanitrodisulphodiphenylene oxide*,



a white powder, m. p. 215°.

Nitration of diphenylene oxide in acetic acid solution yields the mononitro-derivative already described by Borsche and Bothe (*Abstr.*, 1908, i, 528).

W. G.

**Preparation of Homopiperonylamine.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 245523. Compare *Abstr.*, 1908, i, 901; 1911, i, 483).—Homopiperonylamine (*Abstr.*, 1906, i, 421), finds employment in the preparation of hydrastinine; it is now found that it can be readily prepared by the reduction of homopiperonal oxime with sodium amalgam in a mixture of equal parts of alcohol and acetic acid, and that the foregoing oxime can be obtained by the reduction of methylenedioxy- $\omega$ -nitrostyrene (obtained by the action of nitromethane on piperonal) with zinc dust in alcoholic acetic acid solution.

F. M. G. M.

**Action of Sodium Methoxide on Trinitroveratrole.** JAN J. BLANKSMA (*Chem. Weekblad*, 1912, 9, 440—441).—The constitution of the compound with m. p. 152° obtained from trinitroveratrole by the action of sodium methoxide (*Abstr.*, 1905, i, 277) is proved to be 5:6-dinitro-1:2:4-trimethoxybenzene. There is simultaneously formed the isomeride with m. p. 92°, 3:5-dinitro-1:2:4-trimethoxybenzene, the proportion of the first isomeride to the second being as 3:1.

The diethyl ether of 3:4:5-trinitrocatechol is converted by sodium ethoxide into 5:6-dinitro-1:2:4-triethoxybenzene, m. p. 133°.

A. J. W.

**Optically Active Phenylmethylcarbinols.** ROBERT H. PICKARD and JOSEPH KENYON (*Ber.*, 1912, 45, 1592—1593. Compare Holmberg, this vol., i, 448).—The value for the optical rotatory power of *d*-phenylmethylcarbinol given by Holmberg indicates that much racemisation had occurred in his material (compare Pickard, *Trans.*, 1911, 99, 45).

The two secondary octyl alcohols,  $[\alpha]_D^{20} \pm 9.9^\circ$ , are converted quantitatively into the corresponding bromo-compounds,  $[\alpha]_D^{20} \pm 27.5^\circ$ , from which by means of moist silver oxide the alcohols can be recovered. Some octylene is also formed. E. F. A.

**Search for Cholesterol in Java Petroleum.** WILHELM STEINKOPF, A. K. KOSS, and S. LIEBMANN (*Chem. Zeit.*, 1912, 36, 653—654. Compare Molinari and Fenaroli, *Abstr.*, 1908, i, 933, and Koss, *Abstr.*, 1911, i, 761).—Application of Windaus' digitonin test for cholesterol to the laevorotatory fractions of Java petroleum show that these do not contain cholesterol. It is further shown that on distilling petroleum containing cholesterol, the latter does not pass over in the lower fractions, so that if it occurs in petroleum it will probably be found in the portions boiling at about  $300^\circ$  under reduced pressure. These results show that the laevorotation of the lower boiling fractions of Java petroleum cannot be due to the presence of unchanged cholesterol, although it may be due to its decomposition.

T. A. H.

**New Halogen Derivatives of Cholesterol.** RICHARD KOLM (*Monatsh.*, 1912, 33, 447—450).—*Cholesteryl bromide*, prepared by the action of phosphorus tribromide on cholesterol in benzene solution, crystallises in nacreous platelets, m. p.  $98^\circ$ . A particularly fine play of colour is obtained on melting it and allowing it to cool again. It has  $[\alpha]_D^{19.5} - 19.14^\circ$ .

It reacts with bromine in acetic acid to form *tribromocholestan*,  $C_{27}H_{43}Br_3$ , which crystallises in well-formed, short prisms, m. p.  $111-112^\circ$ ,  $[\alpha]_D^{19} - 49.82^\circ$  without mutarotation.

Cholesteryl iodide has also been obtained.

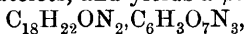
E. F. A.

**Preparation of Glycol Esters.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 245532).—When halogenated glycols are heated with benzoic or substituted benzoic acids (with the exception of salicylic acid), esterification readily occurs; the following compounds have been prepared.

*Ethylene o-toluate*, b. p.  $158^\circ/10$  mm.; *ethylene benzoate*, b. p.  $176-180^\circ/20$  mm., m. p.  $45^\circ$ , is prepared by heating sodium benzoate and ethylene glycol chlorohydrin together during three to four hours at  $145^\circ$ , or by heating  $\beta$ -chloroethyl benzoate during one or two hours with a concentrated solution of sodium acetate at  $130^\circ$ .

*Ethylene o-chlorobenzoate*, b. p.  $205^\circ/20$  mm., is obtained in a similar manner from ethylene dichloride and sodium *o*-chlorobenzoate, and *ethylene p-nitrobenzoate*, m. p.  $63^\circ$ , from *p*-nitrobenzoic acid and glycol in the presence of sulphuric acid. F. M. G. M.

**Condensation of Alkyl-*o*-toluidines with Carbonyl Chloride.** BERTHOLD RASSOW and OTTO REUTER (*J. pr. Chem.*, 1912, [ii], 85, 489—497).—A record of unsuccessful attempts to prepare tetramethyl-diaminodi-*o*-tolyl ketone by the interaction of carbonyl chloride and dimethyl-*o*-toluidine. When heated at 160° in the presence of aluminium chloride, these substances react, yielding (1) methyl chloride; (2) *s-di-o-tolyldimethylcarbamide*,  $\text{CO}(\text{NMe}\cdot\text{C}_6\text{H}_7)_2$ , which crystallises in lustrous, silvery leaflets, m. p. 90°, and yields a *tetranitro*-derivative as a yellow powder sintering at 80° (decomp. 110—115°); (3) *dimethyl-amino-o-toluo-N-methyl-o-toluidide*,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\text{Me}\cdot\text{CO}\cdot\text{NMe}\cdot\text{C}_6\text{H}_4\text{Me}$ , which forms rhombic platelets, and yields a *picrate*,



crystallising in needles, m. p. 158°.

*s-Di-o-tolyldiethylcarbamide*,  $\text{CO}(\text{NEt}\cdot\text{C}_6\text{H}_7)_2$ , prepared by heating *N*-ethyl-*o*-toluidine with carbonyl chloride in the presence of aluminium chloride, has m. p. 37—39°, b. p. 188°/12 mm. F. B.

***aa'*-Ethylenebisimino-acids.** N. SCHLESINGER (*Ber.*, 1912, 45, 1486—1493. Compare Abstr., 1911, i, 427).—*aa'*-Ethylenebisimino-phenylacetoneitrile,  $\text{C}_2\text{H}_4(\text{NH}\cdot\text{CHPh}\cdot\text{CN})_2$ , m. p. 122—123°, is prepared by the addition of benzaldehyde to a methyl alcoholic-aqueous solution of potassium cyanide and ethylenediamine hydrochloride. Its *hydrochloride* decomposes at about 148—154°. Boiling dilute mineral acids transform the nitrile into benzaldehyde, hydrogen cyanide, and ethylenediamine. Hydrolysis to the corresponding *acid* can be effected, however, by treatment of the nitrile with a mixture of concentrated sulphuric acid and fuming hydrochloric acid at the ordinary temperature and subsequent boiling of the diluted solution. It undergoes no apparent change when heated to 250°. Its *hydrochloride* is very sparingly soluble in water. Its *copper* salt,  $\text{C}_{18}\text{H}_{18}\text{O}_4\text{N}_2\text{Cu}$ , was analysed. Its *methyl* ester, prepared by the Fischer-Speier method, forms a viscous, yellow liquid, which decomposes when heated, even under diminished pressure, and has  $D_4^{20}$  1.1501,  $n_D^{20}$  1.5448. The similar *ethyl* ester has  $D_4^{20}$  1.1091,  $n_D^{20}$  1.5320, and forms a crystalline *hydrochloride* when its ethereal solution is treated with dry hydrogen chloride.

*aa'*-Ethylenebisiminopropionitrile *hydrochloride*,  $\text{C}_8\text{H}_{14}\text{N}_4\cdot 2\text{HCl}$ , is obtained when dry hydrogen chloride is passed into a dry ethereal solution of the product of the reaction of ethylenediamine hydrochloride, acetaldehyde, and potassium cyanide. Aqueous acids hydrolyse it completely. A mixture of concentrated sulphuric acid and fuming hydrochloric acid converts it into the corresponding *acid*, m. p. about 262° (decomp.), from which the *hydrochloride*, m. p. about 214° (decomp.), *copper* salt,  $\text{C}_8\text{H}_{14}\text{O}_4\text{N}_2\text{Cu}$ , and *ethyl* ester were prepared. The latter has b. p. 170°/14 mm.,  $D_4^{20}$  1.0297,  $n_D^{20}$  1.4483, and appears to be slightly impure.

In a similar manner, *aa'*-ethylenebisimino- $\alpha$ -phenylpropionitrile,  $\text{C}_2\text{H}_4(\text{NH}\cdot\text{CMePh}\cdot\text{CN})_2$ , m. p. 108—109° (decomp.), is formed by the reaction of ethylenediamine hydrochloride, potassium cyanide, and acetophenone. A mixture of concentrated sulphuric and fuming hydrochloric acids transforms it into the corresponding *acid*, the *hydro*-

*chloride* and *copper* salt of which are also described. This acid cannot apparently be esterified by the Fischer-Speier method.

*aa'-Ethylenebisiminodiphenylacetonitrile*,  $C_2H_4(NH \cdot CPh_2 \cdot CN)_2$ , is slowly formed in poor yield when ethylenediamine hydrochloride, benzophenone, and potassium cyanide react at the ordinary temperature in aqueous-methyl alcoholic solution. It melts indefinitely at  $158-163^\circ$  (decomp.). Its hydrolysis has not been effected. H. W.

**Diphenylisopropylacetic [*aa*-Diphenyl- $\beta$ -methylbutyric] Acid.** (Mme.) PAULINE RAMART-LUCAS (*Compt. rend.*, 1912, 154, 1617-1620).—The acid obtained earlier (Ramart-Lucas, this vol., i, 449) is monobasic, giving a silver salt,  $C_{17}H_{17}O_2Ag$ , and on treatment with thionyl chloride gives an *acid chloride*,  $C_{17}H_{17}OCl$ , m. p.  $95-96^\circ$ ; this is converted by ammonia into the *amide*, needles, m. p.  $149^\circ$ . It is therefore possibly a diphenyldimethylpropionic acid or *aa*-diphenyl- $\beta$ -methylbutyric acid; the properties do not agree with those of the  $\beta\beta$ -diphenyl-*aa*-dimethylpropionic acid already described by Nef (*Abstr.*, 1902, i, 8), and so attempts were made to synthesise *aa*-diphenyl- $\beta$ -methylbutyric acid for the purpose of comparison.

The condensation of dimethylpyruvic acid with benzene gives an acid, m. p.  $150-151^\circ$ , which proves to be identical with the dimethylatropic acid,  $CMe_2 \cdot CPh \cdot CO_2H$ , of Blaise and Courtot (*Abstr.*, 1906, i, 794); it is evidently produced here by the elimination of a molecule of water from the primarily formed *a*-isopropylmandelic acid.

By the action of diphenylacetyl chloride on excess of benzene in the cold, the main product obtained is triphenylvinyl alcohol,  $CPh_2 \cdot CPh \cdot OH$  (compare Biltz, *Abstr.*, 1893, i, 718), but in the warm the product is the ketonic isomeride diphenylacetophenone,  $CHPh_2 \cdot CPh$  (oxime, m. p.  $180^\circ$ ; compare Kohler, *Abstr.*, 1906, i, 756). All endeavours to introduce the isopropyl group into either of these substances were unsuccessful, the sodium amide causing scission into diphenylmethane and benzamide.

By treating diphenylacetonitrile with sodium amide and isopropyl iodide in benzene, *aa*-diphenyl- $\beta$ -methylbutyronitrile is obtained as a viscous liquid, b. p.  $193-195^\circ/15$  mm., which can be hydrolysed by a mixture of hydrochloric and acetic acids to *aa*-diphenyl- $\beta$ -methylbutyric acid, m. p.  $163^\circ$ , and the *anhydride*, m. p.  $166^\circ$ ; a neutral substance,  $C_{16}H_{16}O_2$ , m. p.  $109-110^\circ$ , is obtained as a by-product. The acid is not identical with the acid the constitution of which is under investigation. D. F. T.

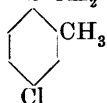
**Preparation of Acetonechloroform Acetylsalicylate [*o*-Acetoxybenzoate].** RICHARD WOLFFENSTEIN (D.R.-P. 245533).—*Acetonechloroform o-acetoxybenzoate*, fine needles, m. p.  $54-57^\circ$  (sintering about  $49^\circ$ ), b. p. about  $185^\circ$  in a vacuum, with partial decomposition, is readily prepared by heating acetonechloroform with *o*-acetoxybenzoyl chloride in the presence of a tertiary base, such as quinoline; it is of therapeutic value. F. M. G. M.

**Preparation of Menthyl Acetylsalicylate [*o*-Acetoxybenzoate].** KONTOR CHEMISCHER PRÄPARATE ERNST ALEXANDER (D.R.-P. 244787).—*Menthyl o-acetoxybenzoate*, an odourless, tasteless liquid,

D<sup>15</sup> 1.0635, b. p. 212—215°/14 mm., is obtained by treating menthyl salicylate (prepared from menthol and salicylic acid) with the ordinary acetylating agents. The following yields are obtainable: with acetyl chloride in xylene, 75%; acetic acid with sulphuric acid, 60%, and with acetic anhydride, 90—95%. F. M. G. M.

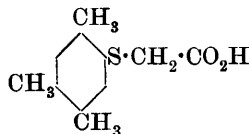
[Preparation of 3:4-Dichlorophenylthiolacetic Acid.] KALLE & Co. (D.R.-P. 245633).—3:4-Dichlorophenylthiolacetic acid, colourless needles, is prepared from 3:4-dichloroaniline by methods described previously; when treated with fuming sulphuric acid, it furnishes a dye in the form of a violet powder. F. M. G. M.

Preparation of 4-Chloro-*o*-tolylthiolacetic Acid. KALLE & Co. (D.R.-P. 245631. Compare this vol., i, 354).—4-Chloro-*o*-tolylthiolacetic acid (annexed formula), colourless needles, is prepared from *p*-chloro-*o*-toluidine; the dye it furnishes with sulphuric acid is a bluish-red powder and suitable for wool or cotton. F. M. G. M.

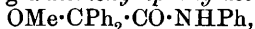


[Preparation of 4-Chloro-*m*-tolylthiolacetic Acid.] KALLE & Co. (D.R.-P. 245632).—4-Chloro-*m*-tolylthiolacetic acid, colourless needles, is prepared from *p*-chloro-*m*-toluidine; when treated with fuming sulphuric acid it furnishes a reddish-violet powder, the tinctorial properties of which are described in the original. F. M. G. M.

[Preparation of  $\psi$ -Cumylthiolacetic Acid.] KALLE & Co. (D.R.-P. 245630. Compare this vol., i, 354).— $\psi$ -Cumylthiolacetic acid (annexed formula), colourless needles, is prepared by previously described methods from  $\psi$ -cumidine; the dye formed by treating it with concentrated or fuming sulphuric acid is a dark violet powder, which dyes cotton a bluish-violet shade, and wool a violet-red tone. F. M. G. M.

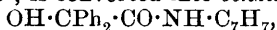


Derivatives of Benzilic Acid and of Chlorodiphenylacetic Acid. HEINRICH KLINGER (*Annalen*, 1912, 389, 253—264).— $\alpha$ -Chlorodiphenylacetanilide,  $\text{CPh}_2\text{Cl}\cdot\text{CO}\cdot\text{NHPh}$ , m. p. 88°, is prepared from aniline and chlorodiphenylacetyl chloride in ether. Its chlorine is very reactive, and is easily substituted by boiling methyl or ethyl alcohol, yielding  $\alpha$ -methoxydiphenylacetanilide,



m. p. 149—150°, rhombic crystals [ $a:b:c=0.64344:1:0.48788$ ], or  $\alpha$ -ethoxydiphenylacetanilide, m. p. 130—131°.  $\alpha$ -Anilinodiphenylacetanilide,  $\text{NHPh}\cdot\text{CPh}_2\cdot\text{CO}\cdot\text{NHPh}$ , m. p. 181—182°, obtained by warming chlorodiphenylacetanilide and aniline (4 mols.) on the water-bath, yields by hydrolysis benzilanilide,  $\text{OH}\cdot\text{CPh}_2\cdot\text{CO}\cdot\text{NHPh}$ , m. p. 175°, monoclinic crystals [ $a:b:c=0.97296:1:0.89641$ ;  $\beta=86^\circ 16' 47''$ ].

$\alpha$ -*p*-Toluidinodiphenylaceto-*p*-toluidide,  $\text{C}_7\text{H}_7\cdot\text{NH}\cdot\text{CPh}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$ , m. p. 168°, obtained from  $\alpha$ -chlorodiphenylacetyl chloride and *p*-toluidine at 125—130°, is converted into benzilo-*p*-toluidide,



m. p. 189—190°, by boiling concentrated hydrochloric acid. When gently warmed and finally heated at 150°,  $\alpha$ -chlorodiphenylacetyl chloride and methylaniline (4 mols.) yield  $\alpha$ -methylanilindiphenylacetomethylanilide,  $\text{NMePh} \cdot \text{CPh}_2 \cdot \text{CO} \cdot \text{NMePh}$ , m. p. 212°.

Ethyl  $\alpha$ -chlorodiphenylacetate and methyl  $\alpha$ -chlorodiphenylacetate (impure), obtained by passing hydrogen chloride into an ethyl or methyl-alcoholic solution of benzoic acid, yield with *p*-toluidine on the water-bath ethyl  $\alpha$ -*p*-toluidinodiphenylacetate,  $\text{C}_7\text{H}_7 \cdot \text{NH} \cdot \text{CPh}_2 \cdot \text{CO}_2\text{Et}$ , m. p. 137°, monoclinic crystals [ $a:b:c = 1.4383:1:0.9503$ ;  $\beta = 48^\circ 25' 58''$ ], or the methyl ester, m. p. 134—135°.  $\alpha$ -*p*-Toluidinodiphenylacetic acid, obtained by the hydrolysis of the preceding esters, has decomp. 150°. C. S.

Diphenyleneglycollic,  $\alpha$ -Chlorodiphenyleneacetic, and  $\alpha$ -Bromodiphenyleneacetic Acids. HEINRICH KLINGER (*Annalen*, 1912, 389, 237—253)—Diphenyleneglycollic acid is obtained in 94% yield by heating phenanthraquinone with 10 parts of 20% sodium hydroxide for two and a-half to three hours at 70—80° in a current of air. It has m. p. 166—167°, and forms a methyl ester, m. p. 159°. This ester or the ethyl ester is obtained by passing a little hydrogen chloride into a dilute methyl or ethyl alcoholic solution (1:25) of the acid; with more concentrated solutions, at higher temperatures, and with an increased quantity of hydrogen chloride, the alcoholic hydroxyl group of the acid is replaced by chlorine; thus a solution of the acid in methyl alcohol (1:5), saturated at 0° with hydrogen chloride and then heated at 100° for six hours, yields methyl  $\alpha$ -chlorodiphenyleneacetate [9-chlorofluorene-9-carboxylate],  $\begin{matrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{matrix} > \text{CCl} \cdot \text{CO}_2\text{Me}$ ,

m. p. 113°, which is also prepared by the action of chlorodiphenyleneacetyl chloride on cold methyl alcohol. Chlorodiphenyleneacetamide, obtained from the chloride and cold ethereal ammonia, has m. p. 194°. Chlorodiphenyleneacetyl chloride and aniline (2 mols.) in ether yield chlorodiphenyleneacetanilide, which is converted into  $\alpha$ -ethoxydiphenyleneacetanilide,  $\begin{matrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{matrix} > \text{C}(\text{OEt}) \cdot \text{CO} \cdot \text{NHPh}$ , m. p. 129°, by prolonged boiling with alcohol. The chloride and aniline (4 mols.) in ether yield  $\alpha$ -anilindiphenyleneacetanilide,  $\begin{matrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{matrix} > \text{C}(\text{NHPh}) \cdot \text{CO} \cdot \text{NHPh}$ , m. p. 199—200°, which is scarcely attacked by boiling concentrated hydrochloric acid, but is converted into diphenyleneglycollanilide, m. p. 247°, by hydrochloric acid at 110—120°.

$\alpha$ -Bromodiphenyleneacetyl bromide,  $\begin{matrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{matrix} > \text{CBr} \cdot \text{COBr}$ , m. p. 137—138°, yellow prisms, obtained from diphenyleneglycollic acid and phosphorus pentabromide, is converted into methyl  $\alpha$ -bromodiphenyleneacetate, m. p. 108.5—109°, or the ethyl ester, m. p. 76°, by cold methyl or ethyl alcohol, into  $\alpha$ -bromodiphenyleneacetamide, m. p. 175°, by ammonia in benzene, and into  $\alpha$ -bromodiphenyleneacetanilide, m. p. 166°, by aniline in cold benzene. C. S.

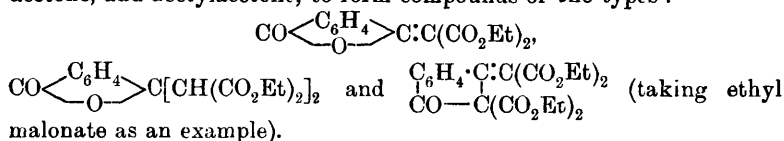
**Methylcarbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetic Operations.** VI. **Partial Methylation of Phenolcarboxylic Acids.** EMIL FISCHER and OTTO PFEFFER (*Annalen*, 1912, 389, 198—214. Compare Abstr., 1911, i, 874).—The ortho-methylated derivatives of gentisic,  $\beta$ -resorcylic, and phloroglucinolcarboxylic acids have been obtained by treating the methylcarbonato-derivatives with diazomethane and hydrolysing the products.

5-Methylcarbonato-2-hydroxybenzoic acid is converted by cold ethereal diazomethane by rapid treatment into *methyl 5-methylcarbonato-2-hydroxybenzoate*,  $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{CO}_2\text{Me}$ , colourless needles, m. p.  $75\text{--}76^\circ$  (corr.) (reddish-violet coloration with alcoholic ferric chloride), and by prolonged treatment (twenty hours at  $25^\circ$ ) into *methyl 5-methylcarbonato-2-methoxybenzoate*, m. p.  $92\text{--}93^\circ$  (corr.). The latter does not develop a coloration with ferric chloride, and in alcoholic solution is converted by 2*N*-sodium hydroxide on the water-bath, and subsequent acidification, into *5-hydroxy-2-methoxybenzoic acid*, m. p.  $155\text{--}156^\circ$  (corr.). In a similar manner, by prolonged treatment with ethereal diazomethane at  $25^\circ$ , 4-methylcarbonato-2-hydroxybenzoic acid yields *methyl 4-methylcarbonato-2-methoxybenzoate*, m. p.  $64\text{--}65^\circ$  (corr.), the hydrolysis of which by 2*N*-sodium hydroxide (4 mols.) at  $25^\circ$  for twenty-four hours and subsequent acidification followed by treatment of the product with 8% potassium hydrogen carbonate yields *4-hydroxy-2-methoxybenzoic acid*, m. p.  $185\text{--}187^\circ$  (decomp. corr.). *Methyl 4-methylcarbonato-2:6-dimethoxybenzoate*, m. p.  $105\text{--}106^\circ$  (corr.), obtained from 4-methylcarbonato-2:6-dihydroxybenzoic acid and ethereal diazomethane, is hydrolysed by 2*N*-sodium hydroxide at  $25^\circ$ , yielding *methyl 4-hydroxy-2:6-dimethoxybenzoate*, m. p.  $189^\circ$  (corr.), which is then hydrolysed by concentrated sulphuric acid at  $25^\circ$  to *4-hydroxy-2:6-dimethoxybenzoic acid*, decomp.  $175^\circ$  (corr.). By direct hydrolysis with cold concentrated sulphuric acid, *methyl 4-methylcarbonato-2:6-dimethoxybenzoate* yields *4-methylcarbonato-2:6-dimethoxybenzoic acid*, m. p.  $160^\circ$  (corr.). It has been found that the methylcarbonato-derivatives of other phenolcarboxylic acids are stable to cold concentrated sulphuric acid.

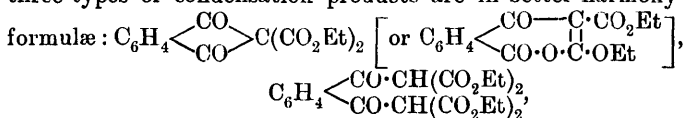
*Methyl 3:5-dimethylcarbonato-4-methoxybenzoate*, m. p.  $66\text{--}67^\circ$ , obtained from 3:5-dimethylcarbonato-4-hydroxybenzoic acid and diazomethane, is hydrolysed by 2*N*-sodium hydroxide at  $40^\circ$  in an atmosphere of hydrogen, yielding after acidification 3:5-dihydroxy-4-methoxybenzoic acid.  
C. S.

**Phthalyl Chloride.** JOHANNES SCHEIBER (*Annalen*, 1912, 389, 121—168).—The asymmetric constitution,  $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CCl}_2 \\ \text{CO}\end{smallmatrix}\right\rangle\text{O}$ , of phthalyl chloride is based on, amongst other evidence, its behaviour on reduction, its interaction with benzene to form phthalophenone in the Friedel-Crafts' reaction, the formation of diethylphthalide from the chloride and zinc ethyl, and its condensation with the sodium derivatives of substances containing the group  $\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot$ , such as ethyl malonate, ethyl acetoacetate, ethyl benzoylacetate, ethyl cyanoacetate, benzoyl-

acetone, and acetylacetone, to form compounds of the types :



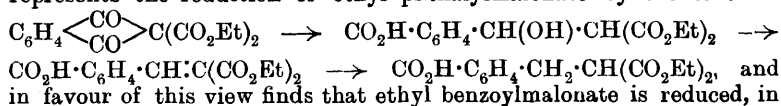
The author is of opinion, however, that this evidence is by no means conclusive. The formation of phthalophenone from phthalyl chloride, benzene, and aluminium chloride is conditioned by the temperature, since in cold carbon disulphide the chief product of the reaction is benzoylbenzoic acid, the formation of which is evidence in favour of the symmetric constitution of phthalyl chloride. Again, the formation of the preceding three types of condensation products has been regarded as proving the asymmetric constitution of phthalyl chloride (compare Bülow, *Abstr.*, 1905, i, 529). The constitutions of these products are deduced from their behaviour on hydrolysis, on reduction by zinc and acetic acid, and additive behaviour with sodium ethoxide. The author shows, however, that the properties and behaviour of the three types of condensation products are in better harmony with the formulæ :



and  $\text{C}_6\text{H}_4 \begin{array}{c} \text{C}[:\text{C}(\text{CO}_2\text{Et})_2] \\ \diagup \quad \diagdown \\ \text{C}[:\text{C}(\text{CO}_2\text{Et})_2] \end{array} \text{O}$ , which represent the products as derivatives of a phthalyl chloride of symmetric structure. The only way in which products of the first type can be derived from a phthalyl chloride of asymmetric structure is for the initially formed phthalide derivatives to change to substituted indandiones by a process similar to that whereby benzylidenephthalide is converted into 2-phenyl-indandione. This rearrangement, however, requires the presence of alcohol (Eibner, *Abstr.*, 1906, i, 588). The author shows that in ethereal solution benzylidenephthalide is unchanged by ethyl sodioacetoacetate, and acetylidenephthalide is not rearranged to 2-acetyl-indandione by sodioacetylacetone.

The proposed new formulæ of substances of the first-mentioned type explain the behaviour of these substances on hydrolysis, particularly the formation of phthalamide by hydrolysis with ammonia. With regard to the action of zinc and acetic acid, Wislicenus regards the change  $\text{CO} \begin{array}{c} \text{C}_6\text{H}_4 \\ \diagup \quad \diagdown \\ \text{O} \end{array} \text{C}:\text{C}(\text{CO}_2\text{Et})_2 \rightarrow \text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{Et})_2$

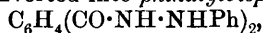
as conclusive evidence of the constitution of ethyl phthalylmalonate. It is open to question, however, whether substances with such constitutions undergo reduction and fission as indicated; for example, benzylidenephthalide is unchanged by zinc and acetic acid. The author represents the reduction of ethyl phthalylmalonate by the scheme :



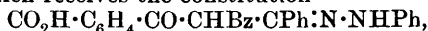
part, to ethyl benzylmalonate by zinc and boiling acetic acid. The constitution,  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C}:\text{CAcBz}$ , of phthalylbenzoylacetone cannot be regarded as definitely proved by the reduction of the substance to phthalidylbenzoylacetone (Bülow and Koch, Abstr., 1904, i, 321), because the similarly constituted compounds, ethyl phthalylmalonate and ethyl phthalylacetoacetate, do not yield phthalidyl derivatives by reduction; the former yields a little ethyl *o*-carboxybenzylmalonate, whilst the latter is converted partly into an isomeride, m. p. 96—97° (see below), partly into ethyl *o*-carboxybenzylacetoacetate.

The fact that the additive compound of ethyl phthalylmalonate and sodium ethoxide yields by acidification a substance which develops an intense red coloration with ferric chloride, is in favour of the author's new constitution of ethyl phthalylmalonate, which permits of the production of an additive compound,  $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CH}(\text{CO}_2\text{Et})_2$  or  $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{C}(\text{CO}_2\text{Et}) : \text{C}(\text{OH}) \cdot \text{OEt}$ , containing, or giving by enolisation, a hydroxyl group. The properties of the additive compound of sodium ethoxide and ethyl phthalylacetoacetate are explained best by ascribing to the latter the constitution  $\text{C}_6\text{H}_4 \langle \text{CO} \rangle \text{CAc} \cdot \text{CO}_2\text{Et}$ ,

rather than  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C}:\text{CAc} \cdot \text{CO}_2\text{Et}$ . Bülow's phenylhydrazone, m. p. 236°, of ethyl phthalylacetoacetate (Abstr., 1905, i, 529) is shown to be a pyrazole derivative. Also the so-called bishydrazones obtained by Bülow and Koch from phthalylbenzoylacetone and phenylhydrazine, *p*-nitrophenylhydrazine, and *p*-bromophenylhydrazine respectively in boiling acetic acid (*loc. cit.*) are proved to be anilino-phthalimides,  $\text{C}_6\text{H}_4 \langle \text{CO} \rangle \text{N} \cdot \text{NHAr}$ , since the same substances are produced from phthalic anhydride and the corresponding hydrazine. The fission which phthalylbenzoylacetone must have undergone to yield these anilinophthalimides is also experienced by ethyl phthalylmalonate and by ethyl phthalylcyanoacetate under similar conditions. Both substances are converted into *phthalylbisphenylhydrazide*,



m. p. 161°, by phenylhydrazine; the former, however, in cold glacial acetic acid solution yields anilinophthalimide. *Phthalylidibenzoylmethane*,  $\text{C}_{23}\text{H}_{14}\text{O}_4$ , m. p. 162°, prepared from sodiodibenzoylmethane and phthalyl chloride in cold ether, reacts with phenylhydrazine in acetic acid or ether to form a *substance*, m. p. 234—236°, yellowish-red crystals, which receives the constitution

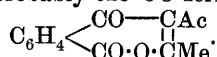


because it is soluble in sodium carbonate and develops a red coloration with ferric chloride, but does not respond to Bülow's reaction.

Ethyl phthalylmalonate and ethyl phthalylacetoacetate do not react additively with bromine or with ethyl diazoacetate. Ethyl  $\alpha$ -cyano-cinnamate and ethyl diazoacetate react at 100° to form nitrogen and *ethyl  $\alpha$ -cyano- $\gamma$ -phenylcyclopropan- $\alpha$ , $\beta$ -dicarboxylate*, a viscous oil.

By treatment with boiling glacial acetic acid for two hours, ethyl phthalylacetoacetate, m. p. 124°, is converted into an *isomeride*, m. p. 96—97°, colourless needles, which is reconverted into the original sub-

stance by a suspension of ethyl sodioacetoacetate in boiling ether. Both isomerides yield the same pyrazole and behave alike towards sodium ethoxide and towards zinc and acetic acid. The constitutions  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} CAc \cdot CO_2Et$  and  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} \begin{smallmatrix} C \\ | \\ CO \cdot O \cdot CMe \end{smallmatrix} \cdot CO_2Et$  are proposed for the esters, m. p.  $124^\circ$  and  $96-97^\circ$  respectively. In a similar manner, phthalylbenzoylacetone, m. p.  $175^\circ$ ,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} CAcBz$ , is converted into an *isomeride*, m. p.  $102^\circ$ ,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} \begin{smallmatrix} C \\ | \\ CO \cdot O \cdot CMe \end{smallmatrix} \cdot CBz$ . The two known forms of ethyl phthalylecyanoacetate, m. p.  $190-192^\circ$  and  $140-141^\circ$  respectively, are represented by the formulæ  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C(CN) \cdot CO_2Et$  and  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} \begin{smallmatrix} C \\ | \\ CO \cdot O \cdot CMe \end{smallmatrix} \cdot CN$ . Ethyl phthalylmalonate, phthalylacetylacetone, and phthalyl dibenzoylmethane have been obtained only in one form; the first and the last are respectively represented by the formulæ  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C(CO_2Et)_2$  and  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} CBz_2$ , whilst phthalylacetylacetone is probably the OC-derivative,



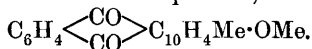
Bülow and Deseniss obtained phthalylacetylacetone in 50% and 1:3-diketo-2-acetylhydriindene in 15-20% yield by adding phthalyl chloride (1 mol.) to an ethereal suspension of sodioacetylacetone (2 mols.) (Abstr., 1905, i, 42). The yields are 75% and 5-10% respectively when the order of the addition is reversed; the yield of diketoacetylhydriindene is increased by working at a higher temperature and by lessening the proportion of phthalyl chloride. Phthalyl chloride and ethyl sodioacetoacetate in ether react to form, in the proportions 1:1 or 1:2, the two forms, m. p.  $124^\circ$  and  $96-97^\circ$  respectively, of ethyl phthalylacetoacetate, in the proportions 1:3, *ethyl phthaloxyl diacetoacetate*,  $C_6H_4 \begin{smallmatrix} \diagup C(:CAc \cdot CO_2Et) \\ \diagdown C(:CAc \cdot CO_2Et) \end{smallmatrix} O$ , m. p.  $112^\circ$ , and in the proportions 1:4, ethyl phthalyl diacetoacetate.

[With P. OPPERMANN.]—As an additional argument in favour of the symmetric structure of phthalyl chloride, the authors advance the fact that its ultraviolet absorption spectrum is similar to those of ethyl phthalate and *isophthalyl* chloride. C. S.

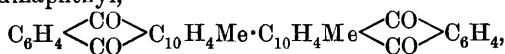
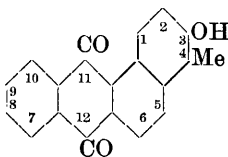
**The Methyl-1:2-benzanthraquinone Series. II.** ROLAND SCHOLL and WALTHER NEUBERGER [with WALTER TRITSCH and JULIUS POTSCHWAUSCHEG] (*Monatsh.*, 1912, 33, 507-533. Compare Scholl and Tritsch, this vol., i, 36).—Unsuccessful attempts were made to condense 2-amino-1-methylnaphthalene or its acetyl or phthaloyl derivatives with phthalic anhydride or with *o*-cyanobenzoyl chloride.

From 2-methoxy-1-methylnaphthalene, phthalic anhydride, and aluminium chloride, 2-methoxy-1-methylnaphthalene-6-phthaloylic acid,  $CO_2H \cdot C_6H_4 \cdot CO \cdot C_{10}H_5Me \cdot OMe$ , is obtained. This is more easily sulphonated than condensed by concentrated sulphuric acid, but the

reduction product, 6-methoxy-5-methyl-2-naphthylphenylmethane-2'-carboxylic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{C}_{10}\text{H}_5\text{Me}\cdot\text{OMe}$ , was converted into 3-methoxy-4-methyl-1 : 2-benzanthraquinone,

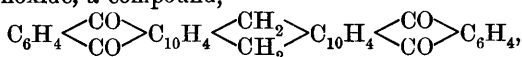


This compound can be demethylated by hydrogen bromide in acetic acid to 3-hydroxy-4-methyl-1 : 2-benzanthraquinone (annexed formula), which could not, however, be converted into the corresponding amine. 2-Hydroxy-1-methylnaphthalene-6-phthaloylic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_{10}\text{H}_5\text{Me}\cdot\text{OH}$ , prepared either from  $\beta$ -1-methylnaphthol, phthalic anhydride, and aluminium chloride, or from the 2-methoxy-1-methylnaphthalene-6-phthaloylic acid, is converted by Buchner's method into 2-amino-1-methylnaphthalene-6-phthaloylic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_{10}\text{H}_5\text{Me}\cdot\text{NH}_2$ , and this by the stages 3-amino-4-methyl-1 : 2-benzanthraquinone and 3-iodo-4-methyl-1 : 2-benzanthraquinone into 1 : 1'-dimethyl-5 : 6 : 5' : 6'-diphthaloyl-2 : 2'-dinaphthyl,



which could not be condensed to a dibenzpyranthrone.

From 3-chloro-4-methyl-1 : 2-benzanthraquinone, on fusion with potassium ethoxide, a compound,



and a hydro-derivative are obtained.

1-Methyl-2-naphthylphthalimide,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{N}\cdot\text{C}_{10}\text{H}_6\text{Me}$ , forms crystals, m. p. 200—201°. 2-Amino-1-methylnaphthalene-N-phthaloylic acid is a colourless, crystalline precipitate, decomposing at 180—190° into the above phthalimide.

o-Cyanobenzoyl chloride separates in lustrous needles, m. p. 73°; it has a mild, aromatic odour.

2-Methoxy-1-methylnaphthalene-6-phthaloylic acid has m. p. 161—163°; it gives at first a brown solution in concentrated sulphuric acid, which soon becomes violet or blue.

6-Methoxy-5-methyl-2-naphthylphenylmethane-2'-carboxylic acid crystallises in colourless platelets or slender needles, m. p. 166°. In concentrated sulphuric acid the coloration is at first yellow, and then becomes red.

6-Hydroxy-5-methylnaphthylphenylmethane-2'-carboxylic acid forms a granular, crystalline mass sintering at 165°, m. p. 179—181°.

3-Methoxy-4-methyl-1 : 2-benzanthraquinone is prepared by the action of sulphuric acid on the naphthylphenylmethane derivative, whereby 3-methoxy-4-methyl-1 : 2-benzanthrone-9 is formed, and subsequent oxidation with chromic anhydride. It crystallises in glistening, yellowish-red or brownish-red needles, m. p. 235—236°. When oxidised with potassium permanganate, anthraquinone-1 : 2-dicarboxylic acid is obtained.

3-Hydroxy-4-methyl-1 : 2-benzanthraquinone crystallises in stellate

aggregates of needles, which begin to sublime at  $275^{\circ}$ , m. p.  $283\text{--}284^{\circ}$ . The solution in sodium hydroxide changes colour with increasing concentration from reddish-violet through bluish-violet and blue to bluish-green.

*2-Hydroxy-1-methylnaphthalene-6-phthaloylic acid* crystallises in small, colourless, silky platelets, m. p.  $264\text{--}265^{\circ}$ , with frothing. The coloration in concentrated sulphuric acid rapidly changes from yellowish-brown to a deep bluish-violet.

*2-Amino-1-methylnaphthalene-6-phthaloylic acid* forms lustrous, yellow, crystalline splinters; it begins to decompose into the amide at  $170^{\circ}$ , sinters at  $206^{\circ}$ , m. p.  $212\text{--}213^{\circ}$  (decomp.).

*3-Amino-4-methyl-1:2-benzanthraquinone* crystallises in brownish-red, prismatic platelets, which begin to sublime at  $180^{\circ}$ , m. p.  $261\text{--}265^{\circ}$  (some decomp.).

*3-Iodo-4-methyl-1:2-benzanthraquinone* separates in golden-yellow, long, prismatic plates, m. p.  $276\text{--}277^{\circ}$ .

*1:1'-Dimethyl-5:6:5':6'-diphthaloyl-2:2'-dinaphthyl* is an insoluble, amorphous, dark yellow powder, which sinters about  $360^{\circ}$ .

E. F. A.

**Aromatic Aldehydo-acids.** HUGO SIMONIS [with ALFRED BOEHME and J. BENENSON] *Ber.*, 1912, 45, 1584—1592).—I.—*isoPhthalaldehydic Acid*.—By the action of bromine on phthalaldehyde, the acid bromide of phthalaldehydic acid,  $\text{CHO}\cdot\text{C}_6\text{H}_4\cdot\text{COBr}$ , is obtained as an intermediate product, and undergoes internal condensation to monobromophthalide,  $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CO} \\ \text{CHBr}\end{smallmatrix}\right\rangle\text{O}$ . This when hydrolysed yields phthalaldehydic acid. Bromine is without action on the isomeric *isophthalaldehyde* and *terephthalaldehyde* at the ordinary pressure, but on heating in sealed tubes at  $140^{\circ}$  or, on a large scale, in an enamel-lined autoclave, the corresponding aldehydic acids are obtained.

*isoPhthalaldehydic acid* (compare Reinglass, *Abstr.*, 1891, 1344) crystallises in colourless needles from water, m. p.  $175^{\circ}$ , or in glistening platelets from chloroform. The *methyl* ester, m. p.  $53^{\circ}$ , forms an *oxime*, m. p.  $104^{\circ}$ ; the *ethyl* ester is a colourless liquid of agreeable odour, solidifying at  $-10^{\circ}$  to large, colourless prisms, b. p.  $278^{\circ}$ ,  $D_{18}^{20}$  1.093.

The *chloride*, an oily liquid, b. p.  $130^{\circ}/20$  mm., on treatment with dry ammonia gas in benzene yields an *amide* crystallising in colourless prisms, decomp.  $190^{\circ}$ .

The *oxime*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH:N}\cdot\text{OH}$ , separates in colourless, microscopic needles (compare Reinglass, *loc. cit.*), m. p.  $188^{\circ}$ . On heating at this temperature, *isophthalamide* is formed.

The *anil* forms stellate groups of colourless prisms, m. p.  $156^{\circ}$ . The compound with *p*-toluidine has m. p.  $165^{\circ}$ , with  $\alpha$ -naphthylamine, m. p.  $164^{\circ}$ , and with  $\beta$ -naphthylamine, m. p.  $210^{\circ}$ ; they all form colourless needles or plates.

The *semicarbazone* has m. p.  $265^{\circ}$ . The *phenylhydrazone* forms colourless, flat, lustrous needles, m. p.  $265^{\circ}$ .

$\omega$ -*Acetylstyrene-m-carboxylic acid*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH:CH}\cdot\text{CO}\cdot\text{CH}_3$ , forms yellow needles which intumesce at  $185^{\circ}$ , m. p.  $194\text{--}196^{\circ}$ . The solution

in alkali hydroxide is yellow, that in concentrated sulphuric acid is brownish-red.

*m*-Carboxycinnamic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ , prepared by heating isophthalaldehydic acid with sodium acetate and acetic anhydride, has m. p.  $264^\circ$ .

The leuco-base of *p,p'*-tetramethyldiaminotriphenylmethane-*m*-carboxylic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , from isophthalaldehyde acid and dimethylaniline, crystallises in pointed, colourless prisms, m. p.  $233^\circ$ . On oxidation, malachite-green-*m*-carboxylic acid is obtained.

II.—Terephthalaldehydic acid,  $\text{COH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , crystallises in colourless, rhombic prisms or flat, streaked needles, m. p.  $256^\circ$ . The methyl ester forms stellar aggregates of colourless needles, m. p.  $60^\circ$ , b. p.  $265^\circ$ . The ethyl ester is a liquid. The chloride has b. p.  $258^\circ$ , and forms colourless prisms, m. p.  $48^\circ$ .

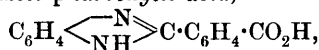
The anil forms rhombic prisms, m. p.  $222^\circ$ ; the *o*-chloroanil separates in light yellow crystals, m. p.  $217$ — $218^\circ$ ; the *m*-nitroanil consists of yellow needles, m. p.  $268$ ; the *p*-tolil crystallises in lustrous, pale yellow platelets, which soften at  $237^\circ$ , m. p.  $261$ — $263^\circ$ ; the *p*-acetylanil forms pale yellow, microscopic platelets, m. p.  $215^\circ$  (decomp.); the  $\beta$ -naphthil forms yellow platelets, m. p.  $240$ — $241^\circ$ ; the isomeric  $\alpha$ -naphthil gives pointed prisms, m. p.  $235^\circ$ .

Terephthalaldehydic acid-*m*-aminonil,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , is a canary-yellow, granular precipitate, m. p. above  $300^\circ$ ; it forms a diazonium salt, which couples with  $\beta$ -naphthol in alkaline solution to a bluish-red dye.

With *p*-phenylenediamine, yellow, microscopic prisms of 1:4-bis-[*p*-carboxybenzylideneamino]benzene,  $[\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{N}]_2\text{C}_6\text{H}_4$ , are obtained having m. p. above  $300^\circ$ ; analysis of the silver salt confirms the structure as a dicarboxylic acid.

Terephthalaldehydic acid azine,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{CH}:\text{N}:\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , is a bright yellow, sandy powder, m. p. above  $280^\circ$ .

2-Phenylbenziminazole-*p*-carboxylic acid,



crystallises in yellow, microscopic plates or six-sided prisms.

Mandelonitrile-*p*-carboxylic acid is obtained on heating the bisulphite compound of the aldehyde acid with potassium cyanide solution. On the addition of acid, a yellow, granular precipitate is obtained, which decomposes when heated.

*p*-Carboxycinnamic acid is obtained on heating terephthalaldehyde acid with sodium acetate and acetic anhydride in a stream of carbon dioxide at  $150$ — $160^\circ$ ; it forms an insoluble, colourless, crystalline powder. E. F. A.

Terephthalaldicarbamide and Terephthalaldinitrocarbamide. MICHAEL PFANNL and OTTO DAFERT (*Monatsh.*, 1912, 33, 485—505).—Terephthalaldicarbamide is prepared with a good yield by heating terephthalyl chloride with excess of carbamide. It gives no biuret reaction, and is remarkably stable towards acids, 96% sulphuric acid only hydrolysing it above  $55^\circ$ . It is also resistant to ring formation, and when heated in a stream of hydrogen chloride in a

vacuum it is degraded only to nitrile. It is colourless and amorphous, subliming above  $200^{\circ}$  (decomp.).

*Terephthalaldinitrocarbamide*,  $C_6H_4(CO \cdot NH \cdot CO \cdot NH \cdot NO_2)_2$ , is remarkable in containing two labile nitroamine groups in the molecule.

It is decomposed by water in a manner analogous to nitrocarbamide, forming amine, carbon dioxide, water, and nitrous oxide. There is no difference in colour between the sodium salt and the acid; they possibly exist in tautomeric modifications. The *sodium* salt crystallises in colourless, stellar aggregates of needles; the *free acid* is colourless, and explodes when heated.

E. F. A.

**Tannin.** KARL FEIST (*Ber.*, 1912, 45, 1493—1494).—The author points out that he has demonstrated the glucosidic nature of tannin previous to the work of Fischer and Freudenberg (this vol., i, 471).

H. W.

**Constitution of Tannin.** RODGER J. MANNING and MAXIMILIAN NIERENSTEIN (*Ber.*, 1912, 45, 1546—1551. Compare this vol., i, 468).—Manning has shown (*Abstr.*, 1910, i, 851) that tannin on esterification forms two pentaethyl esters of pentagalloylglucoside; this behaviour is not in agreement with the constitution ascribed to tannin by Fischer and Freudenberg (this vol., i, 471). Tannin (Schering) yields only ethyl gallate when esterified and no sugar. The change in rotation of tannin solutions on boiling in a stream of hydrogen has been followed, measurements being made also of the tannin and non-tannin matter present. In twelve hours the rotation falls from  $[\alpha]_D + 68.22^{\circ}$  to  $+59.84^{\circ}$ , the amount of tannin falls from 0.4274 to 0.3986, and the amount of non-tannin rises from 0.0244 to 0.0532; it is always optically inactive, which excludes the possibility of dextrose being eliminated.

E. F. A.

**The Behaviour of Acetylacetone towards  $\beta$ -Dialdehydes.** WILLIAM J. HALE (*Ber.*, 1912, 45, 1596—1603. Compare *Abstr.*, 1908, i, 634).—The condensation of acetylacetone with nitromalonaldehyde in presence of small quantities of sodium hydroxide yields some 4-nitro-2-acetylphenol, but also four times as much of a second product. The possibility of this being a diphenol was previously discredited by the fact that nitroacetylphenol and nitromalonaldehyde only condense in excess of alkali or piperidine, and a second supposition, that the nitroacetylphenol itself undergoes condensation to a cumarone derivative, is now shown to be improbable, for such a change can only be brought about by means of sulphuric acid or zinc chloride. Since the reaction takes place between equimolecular proportions, there remains the explanation that the two aldehyde groups condense with the two methylene groups, producing 5-nitro-2:3-diacetylcyclopentadiene, and this substance is actually obtained on adding hydrochloric acid to the mother liquor after the acetylnitrophenol has been precipitated by carbon dioxide.

5-Nitro-2:3-diacetylcyclopentadiene,  $NO_2 \cdot C_5H_3(COMe)_2$ , is a faintly coloured substance, crystallising from ethyl acetate in glistening needles, m. p.  $195^{\circ}$ . It is fairly acid, does not absorb bromine, but

is readily attacked by permanganate or concentrated nitric acid. *4-Nitro-1-methylcumarone*,  $\text{NO}_2 \cdot \text{C}_8\text{H}_4\text{OMe}$ , is obtained quantitatively from 4-nitro-2-acetonylphenol by condensation with zinc chloride in glacial acetic acid (compare Stoermer, Abstr., 1900, i, 650). It separates in short needles, m. p.  $97^\circ$ , from diluted alcohol, gives a deep red solution in sulphuric acid, and is converted by nitric acid into 4:6-dinitro-1-methylcumarone,  $\text{C}_8\text{H}_3\text{OMe}(\text{NO}_2)_2$ , which may also be obtained from 4:6-dinitro-2-acetonylphenol (Abstr., 1908, i, 634) in colourless needles, m. p.  $165^\circ$ . Improvements in the production of acetonylphenols will render this cumarone synthesis valuable.

J. C. W.

**Oxalyl Chloride. IV. The Friedel and Crafts' Reaction with Oxalyl Chloride and Oxalyl Bromide.** HERMANN STAUDINGER [with E. ANTHERS and MAX SCHÖLLER (*Ber.*, 1912, 45, 1594—1596).—The action of oxalyl chloride on aromatic hydrocarbons under the influence of aluminium chloride results usually in the formation of mono-ketones (compare Abstr., 1909, i, 905), but Liebermann has shown that some highly reactive aromatic compounds produce the expected diketones (compare Abstr., 1911, i, 656). This is explained by the fact that the decomposition of oxalyl chloride by aluminium chloride into carbonyl chloride and carbon monoxide takes place more slowly than the condensation with these reactive substances, and in support of this view it is shown that anisole is converted into anisil, and that in the presence of carbon monoxide under a pressure of 150 atmospheres, dimethylaniline can be converted into tetramethyldiaminobenzil.

Oxalyl bromide, b. p.  $103\text{--}105^\circ$ , which will be described in a future paper, decomposes most easily in presence of aluminium chloride into bromine and carbon monoxide, but it condenses even more readily with benzene, so that benzil may be obtained and not merely benzophenone or bromobenzenes. It seems, therefore, more suitable than the chloride for the preparation of diketones.

J. C. W.

**Bromination of cycloHexanone and cycloHexanol.** FERNAND BODROUX and FELIX TABOURY (*Compt. rend.*, 1912, 154, 1509—1511\*).—The tetrabromo-derivative obtained by the action of bromine in the presence of aluminium bromide on cyclohexanone (compare Abstr., 1911, i, 779) is identical with that obtained by Wallach (*Annalen*, 1905, 343, 133). It is, however, best prepared by the action of bromine in carbon tetrachloride solution. The liquid obtained by its decomposition on heating to  $120\text{--}125^\circ$  is a mixture of several monobromophenols and 2:6-dibromophenol.

cycloHexanol when treated with bromine in carbon tetrachloride yields tetrabromocyclohexanone and dibromocyclohexane. Temperature and duration of the reaction do not affect the result. Bromine in boiling acetic acid converts both the ketone and the alcohol into 2:4:6-tribromophenol.

W. G.

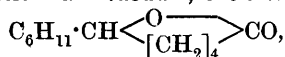
**Terpenes and Ethereal Oils. CIX.** OTTO WALLACH (*Annalen*, 1912, 389, 169—184).—[With WALTHER OST.]—cycloHexyl-2-cyclo-

\* and *Bull. Soc. chim.*, 1912, [iv], 11, 658—665.

hexanonoxime (Abstr., 1911, i, 473), unlike methyl-3-cyclohexanonoxime (Abstr., 1906, i, 514), yields by treatment with diluted sulphuric acid (5:1H<sub>2</sub>O) on the water-bath for five minutes only one

iso-oxime,  $C_6H_{11} \cdot CH \begin{smallmatrix} \nearrow NH \cdot CO \cdot CH_2 \\ \searrow CH_2 \cdot CH_2 \cdot CH_2 \end{smallmatrix}$ , m. p. 145—146°, which is con-

verted by 25% hydrochloric acid at 130—140° into  $\epsilon$ -amino- $\epsilon$ -cyclohexylhexoic acid,  $C_6H_{11} \cdot CH(NH_2) \cdot [CH_2]_4 \cdot CO_2H$ , m. p. 203° (decomp.) (benzoyl derivative, m. p. 228°). By oxidation with 5% potassium permanganate in faintly alkaline solution, the amino-acid yields  $\delta$ -hexahydrobenzoylvaleric acid, identical with that obtained by the direct oxidation of cyclohexyl-2-cyclohexanone (*loc. cit.*). The constitution of this ketonic acid is definitely proved by treating an ethereal solution of its oxime with phosphorus pentachloride, whereby the isomeric amide,  $C_6H_{11} \cdot NH \cdot CO \cdot [CH_2]_4 \cdot CO_2H$ , m. p. 133—134°, is produced, which is hydrolysed to cyclohexylamine and adipic acid by 25% hydrochloric acid at 140°. The reduction of  $\delta$ -hexahydrobenzoylvaleric acid by sodium and boiling alcohol yields, after purification of the product by distillation in a vacuum, the lactone,



m. p. 56°, b. p. 175°/12 mm., of  $\epsilon$ -hydroxy- $\epsilon$ -cyclohexylhexoic acid. The hydroxy-acid itself, which is an oil and is also obtained by the action of nitrous acid on  $\epsilon$ -amino- $\epsilon$ -cyclohexylhexoic acid, is converted by boiling dilute sulphuric acid into an unsaturated acid,  $C_{12}H_{20}O_2$ , b. p. 182—186°/20 mm. This acid, which is more easily obtained from the preceding lactone and boiling dilute sulphuric acid, is oxidised to  $\delta$ -hexahydrobenzoylvaleric acid by successive treatment with faintly alkaline 2% potassium permanganate and with chromic and sulphuric acids.

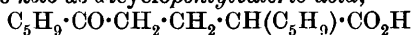
The dicyclic ketone obtained by the auto-condensation of 1-methyl-3-cyclohexanone is reduced by Paal's method to dimethyldicyclohexylhexanone,  $C_{14}H_{24}O$ , b. p. 146—148°/12 mm., which forms a semicarbazone, m. p. 163°, and an oxime, m. p. 95—96°, and yields by oxidation a ketonic acid, b. p. 222—225°/14 mm (silver salt,  $C_{14}H_{23}O_3Ag$ ; semicarbazone, m. p. 169—171°).

cyclopentene-2-cyclopentanone is reduced quantitatively by Paal's method to cyclopentyl-2-cyclopentanone (Godehot and Taboury, Abstr., 1911, i, 385), b. p. 232—233°,  $D^{21}_D$  0.9745,  $n_D$  1.4763 (oxime, m. p. 78—79°, and its hydrochloride, m. p. 112—113°), which forms a benzylidene derivative, m. p. 97—98°, and is oxidised by chromic acid to  $\delta$ -keto- $\delta$ -cyclopentylvaleric acid,  $C_5H_9 \cdot CO \cdot [CH_2]_3 \cdot CO_2H$  (semicarbazone, m. p. 181—183°). This oily acid is also readily obtained by oxidising cyclopentyl-2-cyclopentanone with cold 2% potassium permanganate.

2-cyclopentylcyclopentanol,  $C_5H_9 \cdot C_5H_8 \cdot OH$ , b. p. 235—236°,  $D^{17}_D$  0.9785,  $n_D^{17}$  1.4884 (phenylurethane, m. p. 88—89°), obtained by reducing cyclopentyl-2-cyclopentanone by sodium and alcohol, is converted by zinc chloride at 150° into cyclopentyl- $\Delta'$ -cyclopentene,  $C_5H_9 \cdot C_5H_7$ , b. p. 196.5—198°,  $D^{19.5}_D$  0.9080,  $n_D^{19.5}$  1.4938, which forms a nitrosochloride, m. p. 113—114°.

The yellow 1:3-dicyclopentene-2-cyclopentanone, which is obtained in 12—13% yield by the action of alcoholic sodium ethoxide on cyclo-

pentanone, is reduced by Paal's method to 1:3-dicyclopentyl-2-cyclopentanone,  $C_5H_9 \cdot C_5H_6O \cdot C_5H_9$ , which is colourless, has b. p.  $165-170^\circ/12$  mm.,  $D^{19}_D 0.9925$ , and  $n^{19}_D 1.4956$ , forms a semicarbazone, m. p.  $188-190^\circ$ , and an oxime, m. p.  $85-86^\circ$ , and is oxidised by chromic acid to  $\delta$ -keto- $\alpha\delta$ -dicyclopentylvaleric acid,

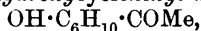


(semicarbazone, m. p.  $195-196^\circ$ ).

2:5-Dicyclopentylcyclopentanol,  $C_5H_9 \cdot C_5H_6(OH) \cdot C_5H_9$ , m. p.  $68^\circ$ , b. p.  $210^\circ/100$  mm., obtained by reducing the dicyclopentylcyclopentanone by sodium and alcohol, is converted into 1:3-dicyclopentyl- $\Delta'$ -cyclopentene, b. p.  $210^\circ/100$  mm.,  $D^{20}_D 0.939$ ,  $n^{20}_D 1.5065$ , by zinc chloride at  $150-200^\circ$ . C. S.

Terpenes and Ethereal Oils. CX. OTTO WALLACH (*Annalen*, 1912, 389, 185-198).—[With WALTHER OST.]—In accordance with expectation, nitrosopinene in methyl alcohol is reduced by hydrogen in the presence of a little colloidal palladium, the addition of hydrogen occurring at the ethylenic linking. However, the product is not pinocamphonoxime itself, but a stereoisomeric pinocamphonoxime, m. p.  $87^\circ$ ; the ketone obtained by its hydrolysis by acids yields a semicarbazone and an oxime identical with those from pinocamphone. When pinocarveol (from pinylamine) is reduced by Paal's method and the resulting saturated alcohol is oxidised, the ketone obtained yields an oxime and a semicarbazone identical with those of pinocamphone. It follows, therefore, that pinene, pinocarvone, carvopinone, and pinocamphone are mutually related as represented by the formulæ previously ascribed to these substances by the author.

[With WALTER N. HAWORTH.]—It has already been shown that the halogen in the nitrosochlorides of unsaturated hydrocarbons can be replaced by the acetoxy-group (Abstr., 1910, i, 569) and that the nitrosochlorides can be reduced directly to saturated bases and ketones by zinc and acetic acid (Abstr., 1911, i, 469). These processes have now been applied in the following cases. Ethylidenecyclohexane nitrosochloride, m. p.  $132^\circ$  (Abstr., 1908, i, 402), is converted by sodium acetate and glacial acetic acid at  $60-65^\circ$  into the oxime of 1-acetoxycyclohexyl methyl ketone,  $OAc \cdot C_6H_{10} \cdot CMe : NOH$ , m. p.  $103^\circ$ , the hydrolysis of which by 2% sulphuric acid yields  $\Delta^1$ -tetrahydroacetophenone and 1-hydroxycyclohexyl methyl ketone,

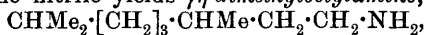


b. p.  $125-126^\circ/50$  mm. (semicarbazone, m. p.  $196^\circ$ ). The reduction of ethylidenecyclohexane nitrosochloride by zinc and acetic acid yields hexahydroacetophenone and  $\alpha$ -cyclohexylethylamine,  $C_6H_{11} \cdot CHMe \cdot NH_2$  (platinichloride,  $2C_6H_{11}N, H_2PtCl_6$ , m. p.  $218^\circ$  [decomp.]).

The reduction of 1-methyl-3-ethylidenecyclohexane by zinc and acetic acid yields a base (unexamined) and 1-methylcyclohexyl methyl ketone,  $C_6H_{10}Me \cdot CMe$ , b. p.  $196-197^\circ$  (semicarbazone, m. p.  $180-181^\circ$ ).

[With MAX BEHNKE.]—When heated with potassium hydroxide, monocyclic ketones tend to form condensation products (Abstr., 1909, i, 811); their oximes, however, undergo fission of the ring; thus menthoneoxime and potassium hydroxide, heated at  $220^\circ$  for thirty-

six hours in an autoclave, yield ammonia, thymol,  $\beta\zeta$ -dimethyloctoic acid,  $\text{CHMe}_2\cdot[\text{CH}_2]_3\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$  (Abstr., 1897, i, 428), and lower fatty acids. The decoic acid forms a *methyl* ester, b. p. 212—215°, *amyl* ester, b. p. 265—266°, *chloride*, b. p. 106—109°/20 mm. (*anilide*, m. p. 91—92°), and *amide*, m. p. 108—109°, from which is prepared the *nitrile*, b. p. 220—225°,  $D_D^{20}$  0.821,  $n_D^{20}$  1.4276. By reduction, the nitrile yields  $\gamma\eta$ -dimethyloctylamine,



b. p. 202—203°,  $D_D^{21}$  0.791,  $n_D^{21}$  1.4316, which forms a *phenylthiocarbamide*, m. p. 78—79°, and *oxamide*, m. p. 76—77°, and is converted by nitrous acid into  $\gamma\eta$ -dimethyloctyl alcohol, b. p. 100—102°/13 mm., and a *decylene*,  $\text{C}_{10}\text{H}_{20}$ , b. p. 152—155°,  $D_D^{19}$  0.744,  $n_D^{19}$  1.4213. C. S.

**Action of Sodamide and Alkyl Halides on Benzoylcyclopropane.** ALBIN HALLER and EUGÈNE BENOIST (*Compt. rend.*, 1912, 154, 1567—1570).—An investigation for the comparison of the behaviour of ketones containing a trimethylene ring with that of ordinary ketones.

Ethyl benzoylcyclopropanecarboxylate (*oxime*, m. p. 152°: Perkin, Trans., 1885, 47, 840) is converted successively into the corresponding acid and benzoylcyclopropane (*oxime*, m. p. 95—96°).

A more convenient method of preparation is by the series of changes trimethylene chlorobromide  $\rightarrow$  trimethylene chlorocyanide  $\rightarrow$  cyclopropanecarboxylonitrile  $\rightarrow$  cyclopropanecarboxylic acid; the acid (b. p. 181—182°/760 mm.) is converted by thionyl chloride into the acid chloride, which condenses with benzene in the presence of aluminium chloride, giving benzoylcyclopropane.

When warmed with sodamide in dried benzene, benzoylcyclopropane gives a sodium derivative, but in moist benzene, cyclopropane is evolved and benzamide remains. When sodium benzoylcyclopropane is treated in warm benzene with methyl iodide, 1-benzoyl-1-methylcyclopropane,  $\text{COPh}\cdot\text{CMe}\cdot\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix}$ , is obtained, b. p. 127—128°/18 mm.; *oxime*, m. p. 115° (decomp.); *p*-nitrophenylhydrazone, orange leaflets, m. p. 112°. From these properties the substance is evidently distinct from that obtained by Blaise and Herman (Abstr., 1911, i, 881); when warmed with sodamide and benzene, methylcyclopropane and benzamide are obtained.

1-Benzoyl-1-allylcyclopropane, obtained in an analogous manner to the above methyl compound, has b. p. 136—137°/16 mm.; a mixture of sodamide and benzene is without effect on this substance.

1-Benzoyl-1-benzylcyclopropane, b. p. 203—204°/20 mm., crystallises in tablets, m. p. 33.5°; when heated with sodamide and moist benzene it undergoes scission into benzene and the *amide* of benzylcyclopropanecarboxylic acid (m. p. 84°), which is easily hydrolysed to the corresponding free acid (cubes, m. p. 103°).

Oxidation of benzoylbenzylcyclopropane by chromium trioxide in acetic acid solution gives a substance,  $\text{C}_{17}\text{H}_{14}\text{O}_3$ , possibly a dibenzoylcyclopropane, crystallising in cubes, m. p. 87—88°.

The refractivities of benzoylcyclopropane, together with its methyl and benzyl derivatives, and ethyl benzoylcyclopropanecarboxylate,

are given for the  $\alpha$ -,  $D$ -,  $\beta$ -, and  $\gamma$ -lines. The results with the  $D$ -line indicate that in these substances the trimethylene ring exerts a similar effect to an ethylenic linking in causing exaltation when conjugated with a ketonic group.

D. F. T.

***mm'*-Dinitrobenzil.** HEINRICH KLINGER and WALTER MARTINOFF (*Annalen*, 1912, 389, 232—237).—By treatment with colourless nitric acid, D 1.53, at  $-10^\circ$ , benzil is converted into *mm'*-dinitrobenzil, m. p.  $108.5-109^\circ$ , yellow needles. Attempts to convert it into dinitrobenzilic acid by the hydroxide of potassium, sodium, or barium have been unsuccessful. It is converted into *m*-nitrobenzoic acid by boiling water and silver oxide.

C. S.

**Correction Concerning the Formation of Cyananilic Acid.** M. M. RICHTER (*Ber.*, 1912, 45, 1682. Compare this vol., i, 34).—The formation of a very small amount of "cyananilic acid" from chloranilic acid was due to the presence of a little chloranil.

J. C. W.

**Abnormal Behaviour of Some Anthraquinone Derivatives towards Alkaline Reducing Agents.** I. CHRISTIAN SEER [with E. KARL] (*Monatsh.*, 1912, 33, 535—548).—Most anthraquinone derivatives when warmed with alkaline reducing agents yield characteristic coloured solutions. Certain substituting groups attached near the carbonyl groups cause steric hindrance and render the compound indifferent to alkaline reducing agents; thus 1:3:5:7-tetramethylantraquinone is quite indifferent, but anthraquinone-1:3:5:7-tetracarboxylic acid obtained from it on oxidation, gives an intense violet-red on reduction.

Further substitution in 1:3:5:7-tetramethyl anthraquinone, producing 4:8-dinitro- and 2:4:6:8-tetranitro-derivatives, still results in compounds which are almost indifferent to alkaline reducing agents. In these compounds, also, the nitro-groups are reduced to amino-groups only with difficulty.

1:5-Dibenzylaminoanthraquinone is equally resistant, but the compound formed on substituting the remaining hydrogen of the amino-group by the benzoyl radicle gives a red solution with alkaline reducing agents, the negative residues evidently acting to restore the activity of the carbonyl groups.

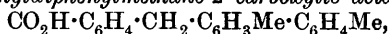
1:4-Dimethylantraquinone gives a red solution on reduction; 1-methyl-4-*p*-tolylantraquinone is, however, indifferent.

4:4'-Dimethyldiphenyl-3-phthaloylic acid is not converted into the anthraquinone derivative by condensation by means of sulphuric acid, zinc chloride, or phosphorus pentachloride. The reduction product, 5-*p*-tolyl-2-methyldiphenylmethane-2'-carboxylic acid, is converted by means of zinc chloride into 1-methyl-4-*p*-tolylanthrone, from which the desired 1-methyl-4-*p*-tolylantraquinone is obtained on oxidation with chromium trioxide.

Oxidation with ferric chloride converts the above anthrone into 1:1'-dimethyl-4:4'-di-*p*-tolyl dianthrone - 10:10'. An additional product of oxidation with chromium trioxide is a small quantity of 4-*p*-carboxyphenylantraquinone-1-carboxylic acid. When a large

excess of the oxidising agent is used, the methyl groups are oxidised to carboxyl, but action proceeds beyond the dicarboxylic acid, and the benzene ring is opened with the formation of a mixture of 4-*p*-carboxylphenylanthraquinone-1-carboxylic acid and anthraquinone-1:4-dicarboxylic acid as the final result. The dicarboxylic acid gives a dark red coloration with alkaline reducing agents.

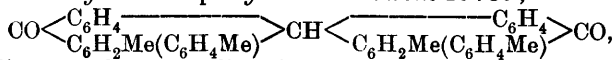
5-*p*-Tolyl-2-methyldiphenylmethane-2'-carboxylic acid,



crystallises in stellar aggregates of colourless needles, m. p. 163—164°. The solution in concentrated sulphuric acid is yellow, becoming reddish-violet when kept.

1-Methyl-4-*p*-tolylanthrone-10,  $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CO}\end{smallmatrix}\right\rangle\text{C}_6\text{H}_3\text{Me}\cdot\text{C}_6\text{H}_4\text{Me}$ , forms pale yellow, long prisms, m. p. 145—146°, dissolving in concentrated sulphuric acid with a reddish-brown coloration.

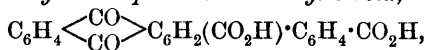
1:1'-Dimethyl-4:4'-di-*p*-tolyl-9:9'-dianthrone-10:10',



crystallises in colourless, glistening, prismatic platelets, m. p. 237°.

1-Methyl-4-*p*-tolylanthraquinone,  $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{CO} \\ \text{CO}\end{smallmatrix}\right\rangle\text{C}_6\text{H}_2\text{Me}\cdot\text{C}_6\text{H}_4\text{Me}$ , crystallises in yellow needles, m. p. 212°; the coloration with concentrated sulphuric acid is red.

4-*p*-Carboxyphenylanthraquinone-1-carboxylic acid,



forms pale yellow, microscopic needles, soluble in concentrated sulphuric acid with a golden-yellow coloration. E. F. A.

**Binary Mixtures Containing Camphor.** JOUNIAUX (*Bull. Soc. chim.*, 1912, [iv], 11, 546—552).—Camphor forms liquid mixtures with naphthalene,  $\alpha$ -nitronaphthalene,  $\beta$ -naphthylamine, pyrogallol, and benzoic acid, and the behaviour of the camphor-naphthalene mixture on cooling has been described already (this vol., i, 198). Binary mixtures with each of the four other substances mentioned behave similarly, and a general curve and tables illustrating this behaviour are given in the original.

The eutectic mixtures have the following molecular compositions, %:  $\alpha$ -nitronaphthalene 46,  $\beta$ -naphthylamine 36, pyrogallol 31 (m. p. 21°), benzoic acid 37 (m. p. 27.2°), the rest being camphor. In all four cases the first crystals, which separate on cooling, consist of camphor, so long as the second constituent does not form more than 30 mols. % of the mixture. The addition of even very minute quantities of the second constituent causes a remarkable lowering in the temperature of commencing solidification.

T. A. H.

**Pinene and Camphor.** MARIO MAYER (*Chem. Zentr.*, 1912, i, 1312; from *Habilitationschr.*, Florence, 1911, 61 pp.).—By fractional crystallisation of *i*- $\alpha$ -pinenehydroxylamineoxime  $\alpha$ -bromo- $\pi$ -camphorsulphonate the author has separated the salt into three fractions, from

which the three corresponding bases have been prepared by treatment with sodium carbonate. The constants of these six substances are as follows: (1) *salt*, m. p.  $195^{\circ}$  (decomp.),  $[\alpha]_D + 79^{\circ}$ : *base*, m. p.  $147^{\circ}$  (decomp.),  $[\alpha]_D + 60.5^{\circ}$ ; (2) *salt*, m. p.  $172^{\circ}$  (decomp.),  $[\alpha]_D + 39^{\circ}$ : *base*, m. p.  $145^{\circ}$  (decomp.),  $[\alpha]_D - 59.6^{\circ}$ ; (3) *salt*, m. p.  $175^{\circ}$  (decomp.),  $[\alpha]_D + 52^{\circ}$ : *base*, m. p.  $140^{\circ}$  (decomp.),  $[\alpha]_D 0^{\circ}$ .

Theoretically the hydroxylamineoxime should exist in four optically active forms, and the author suggests that the two optically active forms described above may be mixtures. A full discussion of the stereochemistry of pinene is given in the original. T. A. H.

**Constitution of 3-Methylpulegene (3-Methylmenthadiene).** HANS RUPE, HEINZ SCHOBEL, and ERWIN ABEGB (*Ber.*, 1912, 45, 1528—1540).—Various formulæ have been assigned to 3-methylpulegene by Grignard, Rupe and Emmerich (*Abstr.*, 1908, i, 556) and, by Auwers and Eisenlohr (*Abstr.*, 1910, ii, 365, 367). On oxidation with ozone, a moderately viscid, greenish-yellow oil is obtained, which analysis indicates to be a mixture of much diozonide with a little mono-ononide. Hydrolysis with water yields acetone in small quantities and an oil, b. p.  $171^{\circ}/14$  mm., which is characterised as a ketonic acid; it yields a semicarbazone crystallising in slender, colourless needles, m. p.  $150^{\circ}$ . On oxidation of this acid with sodium hypobromite,  $\beta$ -methyladipic acid is obtained, whilst on oxidation with nitric acid,  $\alpha$ -methylglutaric acid is formed. This behaviour establishes the constitution of the acid as  $\delta$ -acetyl- $\gamma$ -methylvaleric acid,



but it does not enable any decision to be made between the alternative formulæ for methylpulegene.

A further product of the oxidation with ozone is a soluble brown oil, which distils at  $130$ — $140^{\circ}$  as a viscid, yellow, odourless oil; this has the properties of an aldehyde,  $\text{C}_8\text{H}_{14}\text{O}_2$ , and forms a *semicarbazone*,  $\text{C}_{11}\text{H}_{21}\text{ON}_3$ , crystallising in colourless platelets, m. p.  $266^{\circ}$ . On oxidation of the aldehyde with potassium permanganate, it is converted into the ketonic acid.

*3-Methylpulegol*, obtained as a by-product in the preparation of methylpulegene, has b. p.  $93$ — $94^{\circ}/10.5$  mm., and constitutes a colourless, mobile oil with an odour of menthone.

*Methylmenthone (homomenthone)*, a further by-product of the preparation of the hydrocarbon, has b. p.  $94$ — $97^{\circ}/15$  mm.; the *semicarbazone* crystallises in lustrous, colourless needles, m. p.  $186^{\circ}$ . The ketone prepared from this has b. p.  $93^{\circ}/11$  mm.,  $D_4^{20} 0.905$ ,  $n_D^{20} 1.4642$ ,  $[\alpha]_D^{20} + 43.98^{\circ}$ . E. F. A.

**The Constituents of Essential Oils. Chemical Identity of Synthetic and Natural Cedrene.** FRIEDRICH W. SEMMLER and K. E. SPORNITZ (*Ber.*, 1912, 45, 1553—1557. Compare Semmler and Mayer, this vol., i, 366).—Natural cedrene has a somewhat higher boiling point and considerably lower optical activity than the synthetic product, and the identity of the two compounds has not been established previously. On oxidation of synthetic cedrene with ozone, the methylketonic acid formed is similar to the acid obtained in the

same way from natural cedrene, and is converted into identically the same cedrenedicarboxylic acid. Natural cedrene evidently contains other isomeric sesquiterpenes in addition to the strongly lævorotatory cedrene. E. F. A.

**Essential Oils. III. Basil Oil.** GUSTAVE LALOUÉ (*Bull. Soc. chim.*, 1912, [iv], 11, 491—494).—The author has compared the basil oils obtained from the following four varieties of *Ocimum basilicum*, cultivated near Grasse: var. *thyrsiflorum*, Benth., var. *purpurascens*, Benth., var. *album*, Benth., and var. *crispum*, E. G. Camus. These furnished respectively 0.0855, 0.0370, 0.0780, and 0.1285% of oil, so that the fourth is the best for cultivation. The four oils yielded respectively 35.19, 38.46, 39.66, and 35.19% of total alcohols, calculated as linalool, and their constants, which are tabulated in the original, showed very little variation. The amount of methoxyl in all four oils corresponded with about 55% of estragole. T. A. H.

**Oil of the Southern Cypress.** ALLAN F. ODELL (*J. Amer. Chem. Soc.*, 1912, 34, 824—826).—In an earlier paper (Abstr., 1911, i, 548) it was shown that the wood of the cypress (*Taxodium distichum*) contains an aldehyde. With a view to obtaining larger quantities of this compound, an examination has been made of the volatile oil of the cones. It has been found, however, that the oil does not contain any aldehydes.

Cones collected in September yielded about 1% of a yellowish-green oil with an odour of pinene,  $D_{20} 0.86$ , and  $n_D + 18^\circ$  in a 100 mm. tube. Those collected later in the year furnished  $1\frac{1}{2}$ —2% of an oil of darker colour and citron-like odour, with  $D_{20} 0.85$  and  $n_D + 35.5^\circ$  in a 100 mm. tube. The composition of the oil was found to be approximately as follows: *d*-pinene, 85%; *d*-limonene, 5%; a  $\psi$ -terpene alcohol (probably sabinol), 2%; carvone, 3%; a tricyclic sesquiterpene, 3%; the remainder consisted of substances of b. p. above  $275^\circ$ .

E. G.

**The Oil of Douglas Fir.** H. K. BENSON and MARC DARRIN (*J. Ind. Eng. Chem.*, 1911, 3, 818—820).—A preliminary investigation of the nature and properties of the clear, viscous, yellow oil which is left after removal of the turpentine from the distillation products of Douglas fir. The oil was fractionated, and the constants of each fraction noted and compared (as were those of the crude oil) with the constants of pine oil as recorded by Teeple (Abstr., 1908, i, 355) and Walker (*Mass. Inst. Tech. Bull.*, Sept. 1905). From the result of this and numerous chemical tests which were also applied, the authors consider that not less than one-third of fir oil consists of turpineol, and that it closely resembles pine oil in its properties. F. M. G. M.

**New Synthetic Glucosides.** FERDINAND MAUTHNER (*J. pr. Chem.*, 1912, [ii], 85, 564—568).—*Tetra-acetogluco-p-hydroxyacetophenone*,  $C_{22}H_{26}O_{11}$ , prepared by shaking a solution of *p*-hydroxyacetophenone in aqueous sodium hydroxide with an ethereal solution of  $\beta$ -acetobromoglucose, crystallises from methyl alcohol in colourless needles, m. p.

172—173°, and is hydrolysed by aqueous barium hydroxide to *gluco-p-hydroxyacetophenone*,  $C_{14}H_{18}O_7$ , which forms colourless needles, m. p. 195—196°, and has  $[\alpha]_D^{25} = -87.82^\circ$  in aqueous solution.

*Tetra-acetogluco-p-hydroxybenzaldehyde*,  $C_{21}H_{24}O_{11}$ , prepared in a similar manner, forms colourless needles, m. p. 144—145°, and is hydrolysed to *gluco-p-hydroxybenzaldehyde*,  $C_{13}H_{16}O_7$ , which has m. p. 157—158°, and  $[\alpha]_D^{25} = -94.45^\circ$  in aqueous solution. F. B.

**The Relation of Members of the Digitalin Group towards Enzymes.** ARNOLD HOLSTE (*Arch. exp. Path. Pharm.*, 1912, 68, 323—332).—The various members of the digitalin group are all more or less affected by digestive enzymes, also by diastase and emulsin, being thus rendered inactive. The most resistant towards pancreatin are oleandrin, digitoxin, and strophanthin. Helleborein is easily affected. A good deal of the uncertainty of digitalis therapeutics depends on these facts. W. D. H.

**Sphingosine.** PHÆBUS A. LEVENE and WALTER A. JACOBS (*J. Biol. Chem.*, 1912, 11, 547—554).—A full account of work the results of which have already been described (this vol., i, 284). W. D. H.

**Bilirubic Acid, a New Degradation Product of Bilirubin.** HANS FISCHER and HEINRICH ROSE (*Ber.*, 1912, 45, 1579—1583).—On reduction of bilirubin with hydrogen iodide and acetic acid, a crystalline acid,  $C_{17}H_{24}O_3N_2$ , is obtained. It forms bunches of macroscopic platelets, m. p. 187°. It is very stable, is monobasic, and shows no pyrrole reaction. It is very resistant towards 70% sulphuric acid and towards hydriodic acid and red phosphorus at 125°. On oxidation, methyl ethylmaleinimide and hæmatic acid are obtained. The constitution  $CMe \begin{array}{c} \diagup CMe \cdot CEt \\ \diagdown NH - C \end{array} \begin{array}{c} CO_2H \cdot CH_2 \cdot CH_2 \cdot C \cdot CMe \\ \diagup O \end{array} \begin{array}{c} \diagdown C \cdot NH \\ \diagup \end{array} CMe$  is assigned to bilirubic acid for the following reasons: the degradation product shows it to contain two pyrrole rings in which the position of the  $\beta$ -substituting groups is fixed. It is obviously a tetra-substituted pyrrole, since it gives a negative reaction with dimethylaminobenzaldehyde and no pyrrole reaction or azo-dye. Accordingly, the four hydrogen atoms in the  $\alpha$ -position to nitrogen must be substituted, for which purpose there are two methyl groups and oxygen available; it is assumed that the two pyrrole groups are united through oxygen. This is in agreement with the resistance to hydrogen iodide.

Hemibilirubin yields 20% of the new acid; compound II gives 9%. The yield of methyl ethylmaleinimide on oxidation of hemibilirubin is about half that from bilirubic acid. A by-product in the preparation of bilirubic acid from hemibilirubin and compound II is a pyrrole carboxylic acid which couples with diazobenzenesulphonic acid.

E. F. A.

**Conversion of Oxindole into 2-Ketodihydro-1-thionaphthen.** ("Thio-oxindole"). CHARLES MARSHALK (*Ber.*, 1912, 45, 1481—1485. Compare this vol., i, 303).—*o*-Thiolphenylacetic acid has been transformed by distillation into 2-ketodihydro-1-thionaphthen.

The latter condenses with *p*-dimethylaminobenzaldehyde and with  $\alpha$ -isatinanilide with the formation of dyes.

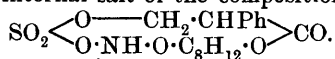
*o*-Thiocyanophenylacetic acid, m. p. 105—106°, was obtained by the addition of a solution of *o*-diazophenylacetic acid to a warm solution of cuprous and potassium thiocyanates. When dissolved in sodium hydroxide, mixed with sodium sulphide and evaporated to dryness, it yielded, after acidification, *o*-thiolphenylacetic acid, m. p. 96—97°, which was, however, more readily prepared by the addition of a solution of *o*-diazophenylacetic acid to a cold solution of potassium xanthate and subsequent warming of the compound so formed with potassium hydroxide solution and liberation of *o*-thiolphenylacetic acid by means of hydrochloric acid. When heated, it formed 2-ketodihydro-1-thionaphthen, a yellow oil, b. p. 260—264°/733 mm., which solidified when cooled. This was insoluble in cold sodium carbonate solution, but dissolved in hot sodium hydroxide with the formation of the sodium salt of *o*-thiolphenylacetic acid. It condensed with *p*-dimethylaminobenzaldehyde in methyl alcoholic solution in the presence of piperidine with formation of 3-*p*-dimethylaminobenzylidene-2-ketothionaphthen, m. p. 164—165°, which dyes wool and silk an orange colour in an acid-bath. When boiled with acetic anhydride and  $\alpha$ -isatinanilide, thio-oxindole formed 2'-indoxyl-3-thionaphthen-2'-one (compare Bedzik and Friedländer, Abstr., 1908, i, 673).

H. W.

**Scopolamine.** RICHARD WILLSTÄTTER and ERNST HUG (*Zeitsch. physiol. Chem.*, 1912, 79, 146—163).—It is supposed generally that scopolamine undergoes changes on keeping, such as racemisation, so that the optical activity vanishes, hydrolysis of the ester group, conversion into an *apo*-compound analogous to *apotropine*, or hydrolysis of the oxide group. Experiments made to test these points prove that scopolamine remains unchanged both in physical and chemical characteristics on keeping, and that probably also the physiological action does not alter.

The alkaloid remains saturated when either atropine or scopoline is mixed with concentrated sulphuric acid, and it is stable towards bromine or permanganate on dilution. When the solution, however, is made neutral, *apopropine* or *aposcopolamine* are obtained quantitatively.

When the solution in concentrated sulphuric acid is diluted and neutralised with ammonia, the sulphuric acid ester of the alkaloid separates. It is an internal salt of the composition



*apo*Scopolamine can also be obtained by means of hydrogen chloride. On treatment of scopolamine with thionyl chloride or phosphorus pentachloride, the alcoholic hydroxyl is replaced by chlorine, and scopoleine of chlorohydrotropic acid is obtained. This is stable in acid solution, but when isolated and the ethereal solution evaporated, isomeric change takes place and *aposcopolamine* hydrochloride is obtained.

*apo*Scopolamine sulphate gives in aqueous solution with bromine

only a flocculent precipitate of perbromide, but in concentrated sulphuric acid one molecule of bromine is decolorised without the formation of perbromide. This enables the estimation of *aposcopolamine* when in admixture with *scopolamine*.

*Scopoline* contains two oxygen atoms, the one in an hydroxyl group, the other is fixed as an ether-like linking. *Scopoline* combines with concentrated sulphuric acid to form an ester acid, but *chloroscopoline* may be heated with this acid to about 100° without change.

*Scopolamine hydrobromide* has  $[\alpha]_D^{18} - 26^\circ$ ; the commercial product reacts very faintly acid, but it is neutral to methyl-red after purification.

*Atropinesulphuric acid* crystallises in lustrous, colourless prisms, m. p. 238—239°.

*Scopolaminesulphuric acid* crystallises in slender, stellar aggregates of matted needles, m. p. 244° (decomp.).

*Homatropinesulphuric acid* crystallises in rhombic platelets, m. p. 240°.

*apoScopolamine* crystallises in long needles from ether or in well-formed prisms from light petroleum, m. p. 97°. The *nitrate* forms nacreous platelets, m. p. 157°; the *aurichloride* separates in feathery clusters of needles or well-formed thin prisms, m. p. 183—184°; the *picrate* consists of slender prisms, m. p. 217°, whilst the *methiodide* crystallises in short, stunted, lustrous prisms, m. p. 238° (decomp.).

[With E. P. HEDLEY].—*Scopolyl chloride* crystallises from ether in long prisms, b. p. 102—103°/8 mm. The *platinichloride* forms stunted prisms, m. p. 229—230° (decomp.).

E. F. A.

**Preparation of Quinine Esters of Aromatic Amino-acids.** VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 244741).—The quinine esters of aromatic amino-acids have not previously been prepared.

*p-Nitrobenzoylquinine*, tasteless, yellow needles, m. p. 154°, obtained from quinine and *p*-nitrobenzoyl chloride, when reduced with stannous chloride furnishes *p-aminobenzoylquinine*, colourless crystals, m. p. 170°. *o-Nitrobenzoylquinine* forms tasteless needles, m. p. 164·5—166·5°, and *o-aminobenzoylquinine*, octahedra, m. p. 135—137·5°; the *hydrochloride*,  $C_{20}H_{23}O_2N_2 \cdot CO \cdot C_6H_4 \cdot NH_2 \cdot 2HCl$ , is a yellow, tasteless powder with anæsthetic properties.

F. M. G. M.

**Buphane disticha** (*Hæmanthus toxicarius*). LOUIS LEWIN (*Arch. exp. Path. Pharm.*, 1912, 68, 333—340).—*Hæmanthine*, the alkaloid obtained from this plant, is a narcotic. Its action on the heart resembles that of the tropeines; it is also an emetic.

W. D. H.

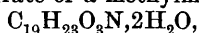
**Trimethyldiapoharmine, a New Base Obtained by the Application of Hofmann's Reaction to apoHarmine.** VICTOR HASENFRATZ (*Compt. rend.*, 1912, 154, 1520—1523. Compare this vol., i, 209, 383).—Hofmann's reaction when applied to *apoharmine* does not bring about its degradation, but on the contrary a complex base containing four atoms of nitrogen is formed.

*Methylapoharmine* unites with methyl iodide, forming *methyl*

*apoharmine methiodide*,  $C_8H_7N_2Me_3I$ , which is not acted on by potassium hydroxide. With moist silver oxide, it yields the corresponding *methohydroxide*,  $C_8H_7N_2Me_3\cdot OH$ , which in solution has a very alkaline reaction and an intense blue fluorescence. On evaporating the solution under reduced pressure and distilling the residue, *trimethylldiapoharmine*,  $C_{16}H_{13}Me_3N_4$ , is obtained as a yellow oil, which finally solidifies and crystallises from alcohol or ether in colourless plates, m. p.  $74\cdot5^\circ$ . It yields a *platinichloride*,  $C_{19}H_{22}N_4\cdot H_2PtCl_6$ , and a *dimethiodide*, which is soluble in water and alcohol. W. G.

**Replacement of the Halogen in Chloro- $\alpha$ -methylmorphimethine by Hydroxyl.** ROBERT PSCHORR and F. DICKHÄUSER (*Ber.*, 1912, 45, 1570—1579).—When the halogen in chlorocodeine is replaced by hydroxyl, the three isomerides of codeine are obtained, instead of codeine itself. Somewhat analogous behaviour has now been observed with chloro- $\alpha$ -methylmorphimethine, which when heated with dilute acids forms  $\gamma$ -,  $\epsilon$ -, or  $\delta$ -methylmorphimethine respectively, with the elimination of hydrogen chloride. The changes causing the isomerism evidently take place in both instances in the reduced benzene nucleus of the phenanthrene residue.

When chloro- $\alpha$ -methylmorphimethine is hydrolysed above  $100^\circ$ , a further product is a dihydrate of a methylmorphimethine,



in which one molecule of water is a part of the molecular structure. This hydrate is obtained from  $\epsilon$ -methylmorphimethine on heating a solution of the acetate, and it can be converted into  $\epsilon$ -methylmorphimethine by heating it in a vacuum at  $80^\circ$ . The *dihydrate* crystallises in lustrous needles, m. p. about  $100^\circ$ ; the *monohydrate* is hygroscopic, m. p.  $112^\circ$  (decomp.).

When heated with acetic anhydride and precipitated by potassium iodide, the *hydriodide* of the *monoacetylated hydrate* is obtained in prisms, decomp.  $170^\circ$ ; the *base* forms slender needles, m. p.  $130$ — $131^\circ$ .

E. F. A.

**Methylation of the Alcoholic Hydroxyl in the Codeines**  
**II. Methylation of *iso*- and  $\psi$ -Codeine.** ROBERT PSCHORR and F. DICKHÄUSER (*Ber.*, 1912, 45, 1567—1570. Compare Abstr., 1911, i, 908).—The method of methylation of codeine previously described (*loc. cit.*), that is, treatment of the aqueous alkaline solution or suspension with excess of methylsulphate or methyl iodide, is extended to *iso*- and  $\psi$ -codeine. The product from  $\psi$ -codeine is identical with the quaternary salt of the codeine methyl ether obtained by Knorr and Roth (Abstr., 1911, i, 1014) by the action of sodium methoxide on  $\alpha$ -chlorocodide, proving that in this reaction of Knorr and Roth conversion into the  $\psi$ -series has taken place.

*Methylisocodeine methiodide* crystallises in lustrous platelets, which sinter at  $196^\circ$ , m. p.  $199$ — $200^\circ$ . On boiling with sodium hydroxide,  $\gamma$ -methylmorphimethine methyl ether is obtained, crystallising from light petroleum in lustrous, four-cornered platelets, m. p.  $41^\circ$ . The *hydroiodide* formed long, lustrous needles, which sinter at  $189^\circ$ , m. p.  $192$ — $193^\circ$ ,  $[\alpha]_D^{25} + 20\cdot31^\circ$ .

When the hydrochloride of  $\gamma$ -methylmorphimethine methyl ether is

heated with sodium acetate in a sealed tube at  $150^{\circ}$ ,  $\delta$ -*methylmorphimethine methyl ether* is obtained in narrow platelets, m. p.  $71-72^{\circ}$ ; the *hydriodide* forms broad needles, m. p.  $212^{\circ}$ .  $\beta$ -*Methylmorphimethine methyl ether*, previously described as an oil, has been obtained from light petroleum in colourless prisms, m. p.  $82^{\circ}$ ,  $[\alpha]_D^{17} + 432^{\circ}$ . The *hydriodide* consists of prisms, decomp.  $243^{\circ}$ .

$\psi$ -*Codeinemethyl ether methiodide* crystallises in large, stunted prisms, m. p.  $270-271^{\circ}$  (decomp.).

$\epsilon$ -*Methylmorphimethine methyl ether* crystallises in large prisms, m. p.  $75^{\circ}$ ,  $[\alpha]_D^{18} - 92.48^{\circ}$ ; the *hydriodide* consists of platelets, which sinter at  $200^{\circ}$ , decomp.  $207^{\circ}$ . E. F. A.

**Preparation of Methylene-dicotarnine.** MARTIN FREUND (D.R.-P. 245622).—*Methylene-dinarcotine*,  $\text{CH}_2(\text{C}_{22}\text{H}_{22}\text{O}_7\text{N})_2$ , m. p.  $215-216^{\circ}$ , is prepared by the action of formaldehyde on narcotine; when treated with oxidising agents, it furnishes *methylene-dicotarnine*,

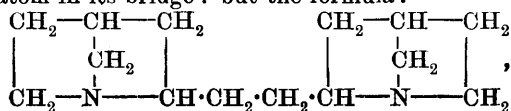


m. p.  $132^{\circ}$  (decomp.); its salts are yellow; the *hydriodide* has m. p.  $235^{\circ}$  (decomp.), and the *hydrobromide* decomposes at about  $240^{\circ}$ . These compounds are of therapeutic value. F. M. G. M.

**Oxidation of Sparteine with Potassium Permanganate.** A. GERMAIN (*Gazzetta*, 1912, 42, i, 447—450; *Boll. Chim. Farm.*, 1912, 51, 111—113).—Bamberger (Abstr., 1887 162) and Ahrens (Abstr., 1887, 1056) having obtained contradictory results in studying the oxidation of sparteine with permanganate, the author has investigated the reaction in sulphuric and in phosphoric acid solution.

In the former case, no change takes place in the cold for a longer or shorter time according to the concentration of the acid, but if this is lowered by addition of increasing quantities of an alkali, the stability is diminished more and more, until, in a neutral medium, oxidation is almost instantaneous. No matter what the concentration of the acid, oxidation proceeds with great rapidity as soon as it begins, and is accompanied by vigorous evolution of carbon dioxide. The principal product of the reaction is oxalic acid, small proportions of ammonia and of a base giving a picrate, m. p.  $168-169^{\circ}$ , being also formed; in no case was a precipitate formed with copper acetate.

In presence of phosphoric acid the oxidation commences immediately, but proceeds very slowly, and is complete only after about a week. The main product is succinic acid, so that the presence of a four-carbon atom chain must be assumed in the sparteine molecule, and Moureu and Valeur's formula (Abstr., 1905, i, 716) requires modification. Numerous investigations have shown that the nuclei of sparteine are piperidinic in character, and hence incapable of undergoing oxidation to a four-carbon atom chain, which must hence be assumed to form the connecting link between the two nuclei. The conclusion is therefore drawn that at least one of the nuclei has only one carbon atom in its bridge: but the formula:



is less by  $\text{CH}_2$  than that of sparteine, which is to be regarded as a higher homologue. Confirmation of this result is afforded by the behaviour of coniine, which gives *n*-butyric acid on oxidation.

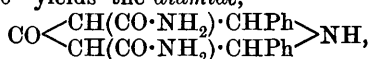
T. H. P.

**Preparation of Readily Soluble Double Compounds from Aminoacylphenetidines, Caffeine, and Mineral Acids.** CHEMISCHE WERKE VORM. HEINRICH BYK (D.R.-P. 244740. Compare this vol., i, 516).—The aminoacylphenetidines combine with caffeine to form readily soluble double salts analogous to those furnished by dialkylaminodimethylpyrazolones; the reaction is carried out with equimolecular proportions of the components (or their salts) in either aqueous or alcoholic solution.

The patent describes a *compound* obtained from caffeine and aminoaceto-*p*-phenetidine ( $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}_2$ ) in dilute hydrochloric acid solution.

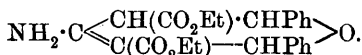
F. M. G. M.

**Action of Ammonia on Derivatives of Piperidone, Pyridone, and Hydropyrone.** N. TSONEFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 662—664).—The interaction of ethyl or methyl diphenylpiperidonedicarboxylate with a small quantity of alcoholic ammonia in a sealed tube at  $100^\circ$  yields the *diamide*,



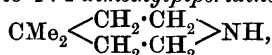
m. p.  $245\text{--}247^\circ$ . With the esters of pyridonedicarboxylic acid, no such reaction occurs with ammonia.

The compound obtained by heating ethyl 1:5-diphenylhydropyrone-2:4-dicarboxylate with alcoholic ammonia in a sealed tube, melts at  $125\text{--}126^\circ$ , and has the constitution  $\text{NH}\cdot\text{C} \begin{array}{c} \text{CH}(\text{CO}_2\text{Et})\cdot\text{CHPh} \\ \text{CH}(\text{CO}_2\text{Et})\cdot\text{CHPh} \end{array} \text{O}$  or



T. H. P.

**4:4-Dimethylpiperidine.** GUSTAV KOMPPA (*Ann. Acad. Sci. Fennicae*, 1911, A, 3, 6 pp. Compare *Chem. Zeit.*, 1906, 30, 1184).— $\beta\beta$ -Dimethylglutarimide (needles, m. p.  $146^\circ$ ), obtained from the corresponding acid anhydride by the action of ammonia, is reducible by sodium and alcohol to 4:4-dimethylpiperidine,



b. p.  $145\text{--}146^\circ$ ; *hydrochloride*, needles, m. p.  $220\text{--}221^\circ$ ; *platini-chloride*, prismatic crystals; *aurichloride*, m. p.  $168^\circ$  (decomp.). The base reacts with phenylthiocarbimide, giving 4:4-dimethylpiperidylphenylthiocarbamide, needles, m. p.  $136^\circ$ .

D. F. T.

[**Hæmopyrrole.**] HANS FISCHER and ERICH BARTHOLOMÄUS (*Zeitsch. physiol. Chem.*, 1912, 78, 420).—Polemical. A reply to Marchlewski (this vol., i, 399).

E. F. A.

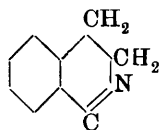
**Preparation of Dibromoisatin.** KALLE & Co. (D.R.-P. 245042). Dibromoisatin has already been prepared by the action of bromine on isatin in acetic acid solution at high temperatures. It is now found

that the reaction goes smoothly and at a lower temperature in sulphuric acid solution. If sulphuric acid (66 Bé) is employed, only monobromoisatin is formed, whereas dibromoisatin, an orange-yellow powder, m. p. 248—250, is obtained in quantitative yield when isatin (14·7 parts) in 150 parts of sulphuric acid (60° Bé) is treated with bromine (32 parts), left at the ordinary temperature during twenty-four hours, then slowly heated to 40°, and subsequently at 80°.

F. M. G. M.

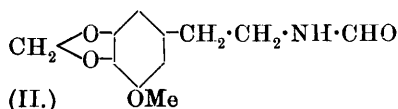
### Preparation of Dihydroisoquinoline Derivatives. HERMANN

DECKER (D.R.-P. 245095. Compare Trans., 1910, 97, 1212; Abstr., 1911, i, 906). — *Oxalylbisphenylethylamine*, glistening needles, m. p. 186°, is prepared by fusing together phenylethylamine (2 mols.) and oxalic acid (1 mol.); when treated with phosphoric



(I.)  $\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_5$  (1 mol.)

oxide in toluene solution it furnishes the base (formula I) [*dihydroisoquinoline-2-carboxyphenylethylamide*]; the *picrate*,  $\text{C}_{24}\text{H}_{21}\text{O}_8\text{N}_5$ , canary-green needles, has m. p. 167—168°, the *hydrochloride*, colourless needles, m. p. 191—193°; when heated under

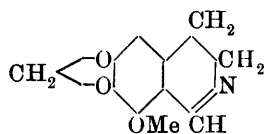


(II.)

pressure during four hours with 15% hydrochloric acid at 180°, it is decomposed into dihydroisoquinoline and phenyl-

ethylamine hydrochlorides with evolution of carbon dioxide.

*Formyl-3-methoxy-4:5-methylenedioxyphenylethylamine* (formula



(III.)

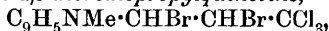
II) has m. p. 105—106°, and when treated with phosphoryl chloride furnishes 8-methoxy-6:7-methylenedioxy-3:4-dihydroisoquinoline (formula III), a dark oily base, which finally solidifies, but has no well defined m. p. (the *picrate* has m. p. 182—184°), and on methylation yields cotarnine hydriodide.

F. M. G. M.

**Condensation Products of 2:4-Dimethylquinoline with Aldehydes.** ROSARIO SPALLINO and A. CUCCHIARONI (*Gazzetta*, 1912, 42, i, 517—525).—In view of the readiness with which a methyl group in the 2-position of the pyridine or quinoline nucleus reacts with aldehydes, the authors have investigated 2:4-dimethylquinoline in this direction in order to ascertain if the 4-methyl group can also be made to react. With all the aldehydes employed, however, it was found that the 4-methyl group did not react, even when an excess of the aldehyde was employed and the reaction was carried out in presence of zinc chloride. This condensing agent has, indeed, a harmful effect, since, in addition to causing resinification, it forms compounds with the quinoline derivatives, from which the latter are separated only with difficulty.

With *chloral*, 2:4-dimethylquinoline forms the condensation product

[4-methyl-2-tri- $\gamma$ -chloropropenylquinoline],  $C_9H_5NMe \cdot CH \cdot CH \cdot CCl_3$ , which forms nacreous, rectangular plates, m. p.  $124^\circ$ , exhibits normal cryoscopic behaviour in benzene, and combines with bromine, giving 4-methyl-2-tri- $\gamma$ -chloro- $\alpha\beta$ -dibromopropylquinoline,



m. p.  $155^\circ$ . The unsaturated condensation product is basic in character, its *hydrochloride* having m. p.  $152^\circ$ ; it is readily hydrolysed by alkali, giving 4-methylquinoline-2-acrylic acid,  $C_9H_5NMe \cdot CH \cdot CH \cdot CO_2H$ , which begins to decompose at  $190^\circ$  and melts at about  $210^\circ$ , and readily reduces permanganate and absorbs bromine.

If the reaction between 2:4-dimethylquinoline and chloral is arrested before its completion, the result is an aldol condensation product,  $C_9H_5NMe \cdot CH_2 \cdot CH(OH) \cdot CCl_3$ , which forms white, prismatic needles, m. p.  $67^\circ$ , and gives the unsaturated product, m. p.  $124^\circ$ , when heated.

With benzaldehyde, 2:4-dimethylquinoline yields the condensation product [2-styryl-4-methylquinoline],  $C_9H_5NMe \cdot CH \cdot CHPh$ , which forms thick, lemon-yellow needles, m. p.  $122-123^\circ$ , gives a *hydrochloride*, m. p.  $259^\circ$  (decomp.), and a *dibromide*, m. p.  $162^\circ$ , decolorises permanganate solution, and yields benzoic and 4-methylquinoline-2-carboxylic acids on oxidation.

The following condensation products [substituted 2-styryl-4-methylquinolines] were also examined:

With o-nitrobenzaldehyde,  $C_9H_5NMe \cdot CH \cdot CH \cdot C_6H_4 \cdot NO_2$ , m. p.  $140-141^\circ$ ; *hydrochloride* decomposes at  $200^\circ$ ; *bromide*, m. p.  $505^\circ$  (decomp.).

With m-nitrobenzaldehyde, m. p.  $184^\circ$ ; the *hydrochloride* and *bromide* decompose on heating.

With vanillin,  $C_9H_5NMe \cdot CH \cdot CH \cdot C_6H_3(OH) \cdot OMe$ , golden-yellow scales, m. p.  $217^\circ$ ; the *hydrochloride* decomposes at  $256^\circ$ . T. H. P.

**Preparation of Aryl Esters of 2-Phenylquinoline-4-carboxylic Acid.** CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 244788).—The methyl and ethyl esters of 2-phenylquinoline-4-carboxylic acid have already found therapeutic employment, and the following additional compounds have now been prepared; the *phenyl* ester, m. p.  $132^\circ$ , and the  $\beta$ -*naphthyl* ester, yellow crystals, m. p.  $130^\circ$ .

F. M. G. M.

**Dibromophenylisooxazolone and Derivatives.** ANDRÉ MEYER (*Compt. rend.*, 1912, 154, 1511—1514).—4:4-Dibromo-3-phenylisooxazolone,  $O \begin{smallmatrix} \diagup CO \cdot CBr_2 \\ \diagdown N = CPh \end{smallmatrix}$ , is obtained as colourless crystals, m. p.  $76-77^\circ$ ,

by the action of bromine on phenylisooxazolone in acetic acid solution. It condenses with phenylhydrazine, giving a phenylhydrazone, which is identical with Claisen's benzeneazophenylisooxazolone (compare Abstr., 1891, 468). With *as*-phenylmethylhydrazine it forms the *hydrazone*,  $C_{16}H_{13}O_2N_3$ , m. p.  $148^\circ$ , and with *as*-phenylbenzylhydrazine the *hydrazone*,  $C_{22}H_{17}O_2N_3$ , m. p.  $126-127^\circ$ . With *as*-benzoylphenylhydrazine no hydrazone is formed, but the product is benzeneazophenylisooxazolone. It gives a *semicarbazone*,  $C_{10}H_8O_3N_4$ , which crystallises in pale yellow

needles, m. p. 230—232°, and an oxime which is identical with oximinophenylisooxazolone.

Amines cause the elimination of bromine, heterocyclic amines giving rise to rubazonic acids. Aminoantipyrine condenses with dibromophenylisooxazolone, giving 1-phenyl-2:3-dimethylpyrazoloneimino-3'-phenylisooxazolone (compare Abstr., 1911, i, 687).

With indoxyl, 3-phenylisooxazolone-2-indole is obtained (compare Wahl, Abstr., 1909, i, 261). W. G.

**Diphenylethylene Leuco-bases and Colouring Matters; Some Alkylaminoethylenic Derivatives.** PAUL LEMOULT (*Compt. rend.*, 1912, 154, 1622—1625. Compare Abstr., 1911, i, 399).—*p*-Alkylaminophenyl ketones, for example, Michler's ketone, when treated with a Grignard reagent produce ethylenic substances (Freund and Mayer, Abstr., 1906, i, 384; Busignies, Abstr., 1909, i, 736). The reaction is now extended by the application of Grignard reagents from other alkyl halides; the reaction product generally consists of a mixture of a grey powder insoluble in alcohol, with the expected ethylenic compound.

Magnesium *n*-propyl iodide with Michler's ketone gives *di-p*-dimethylamino-*aa*-diphenyl- $\Delta^a$ -butylene,  $\text{CH}_2\text{Me}\cdot\text{CH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , colourless needles, m. p. 47·5°.

Magnesium isopropyl iodide in a similar manner gives the isomeric *di-p*-dimethylamino-*aa*-diphenyl- $\beta$ -methyl- $\Delta^a$ -propylene,  $\text{CMe}_2\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , compact crystals with a green tinge, m. p. 89°.

Magnesium *n*-butyl iodide gives *di-p*-dimethylamino-*aa*-diphenyl- $\Delta^a$ -amylene,  $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , colourless needles, m. p. 50·5°.

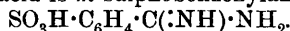
Magnesium isobutyl iodide gives *di-p*-dimethylamino-*aa*-diphenyl- $\gamma$ -methyl- $\Delta^a$ -butylene,  $\text{CHMe}_2\cdot\text{CH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , which refused to crystallise; a reddish-brown, crystalline substance which contained iodine was obtained as a by-product.

Magnesium *sec*-butyl iodide gives *di-p*-dimethylamino-*aa*-diphenyl- $\beta$ -methyl- $\Delta^a$ -butylene,  $\text{CMeEt}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$ , compact, pale yellow crystals, m. p. 79°.

The above products give solutions in acetic acid, which gradually attain an intense blue colour; they also give colour reactions with nitrous acid and with manganese dioxide. D. F. T.

**Hexahydrogenated Malachite-green; an Example of Two Different Leuco-bases which Yield the Same Dye.** PAUL LEMOULT (*Compt. rend.*, 1912, 154, 1354—1356. Compare Abstr., 1911, i, 399).—The author has reduced cyclohexenyltetramethyldiaminodiphenylmethane to cyclohexyltetramethyldiaminodiphenylmethane (Wahl and Meyer, Abstr., 1910, i, 134) by means of hydriodic acid and red phosphorus. The latter compound yields no coloration when oxidised by lead peroxide in acid solution. Chloranil in benzene solution oxidises it to malachite-green, the six additional hydrogen atoms of the cyclohexane group being removed. The conclusion is drawn that the existence of a dye containing the cyclohexyl group is improbable. H. W.

**Reaction between Carboxylic Acids and Benzenesulphonamide at High Temperatures.** CHARLES A. ROUILLER (*Amer. Chem. J.*, 1912, 47, 475—497).—Nakaseko (this vol., i, 452) has suggested that the “infusible diamide” obtained by the action of heat on *m*-sulphamidobenzoic acid is *m*-sulphobenzylamidine,

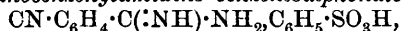


This structure has now been confirmed by the observation that the “infusible diamide” yielded by *p*-sulphamidobenzoic acid (Remsen and Muckenfuss, *Abstr.*, 1896, i, 481) can be obtained by heating *p*-sulphobenzoic acid with benzenesulphonamide. It has also been shown that carbamidobenzenesulphonic acid is probably formed as an intermediate compound in the production of the “infusible diamide,” since benzylamidine benzenesulphonate can be obtained from benzamide and benzenesulphonamide.

When a mixture of benzoic acid (1 mol.) and benzenesulphonamide (2 mols.) is heated at 225°, benzenesulphonic acid and benzylamidine benzenesulphonate are produced, together with small quantities of benzonitrile, cyaphenin, and benzoic acid, the main reaction being represented as follows:  $\text{C}_6\text{H}_5\cdot\text{CO}_2\text{H} + 2\text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{NH}_2 = \text{C}_6\text{H}_5\cdot\text{C}(\text{:NH})\cdot\text{NH}_2\cdot\text{C}_6\text{H}_5\cdot\text{SO}_3\text{H} + \text{C}_6\text{H}_5\cdot\text{SO}_3\text{H}$ , or in two stages, thus:  $\text{C}_6\text{H}_5\cdot\text{CO}_2\text{H} + \text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{NH}_2 = \text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}_2 + \text{C}_6\text{H}_5\cdot\text{SO}_3\text{H}$  and  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}_2 + \text{C}_6\text{H}_5\cdot\text{SO}_2\cdot\text{NH}_2 = \text{C}_6\text{H}_5\cdot\text{C}(\text{:NH})\cdot\text{NH}_2\cdot\text{C}_6\text{H}_5\cdot\text{SO}_3\text{H}$ . Benzylamidine benzenesulphonate, m. p. 173°, first prepared by Robinson (*Diss.*, 1906), behaves towards alkali hydroxides, magnesium hydroxide, and acids in an analogous manner to the “infusible diamide” from *p*-sulphamidobenzoic acid. In order to confirm the view that benzamide is formed as an intermediate product, benzamide (1 mol.) and benzenesulphonamide (1 mol.) were heated together at 220°; it was found that benzylamidine benzenesulphonate could be obtained in this way, but only in presence of benzenesulphonic acid. Benzylamidine *p*-toluenesulphonate (Robinson, *loc. cit.*) melts at 193°.

*Ethenylamidine benzenesulphonate*, m. p. 136°, obtained by heating a mixture of acetic acid (1 mol.) and benzenesulphonamide (2 mols.) at 220°, forms long, transparent needles. This method of preparing amidines was applied to various aliphatic and aromatic acids; in several cases, amidine benzenesulphonates were produced, whilst in others negative results were obtained.

*m*- and *p*-Nitrobenzylamidine benzenesulphonates have m. p. 198—200° and 250° respectively. *m*-Bromobenzylamidine benzenesulphonate has m. p. 156—158°, and phenylethenylamidine benzenesulphonate, m. p. 182—183°. When phthalic acid is heated with benzenesulphonamide, a nearly quantitative yield of phthalimide is produced. *iso*Phthalic and terephthalic acids, however, yield the corresponding nitriles as the main products, together with small quantities of the cyanobenzoic acids; terephthalic acid gives also a small quantity of *p*-cyanobenzylamidine benzenesulphonate,



m. p. 215—218°.

E. G.

**Urocanic Acid.** ANDREW HUNTER (*J. Biol. Chem.*, 1912, 11, 537—546).—The details of analysis given prove that urocanic acid is β-iminazole-4(5)-acrylic acid.

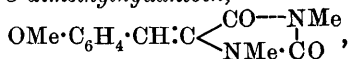
W. D. H.

**Hydantoins. XI. New Method of Synthesising *N*-Alkyl Derivatives of  $\alpha$ -Amino-acids. Methyltyrosine.** TREAT B. JOHNSON and BEN H. NICOLET (*Amer. Chem. J.*, 1912, 47, 459—475). —*N*-Methyltyrosine ( $\alpha$ -methylamino- $\beta$ -*p*-hydroxyphenylpropionic acid) has been prepared by Friedmann and Gutmann (*Abstr.*, 1910, i, 741). It is now shown that this compound can be readily obtained from 4-anisylidenehydantoin (Wheeler and Hoffman, *Abstr.*, 1911, i, 499). By the action of methyl iodide on 4-anisylidenehydantoin, 4-anisylidene-1:3-dimethylhydantoin is produced, which, on reduction with hydriodic acid, yields 1:3-dimethyltyrosinehydantoin, and this when hydrolysed with barium hydroxide furnishes the barium salt of methyltyrosine. The amount of methyltyrosine obtained after removing the barium corresponds with 32% of the theoretical.

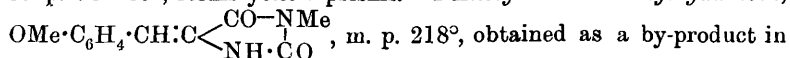
The syntheses can be modified by reducing the 4-anisylidene-1:3-dimethylhydantoin to 4-*p*-methoxybenzyl-1:3-dimethylhydantoin by means of tin and hydrochloric acid and converting this, by hydrolysis with barium hydroxide, into  $\alpha$ -methylamino- $\beta$ -*p*-methoxyphenylpropionic acid (Friedmann and Gutmann, *loc. cit.*), which when heated with hydriodic acid gives a yield of methyltyrosine amounting to 65% of the theoretical.

Methyltyrosine has no definite m. p., but decomposes between 265° and 320°, according to the rate of heating.

4-Anisylidene-1:3-dimethylhydantoin,



m. p. 84—85°, forms yellow prisms. 4-Anisylidene-1-methylhydantoin,



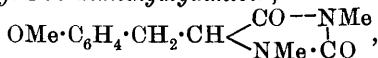
the preparation of the dimethyl compound, crystallises in needles.

4-*p*-Hydroxybenzyl-1:3-dimethylhydantoin (1:3-dimethyltyrosinehydantoin),  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH} \begin{array}{l} \text{CO} \text{---} \text{NMe} \\ \text{NMe} \cdot \text{CO} \end{array}$ , m. p. 149—150°, forms

rhombohedral crystals. 4-*p*-Hydroxybenzyl-1-methylhydantoin (1-methyltyrosinehydantoin),  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH} \begin{array}{l} \text{CO} \text{---} \text{NMe} \\ \text{NH} \cdot \text{CO} \end{array}$ , m. p. 200°, obtained

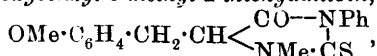
by reducing 4-anisylidene-1-methylhydantoin with hydriodic acid and amorphous phosphorus, crystallises in short, colourless prisms.

4-*p*-Methoxybenzyl-1:3-dimethylhydantoin,



was obtained as a light brown oil; it can also be prepared by treating 4-*p*-methoxybenzylhydantoin with methyl iodide in presence of alkali hydroxide.  $\alpha$ -Methylamino- $\beta$ -*p*-methoxyphenylpropionic acid crystallises in colourless, prismatic needles, and decomposes between 220° and 255°, according to the rate of heating.

1-Phenyl-4-*p*-methoxybenzyl-3-methyl-2-thiohydantoin,



m. p. 105°, prepared by the action of phenylthiocarbimide on

$\alpha$ -methylamino- $\beta$ -*p*-methoxyphenylpropionic acid, crystallises in colourless prisms.

4-*p*-Methoxybenzylhydantoin (Wheeler, Hoffman, and Johnson, Abstr., 1911, i, 923) can be prepared in a yield of 78% of the theoretical by reducing 4-anisylidenehydantoin with tin and alcoholic hydrogen chloride.

By the action of iodine on methyltyrosine in presence of potassium hydroxide,  $\alpha$ -methylamino- $\beta$ -3:5-di-iodo-4-hydroxyphenylpropionic acid (methyliodogorgoic acid),  $\text{OH}\cdot\text{C}_6\text{H}_2\text{I}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NHMe})\cdot\text{CO}_2\text{H}$ , is obtained in 76% yield; it forms nearly colourless crystals and decomposes at about 205°.

E. G.

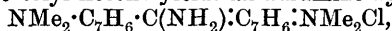
Some Homologues of Auramine and Crystal-violet. BERTHOLD RASSOW and OTTO REUTER (*J. pr. Chem.*, 1912, [ii], 85, 497—513).—The interaction of auramine-G (dimethyldiaminodi-*o*-tolyliminomethane) and methyl sulphate in alcoholic solution in the presence of magnesium oxide yields trimethyldiaminodi-*o*-tolyliminomethane methyl sulphate,  $\text{NHMe}\cdot\text{C}_7\text{H}_6\cdot\text{C}(\text{NH}_2)_2\cdot\text{C}_7\text{H}_6\cdot\text{NMe}_2\cdot\text{SO}_4\text{Me}$ , which crystallises in small, reddish-brown, basalt-like prisms, m. p. 243—244°, and when boiled with hydrochloric acid is converted into trimethyldiaminodi-*o*-tolyl ketone,  $\text{NHMe}\cdot\text{C}_7\text{H}_6\cdot\text{CO}\cdot\text{C}_7\text{H}_6\cdot\text{NMe}_2$ . This forms a light yellow, crystalline powder, m. p. 128—129°, and yields a dihydrochloride, crystallising in small, lustrous, silvery leaflets, m. p. 216°; the picrate forms light orange crystals, m. p. 171°.

Tetramethyldiaminodi-*o*-tolyl ketone,  $\text{CO}(\text{C}_7\text{H}_6\cdot\text{NMe}_2)_2$ , prepared by methylating dimethyldiaminodi-*o*-tolyl ketone (Gnehm and Wright, Abstr., 1902, i, 295) with methyl sulphate and magnesium oxide in benzene solution, crystallises in clusters of long, flat, pale yellow needles, m. p. 85·5°, b. p. 240—250°/12 mm.; the dihydrochloride forms slender, white needles, m. p. 204—206° (decomp.); the platinichloride,  $\text{C}_{19}\text{H}_{24}\text{ON}_2\cdot\text{H}_2\text{PtCl}_6$ , crystallises with alcohol (1 mol.) and decomposes at 240°; the oxalate, m. p. 171—172°, and picrate, small yellow needles, m. p. 192°, are also described.

The methyl sulphate is obtained as a viscid, reddish-brown oil by carrying out the methylation in the absence of magnesium oxide.

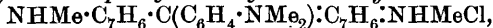
Tetramethyldiaminodi-*o*-tolylcarbinol,  $\text{OH}\cdot\text{CH}(\text{C}_7\text{H}_6\cdot\text{NMe}_2)_2$ , prepared by reducing the preceding ketone with sodium amalgam and alcohol, forms a white powder, m. p. 76°; the picrate becomes green at 140°, and has m. p. 145°.

When heated with ammonium chloride and zinc chloride, tetramethyldiaminodi-*o*-tolyl ketone yields an auramine dye,



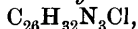
as a yellow powder which chars at 250°.

Tetramethyltriaminophenyl-di-*o*-tolylcarbinol hydrochloride,



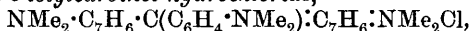
prepared by condensing dimethyldiaminodi-*o*-tolyl ketone and dimethylaniline with phosphorus trichloride, forms small, green, lustrous crystals, and dyes cotton, mordanted with tannin, reddish-violet; the corresponding carbinol is precipitated in brownish-red flocks on the addition of aqueous sodium hydroxide to the hydrochloride.

Pentamethyltriaminophenyl-di-*o*-tolylcarbinol hydrochloride,



obtained from trimethyldiaminodi-*o*-tolyl ketone and dimethylaniline in a similar manner, forms a deep blue, hygroscopic, crystalline powder, having a metallic lustre; the reddish-brown *carbinol*,  $C_{26}H_{33}ON_3$ , could not be obtained crystalline.

The condensation of tetramethyldiaminodi-*o*-tolyl ketone and dimethylaniline by means of phosphoryl chloride yields *hexamethyltri-aminophenyldi-o-tolylcarbinol hydrochloride*,



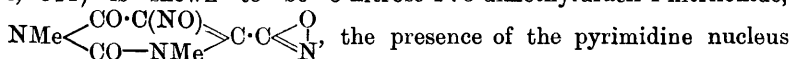
which forms a dark violet, crystalline powder of a feeble metallic lustre; the corresponding *carbinol* forms white crystals, m. p. 115—116°.

The preceding penta- and hexa-methyl derivatives dye cotton, mordanted with tannin, bluish-violet and blue respectively. F. B.

**Tri-indylmethane Dyes.** III. ALEXANDER ELLINGER and CLAUDE FLAMAND (*Zeitsch. physiol. Chem.*, 1912, **78**, 365—372. Compare König, Abstr., 1911, i, 808).—According to König, the formation of the dye,  $C_{19}H_{16}N_2 \cdot HCl$ , from methylindole-aldehyde takes place without oxidation. The authors formulate the change as involving three molecules of methylindole-aldehyde and an atom of oxygen, giving the dye,  $C_{28}H_{23}N_3 \cdot HCl$ . König's formula is supported by analyses of the salts, but these alone are insufficient to decide between the two formulæ. Both molecular-weight determinations and the estimation of the amount of formic acid formed confirm the formula  $C_{28}H_{23}N_3$ .

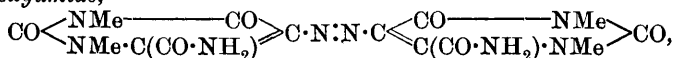
*Indyldichloromethylindylmethane*, prepared from indylaldehyde and chloromethylindole, forms colourless plates, which become yellowish-rose on the surface on exposure to light, and have m. p. 263°. E. F. A.

**Nitrosodimethyluracilnitriloxide.** RUDOLF BEYTHIEN (*Annalen*, 1912, **389**, 214—232).—The green substance obtained by Behrend and Hufschmidt by the nitration of 1:3:4-trimethyluracil (Abstr., 1906, i, 311) is shown to be 5-nitroso-1:3-dimethyluracil-4-nitriloxide,



the presence of the pyrimidine nucleus being proved by the formation of nitrodimethyluracilcarboxylic acid by its further nitration. It has m. p. 170—171° (decomp.), crystallises from alcohol in green needles, from benzene in green prisms, and best from glacial acetic acid in pale green, rhombic plates, and its unimolecular structure is proved by the cryoscopic method in the last solvent. It is converted by 36% hydrochloric acid on the water-bath into *dimethyl-violuric acid*,  $C_6H_7O_4N_3 \cdot H_2O$ , m. p. 123° (decomp.), or 140—141° when anhydrous, which produces a violet coloration with alkalis and is converted into dimethyldiluric acid by nitric and sulphuric acids.

The reduction of nitrosodimethyluracilnitriloxide by tin and hydrochloric acid at the ordinary temperature yields *azodimethyluracil-carboxamide*,

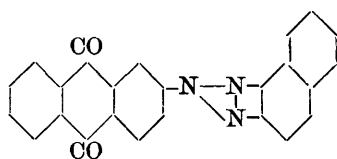


m. p. 227°, orange-yellow needles (which is reduced to aminodimethyluracilcarboxylic acid by further treatment with tin and hydrochloric

acid on the water-bath), and 5-amino-1:3-dimethyluracil-4-carboxylic acid,  $C_7H_9O_4N_3 \cdot H_2O$ , m. p. 215—224° (decomp.), which has strongly acidic properties, contrary to the statement of Behrend and Hufschmidt (*loc. cit.*). When aminodimethyluracilcarboxylic acid is boiled with 5% sodium hydroxide, ammonia is given off, and after acidifying the solution, carbon dioxide is obtained, together with a substance,  $C_6H_8O_3N_2$ , m. p. 224—225°, which has acidic properties, does not give a blue coloration with ferric chloride, and is regarded as 1:3-dimethyl-iminoazole-2-one-4-carboxylic acid,  $CO_2H \cdot C \begin{smallmatrix} \swarrow CH-NMe \\ \searrow NMe \cdot CO \end{smallmatrix}$ , since it does exhibit the murexide reaction and is oxidised to dimethylparabanic acid by chromic acid.

C. S.

**Preparation of Anthraquinone Derivatives Containing the  $\psi$ -Azimino-Ring.** CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 245973).—When the aminoazo-derivatives obtained from diazotised  $\beta$ -aminoanthraquinones and  $\beta$ -naphthylamines are submitted to the action of oxidising agents they yield new compounds containing the  $\psi$ -azimino-ring, which find employment as yellow pigments.



$\beta$ -Naphthylene- $\psi$ -azimino- $\beta$ -anthraquinonyl (annexed formula) crystallises from nitrobenzene, has m. p. 300° (approx.), and is prepared by dissolving the product obtained from diazotised  $\beta$ -aminoanthraquinone coupled with  $\beta$ -naphthylamine in

nitrobenzene and treating it with sodium dichromate in acetic acid.

The preparation of the following analogous compounds are described in the original: from diazotised  $\beta$ -aminoanthraquinone with  $\beta$ -naphthylamine-3:6-disulphonic acid; with  $\beta$ -naphthylamine-6-sulphonic acid, and with 2:6-naphthylenediamine. From diazotised 2:6-diaminoanthraquinone with  $\beta$ -naphthylamine, and with  $\beta$ -naphthylamine-6-sulphonic acid. These compounds are all yellow or brownish-yellow powders.

F. M. G. M.

**Preparation of Aminoanthraquinonyltriazoles.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 245191).—When the anthraquinonyltriazoles which are obtained by the oxidation of *o*-aminoazoanthraquinone derivatives are nitrated and subsequently reduced, they yield compounds of tinctorial value.  $\beta$ -Anthraquinonyl-1:2-naphthylenetriazole (37 parts) dissolved in concentrated sulphuric acid (400 parts) was slowly treated with potassium nitrate (10.1 parts), and the nitro-compound isolated in the form of a yellow powder; this when reduced with sodium sulphide furnished amino- $\beta$ -anthraquinonyl-1:2-naphthylenetriazole, a brown powder which is soluble in concentrated sulphuric acid with an orange coloration. When a larger quantity of potassium nitrate is employed, more highly nitrated products are obtained.

F. M. G. M.

**Purines.** 2:8-Dioxy-6:9-dimethylpurine and 2:8-Dioxy-1-methylpurine. CARL O. JOHNS (*J. Biol. Chem.*, 1912, 11, 393—400).—6-Chloro-2-ethylthiol-4-methylpyrimidine was heated in a

sealed tube with methylamine; the 6-methylamino-2-ethylthiol-4-methylpyrimidine so obtained, flat prisms, m. p.  $87^{\circ}$ , was converted into 6-methylamino-4-methyl-2-pyrimidone, m. p.  $290^{\circ}$ , which when nitrated gave 5-nitro-6-methylamino-4-methyl-2-pyrimidone, stout prisms, m. p.  $250^{\circ}$ ; this was reduced by ferrous hydroxide to 5-amino-6-methylamino-4-methyl-2-pyrimidone, forming anhydrous needles, m. p.  $270^{\circ}$ . By heating this with carbamide, 2:8-dioxy-6:9-dimethylpurine was obtained; it crystallises ( $2\text{H}_2\text{O}$ ) in needles, m. p.  $320^{\circ}$ .

2:8-Dioxy-1-methylpurine was obtained by heating 5:6-diamino-3-methyl-2-pyrimidone with carbamide as small, anhydrous plates, not melting at  $320^{\circ}$ .  
W. D. H.

**Uric Acid Glycol.** HEINRICH BILTZ and MYRON HEYN (*Ber.*, 1912, 45, 1677—1682).—Alluradic acid was obtained by Mulder by the evaporation of an aqueous solution of alloxan and carbimide (this *Journ.*, 1874, 49). On the analogy of the formation of substituted uric acid glycols (compare *Abstr.*, 1910, i, 526, and following abstract), this acid should be the glycol of uric acid itself. It has now been prepared by allowing the mixed solutions to evaporate in a desiccator over lime, in flat prisms with half a molecule of water. When warmed with glacial acetic acid the anhydrous acid is obtained, m. p.  $203\text{--}205^{\circ}$ , and when heated with hydriodic acid it is reduced to hydantoin, which confirms its constitution.

Attempts have been made to convert the glycol into the isomeric 5-hydroxyhydantoinylcarbamide,  $\text{C}_5\text{H}_6\text{O}_5\text{N}_4$ , but this only takes place in warm water; the new compound is very soluble in water, but practically insoluble in organic media, and decomposes at  $204\text{--}206^{\circ}$ . When treated with hydrochloric acid in ethyl acetate, ammonium chloride is precipitated, and a syrupy residue, the caffolide, is formed. Hydrolysis by means of hydrochloric or nitric acid leads to the elimination of carbamide, and the residue of the molecule can be characterised by reduction to hydantoin.  
J. C. W.

**The Reduction of the Uric Acid Glycols to Hydantoins. Some Salts of the Uric Acid Glycols.** HEINRICH BILTZ and MYRON HEYN (*Ber.*, 1912, 45, 1666—1677).—It was hoped that the reduction of uric acid glycols (compare *Abstr.*, 1910, i, 526) would furnish some uric acids which are difficult to obtain. This could not be realised, as many reducing agents are without effect, but hydriodic acid readily reduces these substances to hydantoins, the alloxan nucleus being opened or eliminated.

7:9-Dimethyluric acid glycol gives the new 1:3-dimethylhydantoin; the formation of 3-methyl-(or ethyl)-hydantoin from the glycols produced by condensing alloxan with methyl-(or ethyl)-carbamide decides for position 9 for the alkyl group; and the production of 1-methylhydantoin from 3:7-dimethyluric acid glycol, on the one hand, and from caffeine, on the other, shows that the carbon atom 5 of the uric acid system becomes the methylene carbon of the hydantoin system. Only one glycol, 1:3-dimethyluric acid glycol, behaved differently, amalic acid being produced. This lesser stability of the

glyoxalone nucleus is no doubt due to the fact that neither imino-group is alkylated (compare Biltz, Abstr., 1909, i, 740 ; 1910, i, 523).

E. Fischer's method for the preparation of 1-methylhydantoin from apocaffeine (Abstr., 1883, i, 354) has been shortened by the direct reduction of the latter to hydrocaffuric acid, which is then hydrolysed by baryta, the best results being obtained by this means.

Methylparabanic acid, when reduced by fuming hydriodic acid, is converted into a mixture of 1- and 3-methylhydantoins, which are very difficult to separate (compare Weitzner, Abstr., 1908, i, 841). The reduction of 7:9-dimethyluric acid glycol also requires the concentrated agent, as weaker acid leads partly to dimethylparabanic acid which can scarcely be separated.

1:3-Dimethylhydantoin,  $C_5H_8O_2N_2$ , crystallises from ether in pointed leaflets, m. p. 44—45°, and distils as a colourless, mobile liquid at 262°. Having ascertained its properties, it was found possible to prepare it by the reduction of 1:3:6-trimethylallantoin, from which Fischer could only separate the accompanying methylcarbamide (*loc. cit.*), and by the energetic reduction of dimethylparabanic acid. The latter process gives a yield of 67%, and as the acid is easily obtained by the oxidation of caffeine, it is the best to adopt. This hydantoin is very susceptible towards alkalis, baryta converting it into the barium salt of 1:3-dimethylhydantoic acid, and for this reason it could not be obtained from deoxyalocaffuric acid (Abstr., 1910, i, 523).

When warmed with alcoholic ammonia, 3:7-dimethyl-, 7:9-dimethyl-, 9-methyl-, and unsubstituted uric acid glycols form unstable *mono-ammonium* salts, which give up their ammonia when kept. In the case of the 1:3-dimethyluric acid glycol, however, the glyoxalone ring is opened. When mixed with silver nitrate and then made alkaline with ammonia, *di-silver* salts are precipitated, the imide hydrogens being replaced ; positions 1 and 9 are most readily filled. 7:9-Dimethyluric acid glycol gives no silver salt. When warmed with methyl iodide the silver is replaced, but degradation to caffolides also takes place, highly methylated uric acid glycols being unstable.

J. C. W.

**Dilatometric Investigations on the Precipitation of Proteins.** GINO GALEOTTI (*Zeitsch. physiol. Chem.*, 1912, 78, 421—434).—Coagulation produced by heat and by enzymes causes no change of volume in proteins. There is, however, an increase in volume seen when egg-albumin is precipitated by protein-precipitants. This is maximal when ammonium sulphate is used (a reversible reaction), medium in the case of salts of the heavy metals, and minimal in the case of potassium ferrocyanide, phosphotungstic acid, and tannin.

W. D. H.

**General Chemistry of the Proteins. IV. Protein Scission and Soap-protein Compounds** PETER RONA and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1912, 41, 165—173).—In following out the course of digestion of proteins by a stalagmometric method it was observed that the surface tension of liquids increased when the solution of proteins was digested by means of acids, whereas it

remained unchanged when the proteins were digested with enzymes. This was found to hold with all the proteins investigated, with the exception of gelatin, and the fact indicates that certain products are formed in digestion by ferments (possibly adsorption compounds) which undergo further change when treated with acids. It was also observed that blood diminishes the capacity of soaps for lowering the surface tension, the corpuscles acting, in this respect, about ten times as powerfully as the serum. This also indicates the formation of protein-soap adsorption compounds. A similar action was not found in the case of other substances, such as amyl acetate and tributyrin, which lower the surface tension of water. S. B. S.

**Pseudo-globulin.** H. C. HASLAM (*Proc. physiol. Soc.*, 1912, xiii—xiv; *J. Physiol.*, 44).—Globulin and  $\psi$ -globulin are to be regarded as distinct chemical individuals; they can be separated by fractional precipitation with salts;  $\psi$ -globulin contains no phosphorus, globulin does. W. D. H.

**The Laws of Combination of Hæmoglobin with Oxygen and Carbon Monoxide.** C. G. DOUGLAS, JOHN S. HALDANE, and J. B. S. HALDANE (*J. Physiol.*, 1912, 44, 275—304).—When hæmoglobin (free or in corpuscles) is saturated with a mixture of oxygen and carbon monoxide, the ratio of oxy- and carboxy-hæmoglobin is proportional to the tensions of the two gases, and is not altered by the presence of carbon dioxide or reduced hæmoglobin, by slight changes in reaction, or by dilution, but is appreciably altered by temperature and by light, and varies in the hæmoglobin of different individuals and species. In human blood, the dissociation curves agree closely with Barcroft's, but in mouse's blood there are great differences. When the pressures of oxygen and carbon monoxide are so low that reduced hæmoglobin is present, the proportions of oxy-, carboxy-, and reduced hæmoglobin can be calculated if the dissociation curves of the two former are known; in consequence of the form of these curves, it follows that a small proportion of oxygen may increase the formation of carboxyhæmoglobin. W. D. H.

**The Cataphoresis of Oxyhæmoglobin.** LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1912, 41, 102—110. Compare Abstr., 1910, ii, 48).—The authors confirm their previous determinations of the isoelectric point of oxyhæmoglobin and show that it is not affected by the presence of small quantities of impurities in the form of either colloids or salts. In carrying out the experiments with salt mixtures of higher concentration (phosphates), it was found that the isoelectric zone was broadened. The isoelectric point was also determined in mixtures of cacodylic acid and its sodium salt.

S. B. S.

**Sturine.** ALBRECHT KOSSEL and FR. WEISS (*Zeitsch. physiol. Chem.*, 1912, 78, 402—413).—Sturine contains a repetition of the grouping  $-\text{NH}\cdot\text{CHR}\cdot\text{CO}-$ ; it breaks down into arginine, histidine, lysine, alanine, and leucine, or an isomeride. Of the total nitrogen, between

67.4 and 66.7% is present as arginine, 10.1 to 9% as histidine, 7.5 to 5.5% as lysine, the numbers representing the maximal and minimal amounts possible.

The basicity of sturine corresponds with 24 atoms of nitrogen per 100 atoms of nitrogen present, whilst the arginine in it is equivalent only to 17 atoms; histidine and lysine must, therefore, be concerned in the basicity.

All three hydrogen atoms in the iminazole (histidine) nucleus of sturine are free and not concerned in the peptide formation. On treatment with nitrous acid, a *deaminosturine* is obtained, which contains the same percentage of arginine and histidine, no lysine, and more monoamino-acid than sturine.

With nitric acid, a nitrosturine is obtained, which forms nitro-arginine on hydrolysis.

On treatment with  $N/2$ -sodium hydroxide at  $37^\circ$  for some days and subsequent hydrolysis, inactive amino-acids are obtained. The change, as Dakin has explained (Abstr., 1910, i, 590), is due to the enolisation of the carbonyl group, and its occurrence proves that the acid carboxyl groups were bound in the molecule as suggested; it has become  $\cdots \text{NH}\cdot\text{CH}:\text{C}(\text{OH})\cdot\text{NH}\cdot\text{CR}''\text{C}(\text{OH})\cdots$  after treatment.

On partial hydrolysis of sturine, protones are obtained containing varying proportions of arginine, histidine, and lysine. E. F. A.

**Preparation of Secretin.** HENRY H. DALE and PATRICK P. LAIDLAW (*Proc. physiol. Soc.*, 1912, xi—xii; *J. Physiol.*, 44).—Secretin can be prepared by precipitating it in the form of a mercury compound; the mercury is removed by hydrogen sulphide, and a very active preparation is thus obtained when required for use. It is relatively free from the depressor substance. The composition of secretin itself is still unknown. W. D. H.

**A Synthetic Action of Emulsin.** ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1912, 154, 1375—1378; *J. Pharm. Chim.*, 1912, [vii], 5, 569—573).—With the object of demonstrating the synthetic action of enzymes, the authors have submitted an alcoholic solution of dextrose and saligenin to the action of emulsin. The course of the action was followed by means of the polarimeter, the final readings of which corresponded with that deduced for the quantity of salicin expected. Attempts to isolate salicin from the reaction product were unsuccessful. In its place a non-crystalline substance,  $[\alpha]_D - 30.02^\circ$ , was obtained, which scarcely reduced Fehling's solution, and was rapidly hydrolysed by emulsin. It is possibly  $\beta$ -ethylglucoside (Koenigs and Knorr, Abstr., 1901, i, 369). H. W.

**The Supposed Reversibility of the Hydrolysis of Salicin by Enzymes.** GABRIEL BERTRAND and ARTHUR COMPTON (*Compt. rend.*, 1912, 154, 1646—1648. Compare Bourquelot and Bridel, this vol., i, 522, and preceding abstract; Visser, Abstr., 1905, ii, 577; Tammann, Abstr., 1892, 899).—The authors view with suspicion the experi-

mental proofs adduced as to the reversible nature of the hydrolysis of salicin by emulsin.

In a careful series of experiments in which the amount of hydrolysis was determined by the reducing effect of the dextrose formed (Bertrand, *Abstr.*, 1907, ii, 136), they find that salicin in 1% and 3% solutions at various temperatures is completely hydrolysed in a comparatively short time. Even if a little salicin is introduced into a solution of equimolecular quantities of the products of hydrolysis (dextrose and saligenin), the addition of emulsin causes hydrolysis of the salicin.

D. F. T.

**Action of Emulsin on Gentiopicroin in Solution in Neutral Organic Liquids.** ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1912, 154, 1259—1261; *J. Pharm. Chim.*, 1912, [vii], 5, 534—549).—It has been shown previously that the decomposition of gentiopicroin or salicin by emulsin must take place by direct contact, since hydrolysis goes on in alcohol in which emulsin is insoluble (*Abstr.*, 1911, i, 1053; this vol., i, 522). It is now shown that gentiopicroin is not hydrolysed by emulsin suspended in dry acetone, but that hydrolysis takes place slowly with acetone containing 10% of water, and more rapidly when larger proportions of water are added, being complete in thirty-seven days when acetone containing 40% of water is used. Similarly, no hydrolysis takes place in dry ethyl acetate, but complete hydrolysis occurs in ten days when 20% of the ester saturated with water is added, and more rapidly when larger proportions of the wet ester are employed. Hydrolysis also takes place when solutions made by macerating emulsin in acetone containing at least 50% of water are used, but not with liquids prepared by macerating emulsin in wet ethyl acetate.

T. A. H.

**Enzyme Action. II. Hydrolytic Action of Some Amino-acids and Polypeptides on Certain Esters.** K. GEORGE FALK and JOHN M. NELSON (*J. Amer. Chem. Soc.*, 1912, 34, 828—845. Compare this vol., i, 522).—It is suggested that the hydrolytic action of lipase is due to an active protein, which is readily hydrolysed in aqueous solution to form lipolytically inactive substances. In order to test this hypothesis, the hydrolytic action of various amino-acids and polypeptides on methyl acetate, ethyl butyrate, and olive oil has been studied.

The results indicate a peculiar selective character in the action of the amino-acids and polypeptides; thus glycine exerts its greatest hydrolytic action on ethyl butyrate, and phenylalanine on methyl acetate. This selective action is suggestive of that of lipases from different sources with different esters, and it seems probable that many of these selective actions of the lipases may be reproduced with amino-acids and polypeptides of varying structure or in presence of other substances.

There is no evidence, however, that the hydrolytic action of lipase is due to amino-acids or polypeptides, but the specific groups in these substances which show this activity may be also present in the proteins, and it is therefore considered probable that a study of the

decomposition products, such as amino-acids, from preparations showing lipolytic activity, or of the more complex polypeptides or other substances synthesised from them, may throw light on the substances capable of causing lipolytic action. E. G.

**Enzyme Action. Urease: a Selective Enzyme.** HENRY EDWARD ARMSTRONG and EDWARD HORTON (*Proc. Roy. Soc.*, 1912, B, 85, 109—127).—The enzyme in these experiments was prepared from Soja beans (compare Takeuchi, *Abstr.*, 1909, ii, 925), and was found to hydrolyse carbamide with ease. The action of the enzyme on the substituted carbamides (methylcarbamide, *s*-dimethylcarbamide, *as*-dimethylcarbamide, ethylcarbamide, *s*-diethylcarbamide, and on biuret) was tested, and the results indicate that it is capable of acting only on carbamide itself. It is, therefore, specific in effect, and must correspond closely in structure with carbamide.

The rate of change is dependent to a certain extent on the concentration of the solution of carbamide employed, since the amount of action in *M*/5-solutions is equal to that in *M*-solution, and more than twice as much as in 5*M*-solutions.

The effects of the products of change were investigated, and it was found that the addition of ammonia, equal to one-tenth of the amount producible from the carbamide added, limited the conversion to a decided extent. On the other hand, ammonium carbonate had a much less effect, whilst carbon dioxide increased the activity of the enzyme. Similar stimulation was obtained by the use of glycine. It appeared conceivable that the ammonia limited the change either by its action as an alkali or by promoting the destruction of the enzyme, but this was shown by experiment not to be the case.

The effect of various salts and non-electrolytes on hydrolysis was tested, and it was found that whilst ammonium chloride and dextrose have a slight accelerating action, potassium and sodium chlorides retard the change.

The process of conversion is regarded as being one of hydration and hydrolysis, the hydrolyte being the hydrated form of carbamide,  $C(OH)_2(NH_2)_2$ . This compound can give rise to cyanic acid if deprived of ammonia and hydrone; if hydrolysed, it can give rise to orthocarbonic acid and ammonia.

The function of urease would seem to be to determine the change in the latter direction; in other words, to condition the direct hydrolysis of carbamide and thereby prevent its reversion into cyanate. The repressing and stimulating action exercised by certain salts and non-electrolytes can be accounted for by assuming the enzyme to be a feebly acidic substance, and that in order to effect change it must unite with the feebly basic carbamide. A more basic substance, such as ammonia, would interfere with such union and consequently retard change. Carbon dioxide by fixing the ammonia would facilitate the action of the enzyme by leaving it free to act as hydrolyst.

H. B. H.

**The Mode of Action of Phosphatase. III.** HANS EULER (*Biochem. Zeitsch.*, 1912, 41, 215—223. Compare *Abstr.*, 1911, i, 1057; this vol. i, 403).—In view of the controversy between Iwanoff

and Harden and Young as to whether the synthesis of organic compounds of phosphorus from phosphates by yeast can take place without fermentation, the view held by Iwanoff as opposed to that held by Harden and Young, the author calls attention to two facts: (1) Under the influence of extract of dried yeast, a synthesis of dextrose-phosphoric acid esters can take place, provided that the dextrose is first submitted to fermentation by yeast; (2) that such a synthesis can take place without evolution of carbon dioxide. The author draws attention to the fact that the various yeasts differ considerably with regard to the amount of synthesising enzyme (phosphatase) which can be extracted by maceration. He also replies to criticisms on his work by Lebedeff.

S. B. S.

**Preparation of Nitrohydroxyarylsarinic Acids.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 245536).—1-Chloro-2-nitrophenyl-4-arsinic acid, colourless leaflets decomposing suddenly without melting, when heated, can be prepared by nitrating 1-chlorophenyl-4-arsinic acid (Abstr., 1908, i, 591); when gently warmed with about five parts of a solution of potassium hydroxide (36° Bé), the chlorine atom is replaced by hydroxyl, yielding the therapeutically valuable 2-nitrophenol-4-arsinic acid (Abstr., 1911, i, 1056).

1-Chloro-o-tolyl-4-arsinic acid, needles, m.p. 180°, can be obtained from o-toluidine-4-arsinic acid (*loc. cit.*) by decomposing its diazonium chloride in the presence of cuprous chloride; when nitrated, it furnishes 1-chloro-6-nitro-o-tolyl-4-arsinic acid, yellow needles, m.p. 310°, which by the action of sodium hydroxide is converted into nitro-o-cresol-4-arsinic acid.

F. M. G. M.

**Preparation of Neutral Aqueous Soluble Derivatives of 3:3'-Diamino-4:4'-dihydroxyarsenobenzene.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 245756).—When 3:3'-diamino-4:4'-dihydroxyarsenobenzene hydrochloride (25 parts) dissolved in 250 c.c. of water is slowly treated with twenty-five grams of formaldehydesulphoxylate dissolved in 125 c.c. of water and after some hours 80 c.c. of a 10% solution of sodium carbonate added, a clear yellow solution is formed, which when treated with mineral acid furnishes a compound in the form of a reddish-yellow powder and containing one acidic sulphur group; the sodium salt can be precipitated by alcohol. If in the foregoing reaction the formaldehyde sulphoxylate is added to a suspension of the free base and the mixture gently warmed at 60–70°, a compound containing two acidic sulphur groups is formed; these compounds are insoluble in the ordinary organic solvents and in acids, but dissolve readily in alkali carbonates or ammonium hydroxide; and the solutions of their alkali salts have a neutral reaction.

F. M. G. M.

**Preparation of 5-Nitro-2-aminophenyl-1-arsinic Acid.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 243693). Compare Abstr., 1909, i, 980; 1910, i, 148).—5-Nitro-2-aminophenyl-1-arsinic acid is obtained in comparatively good yield by heating arsenic acid (20 parts) with *p*-nitroaniline (70 parts) at 210°, with removal of the evolved water by distillation (compare this vol., i, 61).

F. M. G. M.

**Preparation of *p*-Amino-*m*-hydroxyarylsarinic Acids.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 244166. Compare Abstr., 1911, i, 1056).—When diazotised solutions of 3-nitro-4-aminoaryl-1-arsinic acids are treated with agents which combine with mineral acids (such as sodium acetate), the nitro-group is replaced by hydroxyl, yielding compounds which combine readily with  $\beta$ -naphthol, resorcinol, 8-amino- $\alpha$ -naphthol-5-sulphonic acid, and 1:8-dihydroxynaphthalene-4-sulphonic acid.

*p*-Amino-*m*-hydroxyphenylarsinic acid, a crystalline powder, is obtained by the cautious reduction at 30° of the foregoing hydroxyazo- $\beta$ -naphthol derivative with sodium hyposulphite in alkaline solution. It is of therapeutic value; the sodium salt forms glistening scales and is readily soluble in water. F. M. G. M.

**Preparation of Aminohydroxy-derivatives and Homologues of Arsenobenzenes.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 244789 and 244790. Compare Abstr., 1910, i, 803; 1911, i, 594, 1056; preceding abstract).—When 2-nitro-1-aminoaryl-4-arsinic acids are diazotised and treated with acid withdrawing agents (such as sodium acetate), the nitro-group is replaced by hydroxyl and the so-obtained hydroxydiazonium compounds combine readily with resorcinol, the naphthols, and the other azo-dye forming components; the compound from 2-nitro-1-aminophenyl-4-arsinic acid and  $\beta$ -naphthol forms glistening coppery crystals, and by energetic reduction furnishes 4:4'-diamino-3:3'-dihydroxyarsenobenzene as a yellow powder. The second patent describes the preparation of the foregoing base by reducing 1-amino-2-hydroxyphenyl-4-arsinic acid (*loc. cit.*) with sodium hyposulphite at 60—65°. F. M. G. M.

**Preparation of Carboxylic Acid Esters Containing Mercury and the Products of their Hydrolysis.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 245571. Compare Trans., 1907, 91, 557).—When the esters of unsaturated cyclic carboxylic acids are treated with mercuric acetate in 98% alcohol, compounds are formed which readily undergo hydrolysis and furnish the corresponding acids containing mercury.

Mercuric acetate (30 parts) in 98% alcohol (20 parts) was slowly treated with ethyl chaulmoograte (25 parts) and left during twenty-four hours, the alcohol was separated under diminished pressure, and the product extracted from the residue (by means of ether) as a colourless oil, containing 33—35% of mercury, which when hydrolysed with alcoholic potassium hydroxide furnished a mercury containing chaulmoogric acid. Ethyl  $\Delta^1$ -cyclohexenecarboxylate yielded a similar compound, which was obtained in crystalline form, and on hydrolysis furnished the anhydride of a carboxylic acid containing mercury.

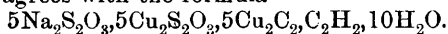
F. M. G. M.

## Organic Chemistry.

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**Remarks on the Nomenclature of Organic Chemistry.** CONSTANTIN I. ISTRATI (*Bull. Soc. chim.*, 1912, [iv], 11, 565—570).—An outline of the principles on which is based a new system of nomenclature, with regard to which a book is shortly to be published by the author. W. G.

**Sodium Copper Thiosulphate and Acetylene Cuproacetylide.** KAHITIBHUSAN BHADURI (*Zeitsch. anorg. Chem.*, 1912, 76, 419—421).—When acetylene is passed into a solution of sodium thiosulphate and copper acetate, a red precipitate is obtained, which dissolves in water, but may be washed with alcohol. It forms a brick-red powder, which burns like gunpowder when heated. It decomposes slowly at 33°, or in ten hours on the water-bath. The red solution is decolorised by acids; the colour is restored on adding alkali immediately, but not after a short time. Alkalis, except ammonia, precipitate a brown, explosive substance. The analysis of the red product agrees with the formula



C. H. D.

**Autoxidation of Trichloroethylene.** ERNST ERDMANN (*J. pr. Chem.*, 1912, 86, [ii], 111—112).—A reply to Staudinger (this vol., i, 330). F. B.

**Synthesis of Compounds of the Nona- and Undeca-methylene Series.** JULIUS VON BRAUN and E. DANZIGER (*Ber.*, 1912, 45, 1970—1979).—When *n*-dibromoheptane is boiled with potassium cyanide in aqueous alcoholic solution the nitrile of azelaic acid,  $\text{CN} \cdot [\text{CH}_2]_7 \cdot \text{CN}$ , is obtained as a colourless liquid, b. p. 183°/11 mm.; on reduction with sodium and alcohol, *α*-diaminononane is formed, yielding a dibenzoyl derivative, m. p. 121°. When this is warmed with phosphorus pentachloride and distilled in a vacuum, *α*-dichlorononane is obtained; this is a colourless liquid of pleasant odour, b. p. 138—139°/17 mm. The residue of the distillation contains the *chlorinated amide*,  $\text{Cl} \cdot [\text{CH}_2]_9 \cdot \text{NHBz}$ , the crystals of which have m. p. 75°. On heating with hydrochloric acid, *chlorononylamine hydrochloride* is obtained as a syrup. The *platinichloride* is egg-yellow in colour; it blackens at 177°, decomp. 193—195°.

When chloromethyl ether is added slowly to a cooled mixture of *n*-dibromoheptane and magnesium, *α*-dimethoxynonane is obtained in good yield, together with other products; it has b. p. 114—115°/10 mm. When warmed with fuming hydrobromic acid at 100°, *α*-dibromononane is obtained, m. p. 154—155°/10 mm.

The dibromononane leads in a similar manner to *nonane-α-dicarboxylonitrile*,  $\text{CN} \cdot [\text{CH}_2]_9 \cdot \text{CN}$ , a transparent, odourless liquid,

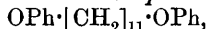
b. p. 195—198°/12 mm., which is converted into nonane- $\alpha$ -dicarboxylic acid, m. p. 109°, on hydrolysis identical with that described by Walker and Lumsden (Trans., 1901, 79, 1194).

On reduction of the nitrile, the *hydrochloride* of  $\alpha\kappa$ -diaminoundecane is obtained in colourless crystals, m. p. 254—255°. The *platini-chloride* is orange-yellow, blackens at 200°, decomp. 221°. The benzoyl derivative of the diamine has m. p. 112°.

$\alpha\lambda$ -Dichloroundecane is a transparent liquid, b. p. 156—158°/16 mm.

$\lambda$ -Chloroundecylbenzamide has m. p. 64—66°.

$\alpha\lambda$ -Diiodoundecane, obtained on heating the dichloro-derivative with sodium iodide, has b. p. 200—208°/15 mm. It reacts with sodium phenoxide readily to form  $\alpha\lambda$ -diphenoxyundecane,



m. p. 52°.

Of the twelve homologous diphenyl ethers, those with an uneven number of carbon atoms have a lower melting point than those with an even number of carbon atoms.

$\alpha\lambda$ -Dimethoxyundecane has b. p. 128—135°/12 mm.; it is converted on heating with hydrogen bromide into  $\alpha\lambda$ -dibromoundecane, b. p. 170—175°/15 mm.

When either dibromo- or di-iodo-undecane is condensed with potassium cyanide, the *nitrile* formed, b. p. 210—215°/16 mm., yields brassylic acid on hydrolysis.

E. F. A.

**Dehydration of Alcohols by means of Sulphonic Acids and the Influence of Phenols on this Reaction.** HENRI WUYTS (*Bull. Soc. chim. Belg.*, 1912, 26, 304—309).—*tert*-Butyl or *tert*-amyl alcohols when heated with one-twentieth to one-sixtieth of their weight of toluene-4-sulphonic acid are converted into *isobutylene* or  $\beta$ -ethyl- $\Delta^{\beta}$ -butylene.

*iso*Propyl and *sec*-butyl alcohols react less readily at their boiling point, but at a higher temperature, or when the proportion of the catalyst is increased to an equimolecular amount, they react quite smoothly and are converted into hydrocarbons.

*sec*-Octyl alcohol is dehydrated at its boiling point; *cyclohexanol* requires an elevated temperature; *menthol* is dehydrated by simple boiling with the sulphonic acid.

Toluene-4-sulphonic acid is decomposed when heated by itself at 155°, but in presence of sufficient alcohol (*cyclohexanol*) no decomposition at this temperature was observed. The addition of a small quantity of phenol greatly facilitates the dehydration of the alcohol. The yield of hydrocarbon is, however, less than the theoretical quantity, and when a considerable proportion of phenol is added, homologues of phenol are obtained. Thus *cyclohexylphenol* has m. p. 128°.

On heating phenol with  $\beta$ -methyl- $\Delta^{\beta}$ -butylene and toluene-4-sulphonic acid in a sealed tube at 100°, *tert*-amylphenol is obtained. E. F. A.

**Some Unsaturated Internal Ethers.** J. W. LE HEUX (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 19—21).—Divinyl glycol (Griner, Abstr., 1893, i, 240) reacts with acetyl chloride to form a *chloroacetin*, b. p. 84—88°/18 mm., which is converted by concentrated,

aqueous sodium hydroxide into *s-divinylethylene oxide*,  $\text{O} \begin{array}{l} \text{CH} \cdot \text{CH} \cdot \text{CH}_2 \\ | \\ \text{CH} \cdot \text{CH} \cdot \text{CH}_2 \end{array}$ , b. p. 108—109°,  $D_4^{15}$  0.8834,  $n_D^{15}$  1.44942. The oxide is a mobile liquid having the pungent odour of allyl compounds, resinifies in the presence of air and alkalis, regenerates the glycol by treatment with warm water, and absorbs hydrogen chloride. The ring is easily ruptured, since the oxide and allylamine yield a molecular additive compound, m. p. 37.5°.

Equal molecular quantities of hypochlorous acid and isoprene react at 0° to form a compound,  $\text{C}_5\text{H}_9\text{OCl}$ , b. p. 142—145°, which is converted by aqueous sodium hydroxide into a substance, b. p. 80—82°, the constitution of which is not yet decided. C. S.

**Chemical Individuality in the Pinacone Series.** MAURICE DELACRE (*Bull. Soc. chim. Belg.*, 1912, 26, 227—236).—A résumé (compare Abstr., 1911, i, 32, 102, 347, 939). E. F. A.

**Mechanism of the Hell-Volhard Reaction.** OSSIAN ASCHAN (*Ber.*, 1912, 45, 1913—1919).—The bromination of carboxylic acids at the  $\alpha$ -carbon atom is rendered explicable if the following changes

occur:  $\text{R} \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot \text{H} \xrightarrow{\text{Br}_2} \text{CHR} \cdot \text{C}(\text{OH})_2 \xrightarrow{\text{Br}_2} \text{CHRB}r \cdot \text{CB}r(\text{OH})_2 \rightarrow \text{CHRB}r \cdot \text{CO}_2 \cdot \text{H} + \text{HBr}$ . The theory can be tested by brominating an acid chloride; in this case an additive compound,  $\text{CHRB}r \cdot \text{CClBr} \cdot \text{OH}$ , would be formed, which should yield a mixture of brominated acid chloride and brominated acid bromide (the latter predominating) by loss of hydrogen bromide and hydrogen chloride.

[With ERIK FALCK.]—The theory has been tested and fully substantiated by the bromination of acetyl chloride, propionyl chloride, valeryl chloride, stearyl chloride, succinyl chloride, and camphoryl chloride; in all cases the acid evolved is a mixture of hydrogen chloride and hydrogen bromide, the former being in excess.

Chloroacetyl chloride is scarcely attacked by bromine even at 150°.

C. S.

**Hydrolysis of Esters of Substituted Aliphatic Acids.** W. A. DRUSHEL (*Amer. J. Sci.*, 1912, [iv], 34, 69—74).—The rates of hydrolysis of ethyl  $\alpha$ - and  $\beta$ -monochloropropionates and of ethyl  $\alpha$ - and  $\beta$ -monobromopropionates in *N*/10-hydrochloric and hydrobromic acid solution and in aqueous solution have been measured. Ethyl  $\alpha\alpha$ -dibromopropionate was found to be too sparingly soluble in water to permit similar determinations.

In the presence of *N*/10-hydrochloric or hydrobromic acid at temperatures not exceeding 35°, the ethyl esters of halogen substituted propionic acids decompose almost quantitatively according to the equation:  $\text{C}_2\text{H}_4\text{X} \cdot \text{CO}_2\text{Et} + \text{H}_2\text{O} \rightarrow \text{C}_2\text{H}_4\text{X} \cdot \text{CO}_2\text{H} + \text{EtOH}$ . Below 35° the halogen substituted propionic acids decompose very slowly according to the equation  $\text{C}_2\text{H}_4\text{X} \cdot \text{CO}_2\text{H} + \text{H}_2\text{O} \rightarrow \text{HX} + \text{OH} \cdot \text{C}_2\text{H}_4 \cdot \text{CO}_2\text{H}$ . When decomposition takes place in this direction, the  $\beta$ -position of the halogen favours the reaction.

The velocity of hydrolysis of the ethyl esters of halogen substituted

propionic acids is much less than that of ethyl propionate in the presence of added catalysing acid, but much greater than when no catalyst is added. Esters with the halogen in the  $\alpha$ -portion hydrolyse more rapidly than those with the halogen in the  $\beta$ -position when hydrolysis is carried out in the presence of added catalysing acid; the same is true when the hydrolysis is made in the absence of added catalysing acid if corrections are applied for the halogen acids set free by the hydrolysis of the halogen substituted propionic acids.

*Ethyl  $\beta$ -chloropropionate*, b. p.  $162^{\circ}$ , and *ethyl  $\beta$ -bromopropionate*, b. p.  $85^{\circ}/25$  mm., were prepared by the action of the corresponding halogen on a solution of ethyl  $\beta$ -iodopropionate in chloroform.

*Ethyl  $\alpha$ -dibromopropionate* had b. p.  $102\text{--}103^{\circ}/38$  mm. H. W.

**Crystallisation of Sodium Palmitate.** ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1912, 26, 193—198).—As the concentration of sodium palmitate solutions is increased, the temperature at which crystallisation begins becomes progressively higher. Separation of the salt takes place almost completely within a small range of temperature. In solutions of 0.05 to 0.025 *N*, which are limpid when warm, acicular crystals are formed at  $47\text{--}45^{\circ}$ , and there is a free separation at  $43\text{--}42^{\circ}$ . Solutions of 0.02 *N* become cloudy at  $45^{\circ}$ , and deposit crystals at  $42.5^{\circ}$ , which separate freely at  $40.5^{\circ}$ . In more dilute solutions the liquids are opalescent at high temperatures and become iridescent at about  $50^{\circ}$ ; very small crystals are formed between  $40^{\circ}$  and  $36^{\circ}$ . Still weaker solutions form granulations which separate as a crystalline deposit.

These results have been confirmed by determinations of the electrical conductivity of the solutions during cooling. The temperature at which crystallisation begins is indicated by a marked fall in the conductivity. The more dilute the solution, the lower is the temperature at which this fall is observed.

The curves connecting temperature and conductivity all show a marked confluence at the lower temperatures, indicating that the mother liquors have the same composition after crystallisation.

Similar curves drawn for sodium oleate show no gradual decrease.

The molecular conductivities of sodium palmitate are very small, and it is deduced that such soap solutions, particularly when not too dilute or warm, constitute colloidal media. E. F. A.

**Glycerides of Fatty Acids. III. Heptadecoic Acid and its Triglyceride.** ALOIS BÖMER and R. LIMPRICH (*Zeitsch. Nahr. Genussm.*, 1912, 23, 641—653. Compare Abstr., 1907, i, 830; 1909, i, 284).—With regard to the question as to the occurrence of certain glycerides in various fats, the authors have prepared, for the purpose of comparison, specimens of heptadecoic acid and its glyceride. The method employed for the synthetic preparation of the acid was that described by Krafft (Abstr., 1880, 34). The pure acid crystallised from ether in the form of rhombic plates, m. p.  $60.5^{\circ}$ , b. p.  $143.6^{\circ}$  in a vacuum (absolute). One hundred c.c. of absolute alcohol dissolved 1.15 grams of the acid at  $0^{\circ}$ , and 3.48 grams at  $15^{\circ}$ . The zinc salt of the acid was practically insoluble in alcohol at  $15^{\circ}$ . The triglyceride of heptadecoic acid was also prepared, and found to have m. p.  $62.7^{\circ}$ .

One hundred c.c. of anhydrous ether dissolved 0.0288 gram of the glyceride at 0°, and 0.322 gram at 15°. Fine needle-shaped crystals of the glyceride were deposited from the ethereal solution. W. P. S.

**Oil of Wallflower Seeds.** HERMANN MATTHES and W. BOLTZE (*Arch. Pharm.*, 1912, 250, 211—230).—The oil extracted by ether from wallflower seeds has a green colour changing to brown after long keeping, and contains 0.027% of ethereal oil (b. p. 120—125°/15 mm.,  $D_{15}^{15}$  0.9034,  $n_D^{20}$  1.692,  $[\alpha]_D -12.73^\circ$ , iodine number 179.40). The residual cheiranthus oil has  $D_{15}^{15}$  0.9240,  $n_D^{40}$  1.4690, acid number 11.50, saponification number 180.30, ester number 168.80, iodine number 124.53, Hehner number 95.66, Reichert-Meissl number 0.33, and Polenske number 1.4. It is classified as a drying oil.

After hydrolysis with alcoholic potassium hydroxide and subsequent neutralisation with acetic acid, the oil is treated with aqueous lead acetate and benzene according to Farnsteiner's method for the separation of the fatty acids. The solid fatty acids obtained from hydrolysed oil of wallflower seeds consist of 5% of linolenic acid, 30% of linoleic acid, and 65% of a new unsaturated acid, *cheiranthic acid*,  $C_{17}H_{33}\cdot CO_2H$ , m. p. 30°, b. p. 240—245°/12 mm.,  $n_D^{40}$  1.4536, iodine number 71.16, which is optically inactive. Cheiranthic acid is converted by nitrous acid into an *isomeride*, m. p. 51—52°,  $n_D^{70}$  1.4520, and is oxidised by alkaline potassium permanganate at 0°, and finally at the b. p., yielding a *dihydroxy-acid*,  $C_{17}H_{33}(OH)_2\cdot CO_2H$ , m. 118°,  $n_D^{60}$  1.4570.

From the unsaponifiable constituents of the oil, a *phytosterol*,  $C_{27}H_{46}O, H_2O$ , has been isolated, which crystallises in colourless plates, and has m. p. 136°,  $[\alpha]_D -31.78^\circ$ , iodine number 77.14; it forms an *acetate*, m. p. 128—129°, *benzoate*, m. p. 142°, and *propionate*, m. p. 108°. C. S.

**Direct Preparation of Organic Per-Acids.** JOH. D'ANS and W. FREY (*Ber.*, 1912, 45, 1845—1852).—The reaction between organic per-acids and water is a reversible one, and can be represented as  $RCO\cdot OOH + H_2O \rightleftharpoons RCO_2H + H_2O_2$ . The reverse reaction has been overlooked (Clover and Richmond, *Abstr.*, 1903, i, 396), probably on account of its slowness, but it is now shown that the necessary catalytic effect can be supplied by sulphuric acid or nitric acid (or less well by hydrofluoric and phosphoric acids, and some salts). Equilibrium is then practically attained in twelve to sixteen hours, and even in two hours for formic acid. For equimolecular mixtures of the various acids with hydrogen peroxide, it is found that when equilibrium is attained, 61% of the formic acid, 68% of the acetic acid, and 68% of the propionic acid are converted into the corresponding per-acids. The reaction product can be distilled under reduced pressure, but it is difficult to obtain the pure per-acids in this way.

To obtain the free per-acids it is better to start with the acid anhydride, which reacts quantitatively with hydrogen peroxide according to the equation:  $(RCO)_2O + H_2O_2 = R\cdot CO\cdot OOH + R\cdot CO\cdot OH$ . The addition of sulphuric acid (preferably more than is necessary for the mere catalytic effect), together with another molecule of hydrogen

peroxide, gives a mixture which by distillation yields a highly concentrated solution, from which the per-acid can be separated by freezing-out and centrifugalising.

Per-acetic acid (compare D'Ans and Friederich, this vol., ii, 151) is obtained by adding cautiously (with cooling) a molecular quantity of hydrogen peroxide to one of acetic anhydride; the reaction may be violent. Sulphuric acid (1% calculated on  $\text{Ac}_2\text{O} + 2\text{H}_2\text{O}_2$ ) and a second molecular quantity of hydrogen peroxide are then added, and the mixture left for twelve hours. On distillation at 10–20 mm. pressure (20–30°), a liquid is obtained containing 78% of peracetic acid; if a larger quantity of sulphuric acid is used in the preparation, the percentage of per-acetic acid in the distillate may rise even above 90. The acid is a pungent and extremely explosive liquid, m. p. +0.1°; it explodes violently when warmed slowly to approximately 110°, near which temperature its b. p. lies; it keeps well in aqueous solution, but acids, alkalis, and salts hasten its hydrolysis to acetic acid and hydrogen peroxide; it is a powerful oxidising agent, and attacks the skin.

*Perpropionic acid* can be prepared in an analogous manner. Using 1% of sulphuric acid as catalyst, the distillate contains 78% of perpropionic acid, whilst with 17.56% of sulphuric acid the distillate contains 89.35% of per-acid. The properties of the acid are similar to those of per-acetic acid; it has m. p. –13.5°.

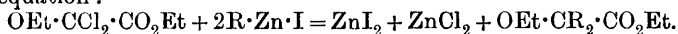
Butyric anhydride is miscible only with difficulty with hydrogen peroxide; the reaction, however, occurs readily, and a distillate can be obtained containing 91.2% of *perbutyric acid* (using 18.7% of sulphuric acid). The acid could not be obtained purer than 95.4%, when it had m. p. –10.5°. Unlike the two previous acids, a dilute solution of perbutyric acid can be concentrated by keeping over anhydrous sodium sulphate.

*Performic acid* could only be obtained as a distillate containing 48% of the substance; it is not stable at room temperature, and forms carbon dioxide; also it is rapidly hydrolysed in aqueous solution.

An even simpler method for the preparation of organic per-acids consists in the action of hydrogen peroxide on the cooled mixture of anhydride with boric acid, according to the equation:  $\text{B}(\text{OAc})_3 + 3\text{H}_2\text{O}_2 = 3\text{AcO}_2\text{H} + \text{B}(\text{OH})_3$ . The per-acid is distilled off under reduced pressure; the yields are excellent, but the mixed acid anhydride is often difficult of preparation in a pure state.

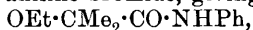
Per-acetic acid is also formed in the action of hydrogen peroxide on keten, but it reacts immediately with more keten, giving as final product, diacetyl peroxide, the reactions being  $\text{CH}_3\text{:CO} + \text{H}_2\text{O}_2 = \text{CH}_3\text{:CO}\cdot\text{OOH}$ ;  $\text{CH}_3\text{:CO}\cdot\text{OOH} + \text{CH}_3\text{:CO} = (\text{CH}_3\text{:CO})_2\text{O}_2$ . D. F. T.

**Syntheses by means of Mixed Organo-metallic Derivatives of Zinc.  $\alpha$ -Ethoxydialkylacetic Acids.** EDMOND E. BLAISE and L. PICARD (*Bull. Soc. chim.*, 1912, [iv], 11, 587–590. Compare this vol., i, 232, 410).—Ethyl dichloroglycollate condenses with mixed organo-zinc derivatives, giving ethyl ethoxydialkylacetates according to the equation:



The condensation is effected at 0° in benzene solution, the ethyl dichloroglycollate being added gradually to the zinc alkyl iodide. The whole is left for two hours and is then treated with water, and the benzene solution separated, dried over anhydrous sodium sulphate, and the benzene driven off under reduced pressure.

*Ethyl α-ethoxyisobutyrate*,  $\text{OEt} \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$ , so prepared is a colourless liquid, b. p. 54°/12.5 mm. On saponification with alcoholic potassium hydroxide, it yields the *acid*,  $\text{C}_6\text{H}_{12}\text{O}_3$ , b. p. 99°/14 mm., of which the *sodium*, *calcium*, and *copper* salts have been prepared. The ester reacts with magnesium aniline bromide, giving the *anilide*,



b. p. 190°/12 mm. The *α-naphthylamide*, m. p. 74°, is similarly prepared.

*Ethyl α-ethoxy-α-ethylbutyrate*,  $\text{OEt} \cdot \text{CET}_2 \cdot \text{CO}_2\text{Et}$ , as prepared by the general method, is a colourless liquid, b. p. 82°/14 mm., which, on saponification, gives the *acid*,  $\text{C}_8\text{H}_{16}\text{O}_3$ , b. p. 112.5°/13 mm. From it the *sodium*, *calcium*, and *copper* salts have been prepared. On boiling with aniline the acid does not yield an anilide, but an *aniline salt*,  $\text{C}_8\text{H}_{16}\text{O}_3 \cdot \text{NH}_2\text{Ph}$ , m. p. 101°. W. G.

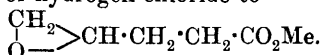
**Reduction of Hydroxymethylene Compounds.** ARTHUR KÖTZ and ERNST SCHAEFFER (*Ber.*, 1912, 45, 1952—1954).—Ethyl hydroxymethyleneacetoacetate, ethyl ethoxymethyleneacetoacetate, 2-hydroxymethylenecyclohexanone, 4-hydroxymethylene-1-methylcyclohexan-3-one, 3-hydroxymethylene-1-methylcyclohexan-2-one, 2-hydroxymethylene-1-methyl-4-isopropylcyclohexan-3-one, and the chloride of hydroxymethylenecamphor have been reduced by hydrogen and palladium by the Paal-Skita method. In each case the hydroxymethylene group is reduced to the methyl group, and two molecular proportions of hydrogen are absorbed. C. S.

**The Walden Rearrangement.** BROR HOLMBERG (*Ber.*, 1912, 45, 1713—1715).—The kinetics of the hydrolysis of *l*-bromosuccinic acid after exactly neutralising the acid with sodium hydroxide have been studied by measuring the change in rotation, the increase in acidity, and the bromine liberated. From the results the conclusion is drawn that the first change is the decomposition of the *l*-bromopropionic acid ion into bromine and propiolactonecarboxylic acid ions, the latter being dextrorotatory. The lactone is only slowly hydrolysed to malic acid; but as the latter is formed, it acts as a catalyst to accelerate this change. The malic acid acts also to retard the formation of the lactone from unchanged bromosuccinic acid.

The Walden change is represented: *l*-bromosuccinic acid → *d*-malic lactone → *d*-malic acid. E. F. A.

**Experiments in the C<sub>5</sub> Series.** 1. Preparation of Ether Lactones and Butyleneoxidecarboxylic Acid Esters. 2. A New Case of Alteration of Configuration (Walden Rearrangement) in Inactive Compounds with Several Asymmetric Carbon Atoms. HERMANN LEUCHS, MICHELE GINA, and JOSEPH F. BREWSTER (*Ber.*, 1912, 45, 1960—1969. Compare Abstr., 1909, i, 361).—By the action of sodium ethoxide or sodium methoxide

on  $\delta$ -chloro- $\gamma$ -valerolactone,  $\delta$ -ethoxy- and  $\delta$ -methoxy- $\gamma$ -valerolactones,  $\text{OR} \cdot \text{CH}_2 \cdot \text{CH} < \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{O} - \text{CO} \end{smallmatrix}$ , are obtained. In addition, isomeric substances of much lower boiling point and a strong ethereal odour are formed. They are butylene oxide derivatives, produced by the opening of the ring to  $\text{CH}_2\text{Cl} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Me}$ , and subsequent elimination of hydrogen chloride to



By the action of dilute hydrogen chloride, the butylene oxide is readily reconverted into the chlorovalerolactone.

Traube and Lehmann (Abstr., 1901, i, 501) have shown that on chlorination of ethyl  $\delta$ -chloro- $\gamma$ -valerolactone- $\alpha$ -carboxylate a solid and an oily chloro-derivative are obtained. These were regarded as isomerides, which is now proved by analysis. They have been converted into  $\gamma$ -hydroxyproline through the  $\alpha\delta$ -dichloro- $\gamma$ -valerolactones, with the result, however, that in both cases a mixture of  $\alpha$ - and  $\beta$ -hydroxyprolines was obtained having the two isomerides in the proportion 3:2. By the substitution, a partial Walden rearrangement takes place, the system  $\begin{pmatrix} d-d \\ l-l \end{pmatrix}$  becoming  $\begin{pmatrix} d-l \\ l-d \end{pmatrix}$  and  $\begin{pmatrix} d-d \\ l-l \end{pmatrix}$ . This is analogous to the rearrangement in the case of dibromo- and *isodibromo*-succinic acid when boiled with water.

$\delta$ -Methoxy- $\gamma$ -valerolactone has b. p. 120—125°/12 mm.; the corresponding  $\delta$ -hydroxy-derivative has b. p. 122—123°/12 mm.,  $D^{19}$  1.113; it has only a faint odour.

Methyl  $\alpha\beta$ -butyleneoxide- $\delta$ -carboxylate is a mobile liquid, b. p. 83—85°/14 mm.,  $D^{19}$  1.069, and has an ethereal, melon-like odour.

$\delta$ -Ethoxy- $\gamma$ -valerolactone has b. p. 123—124°/14 mm.

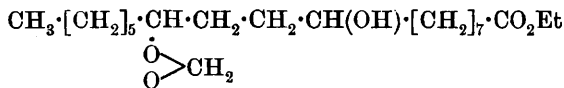
Ethyl  $\alpha\beta$ -butyleneoxide- $\delta$ -carboxylate has b. p. 92—94°/18 mm., 194—196°/760 mm., and resembles the methyl isomeride.

Amyl  $\alpha\beta$ -butyleneoxide- $\delta$ -carboxylate has b. p. 120—121°/10 mm.,  $D^{19}$  1.02. The odour is not strong; when treated with hydrochloric acid, the odour of amyl alcohol is at once perceived.

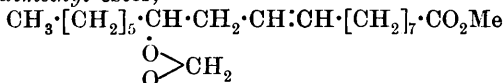
$\alpha\delta$ -Dichloro- $\gamma$ -valerolactone is a thick, colourless oil, b. p. 159—161° (corr.),  $D^{19}$  1.422 E. F. A.

**Turkey Red Oil: New Derivatives of Ricinoleic Acid.** M. TSCHILIKIN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 515—526).—Although, under some conditions, the action of sulphuric acid on ricinoleic acid (compare Grün, Abstr., 1907, i, 111) results in considerable diminution in the extent of unsaturation, the author finds that no such diminution is produced by the action of dry hydrogen chloride on ricinoleic and oleic acids.

In presence of formaldehyde, however, which is capable of reacting in the form  $\text{CH}_2(\text{OH})_2$  and of forming ethers, esters, and mixed ethereal-ester compounds, different results are obtained, the formaldehyde condensing with the hydroxyl of the acid. Thus the passage of dry hydrogen chloride through a mixture of ricinoleic acid, formaldehyde, and alcohol yields *ethyl methylenedioxydistearate*,



$\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \dot{\text{C}}\text{H} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{Et}$   
 a saponification number 164·86 and an acid number zero. The free acid could not be isolated, its liberation being followed by condensation of the carboxyl group of one stearic acid residue with the CH(OH) group of the other, with loss of water. Under other conditions it was found possible to avoid the destruction of the double linking, the *dimethyl* ester,



$\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \dot{\text{C}}\text{H} \cdot \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{Me}$   
 with a saponification number 184·24—184·85, being obtained.

T. H. P.

**Citrophosphate Solutions.** ANTONIO QUARTAROLI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 478—479).—A reply to Pratalongo's criticisms (this vol., i, 412) on the author's conclusions (this vol., i, 238).

T. H. P.

**A New Observation with Angeli's Aldehyde Reaction.** OSKAR BAUDISCH and J. H. COERT (*Ber.*, 1912, 45, 1775—1779).—The reaction between potassium hyponitrite and formaldehyde takes place with the intermediate formation of nitrosomethyl alcohol,  $\text{NO} \cdot \text{CH}_2 \cdot \text{OH}$ , as witnessed by the momentary formation of a bluish-green coloration. The same should happen in Angeli's aldehyde reaction, and to make this visible the Angeli salt is dissolved in a little water, methyl acetate in large excess added, and the whole well shaken. The aqueous formaldehyde solution is now added; the methyl acetate becomes a deep bluish-green, the colour persisting for twenty-five seconds (compare also Steinkopf and Jürgens, *Abstr.*, 1911, i, 530).

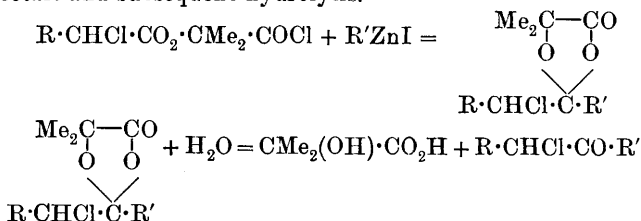
E. F. A.

**Action of Potassium Cyanide on Formaldehyde.** KARL POLSTORFF and HERMANN MEYER (*Ber.*, 1912, 45, 1905—1912).—When 25% aqueous potassium cyanide and about 18% formaldehyde are mixed slowly at 0° and the mixture kept at the ordinary temperature for twenty-four hours, ammonia is evolved, and the solution contains glycollic acid, iminodiacetic acid, and nitrilotriacetic acid. The formation of these acetic acids is due to the initial production of glycollonitrile, the presence of which is proved by treating the alkaline solution, a few minutes after mixing, with methyl sulphate, whereby methoxyacetonitrile (Gauthier, *Abstr.*, 1909, i, 353) is obtained. During the twenty-four hours' keeping, the glycollonitrile is partly hydrolysed to glycollic acid and partly converted into aminoacetonitrile; the latter then reacts with the former to produce, ultimately, iminodiacetic acid and nitrilotriacetic acid.

A good yield of glycollic acid can be obtained by distilling with steam the mixture of potassium cyanide and formaldehyde five to ten minutes after mixing.

C. S.

**Syntheses by means of Mixed Organo-metallic Derivatives of Zinc.  $\alpha$ -Halogenated Ketones.** EDMOND E. BLAISE (*Compt. rend.*, 1912, 155, 46—49. Compare this vol., i, 232).—Chlorinated ketones cannot be prepared by the action of  $\alpha$ -chlorinated acid chlorides on organo-metallic derivatives of zinc, the principal product of this reaction being a chlorinated ester of a tertiary alcohol. The required result is, however, obtained by the preparation of the cycloacetals and subsequent hydrolysis.



$\alpha$ -Hydroxyisobutyric acid when warmed on a water-bath with chloroacetyl chloride and thionyl chloride yields  $\alpha$ -chloroacetoxisobutyryl chloride,  $\text{CH}_2\text{Cl} \cdot \text{CO}_2 \cdot \text{CMe}_2 \cdot \text{COCl}$ , b. p.  $97^\circ/12$  mm., which gives an anilide, m. p.  $127.5^\circ$ . The acid has m. p.  $75^\circ$ . The acid chloride condenses with zinc *n*-propyl iodide, giving the cycloacetal,  $\text{C}_9\text{H}_{15}\text{O}_3\text{Cl}$ , b. p.  $110.5/12$  mm., which on hydrolysis with a mixture of acetic and hydrochloric acids gives a good yield of chloromethyl *n*-propyl ketone,  $\text{CH}_2\text{Cl} \cdot \text{COPr}$ , b. p.  $154.5$ — $156^\circ$  or  $58$ — $59^\circ/17$  mm. Its semicarbazone has m. p.  $157^\circ$ .

Ethyl  $\alpha$ -chloro-*n*-propyl ketone,  $\text{CH}_2\text{Cl} \cdot \text{COEt}$ , b. p.  $53^\circ/17$  mm., is similarly prepared, starting with  $\alpha\alpha$ -chlorobutoxyisobutyric acid, m. p.  $61$ — $62^\circ$ , and condensing its chloride, b. p.  $106^\circ/11$  mm., with zinc ethyl iodide and then hydrolysing the cycloacetal, b. p.  $118.5^\circ/12$  mm. The above acid chloride gives an anilide, m. p.  $65$ — $66^\circ$ . W. G.

**The Photochemical Synthesis of Carbohydrates Under the Action of Ultra-violet Rays.** JULIUS STOKLASA, JOHANN ŠEBOR, and WENZEL ZDOBNICKÝ (*Biochem. Zeitsch.*, 1912, 41, 333—372).—The photochemical action by means of which carbohydrates are produced from carbon dioxide may, in the view of the authors, be represented by the following equations, according to which both formic acid and aldehyde are formed as intermediate products:

- (1)  $\text{K}_2\text{CO}_3 + \text{CO}_2 + \text{H}_2\text{O} = 2\text{KHCO}_3$ .
- (2)  $2\text{KHCO}_3$  (in light)  $= \text{K}_2\text{CO}_3 + \text{H} \cdot \text{CO}_2\text{H} + \text{O}$ .
- (3)  $\text{H} \cdot \text{CO}_2\text{H}$  (in light)  $= \text{H} \cdot \text{CHO} + \text{O}$ .
- (4)  $n\text{H} \cdot \text{CHO} = (\text{H} \cdot \text{CHO})_n$ .

Each reaction has been studied separately by exposure of the various substances to ultra-violet light in an apparatus which is figured in the text. The formaldehyde polymerises in the presence of alkali to a sugar. The reactions, which involve the setting free of oxygen, have been studied in the presence of nascent hydrogen and ferrous sulphate, which in consequence of their reducing properties facilitate the reaction. The sugars formed are hexoses, of which the phenylosazones melt at  $204$ — $205^\circ$ . They appear to consist of ketones and aldoses,

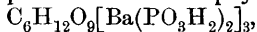
are optically inactive, do not ferment with yeast, and are not degraded by bacteria which assimilate atmospheric nitrogen.

S. B. S.

**Inositol Hexaphosphate.** ANGELO CONTARDI (*Gazzetta*, 1912, 42, i, 408—418. Compare Abstr., 1911, i, 157, 609).—Inositol hexaphosphate is obtained by the action of phosphoric acid, D 1·7, on inosite at 120—130° in the absence of air. This compound is probably identical with that obtained from seeds, as the analysis of both compounds, when dried at 120° in hydrogen under 20 mm. pressure, is the same. The anomalies observed in titration are attributed to the formation of complex salts.

C. H. D.

**Phytin and Phosphoric Acid Esters of Inositol.** R. J. ANDERSON (*J. Biol. Chem.*, 1912, 11, 471—488).—The following salts of phytin have been prepared: Tribarium phytate,



is obtained pure as an amorphous, colourless powder by repeatedly precipitating barium phytate in 0·5% hydrochloric acid with a like volume of alcohol.

*Pentabarium phytate*,  $\text{C}_6\text{H}_{14}\text{O}_{27}\text{P}_6\text{Ba}_5$ , is obtained when a solution of tribarium phytate in 0·5% hydrochloric acid is neutralised with barium hydroxide and then made faintly acid with acetic acid; it is a colourless, amorphous powder.

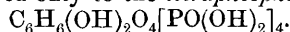
*Pentabarium ammonium phytate*,  $\text{C}_6\text{H}_{12}\text{O}_{27}\text{P}_6\text{Ba}_5(\text{NH}_4)_2$ , obtained by digesting the tribarium salt with dilute ammonia, forms a heavy, colourless, amorphous powder neutral to litmus.

*Pentamagnesium ammonium phytate*,  $\text{C}_6\text{H}_{12}\text{O}_{27}\text{P}_6\text{Mg}_5(\text{NH}_4)_2$ , is formed on adding excess of magnesia mixture to phytic acid; it is a fine colourless, amorphous powder.

*Tetracupric dicalcium phytate*,  $\text{C}_6\text{H}_{12}\text{O}_{27}\text{P}_6\text{Cu}_4\text{Ca}_2$ , is obtained when a slightly acid solution of calcium ammonium phytate is precipitated with excess of copper acetate; it constitutes a light blue, amorphous powder.

Phytin is not decomposed on keeping or on heating to 115°.

Experiments made to synthesise phytic acid and inositol hexaphosphoric acid ester led only to the *tetraphosphoric acid ester*,



This is conveniently isolated by means of its barium salt; it is a well characterised compound very similar in appearance and reactions to phytic acid. By heating with acids, inositol and phosphoric acid are regenerated. It gives a colourless precipitate with ordinary molybdate solution or with excess of silver nitrate.

E. F. A.

**The Higher Carbohydrates Derived from Dextrose.** L. H. PHILIPPE (*Ann. Chim. Phys.*, 1912, [viii], 26, 289—418)—A résumé (compare Abstr., 1909, i, 136; 1911, i, 12, 112, 605). Besides the sugars, the alcohols, lactones, and acids of the series have been studied in detail and their physical properties established. Not one of the sugars derived from dextrose is fermented by yeast. There is no regular variation in the physical properties with an increase in the

number of carbon atoms, each carbohydrate having an individuality of its own.

E. F. A.

**The Reaction between Dextrose and Phenylmethylhydrazine.** CARL NEUBERG (*Ber.*, 1912, 45, 1853).—The author's statement that dextrose does not form an osazone with phenylmethylhydrazine under the ordinary conditions of performing the test (*Abstr.*, 1905, i, 90, etc.) in no wise disagrees with the statement that reaction may occur under protracted digestion of the reagents (Buchner and Meisenheimer, this vol., ii, 671).

D. F. T.

**The Physico-chemical Basis of the Seliwanoff Lævulose Reaction.** ADOLF JOLLES (*Biochem. Zeitsch.*, 1912, 41, 331—332).—Königsfeld (this vol., i, 163) has recently shown that dextrose on treatment with hydrochloric acid yields the Seliwanoff lævulose reaction and has ascribed this fact to the change of dextrose into lævulose. The author does not think this explanation is sufficient, for no change could be detected in the rotation after such treatment. He also shows that when dextrose is treated with very dilute alkalis, there is a formation of acid products.

S. B. S.

**Sugar Solutions and Lime.** JULIUS WEISBERG (*Zeitsch. Ver. deut. Zuckerind.*, 1912, 808—811).—Ginnecken has pointed out that when calcium hydroxide and sucrose solutions are mixed at 80° there is no precipitation of trisucrate, but that when the mixture is made at the ordinary temperature there is a loss in the polarisation due to precipitation of trisucrate. This fact is well known, but it has no practical significance, as the separated juice after treatment of the crude juice with lime is not immediately filtered, being first saturated with carbon dioxide gas.

E. F. A.

**Deflocculation of Starch.** GIOVANNI MALFITANO and [Mlle.] A. MOSCHKOFF (*Bull. Soc. chim.*, 1912, [iv], 11, 606—612).—The authors consider that the system water-starch is never a solution, but always a hydrogel or a hydrosol. By a method of estimation by filtration they arrive at the conclusion that, for a given quantity of starch, the greater the quantity of water used, the higher the temperature to which the system is raised and the longer the time of heating the greater is the number of minute particles (that is, particles which persistently pass through a fine filter paper) formed at the expense of the larger ones.

W. G.

**Conversion of Starch into Dextrin by X-Rays.** H. A. COLWELL and S. RUSS (*Proc. Phys. Soc., London*, 1912, 24, 217—221; *Le Radium*, 1912, 9, 230—232).—When starch solutions are exposed for several hours to X-rays of moderate penetrating power, the opacity and viscosity of the solutions are markedly diminished, and there is a partial conversion into soluble starch and dextrin.

Dextrin under similar conditions could not be converted into dextrose. The effect is attributed to a direct action on the starch molecules, either by the X-rays or by the secondary rays which they produce.

E. F. A.

**Gums and Mucilages.** WOLFGANG SCHIRMER (*Arch. Pharm.*, 1912, 250, 230—251).—The gum obtained from *Anogeissus latifolius* dissolves not quite completely in water, and is very sparingly soluble in glacial acetic acid or 96% alcohol. It is completely soluble in a 60% or 80% solution of chloral hydrate, more easily in the former than in the latter. It yields mucic acid by oxidation with nitric acid, D 1.15, and 26.25% of pentosan and 7.64% of methylpentosan by distillation with 12% hydrochloric acid at 140—150°. By hydrolysis with dilute sulphuric acid on the water-bath for ten hours, the gum yields *l*-arabinose and *d*-galactose. The gum from *Odina Wodier* yields furfuraldehyde by distillation with 12% hydrochloric acid, mucic acid by oxidation with nitric acid, and *d*-galactose and *l*-arabinose by hydrolysis with dilute sulphuric acid.

Both of these gums, therefore, consist largely of arabo-galactans, but in the former the araban, in the latter the galactan, predominates. The mucilage obtained from the pith of *Sassafras variifolium* is purified by repeated maceration with water, decantation, and precipitation from the aqueous solution by alcohol. The purified material is a white, light substance which swells, but is insoluble, in water; also it does not dissolve in other solvents, in dilute acids or alkalis, or even in an 80% solution of chloral hydrate. By oxidation with nitric acid, it yields saccharic acid, but not mucic acid, whilst by hydrolysis with dilute sulphuric acid, it is converted into *l*-arabinose and dextrose, the former in the larger quantity.

The mucilage obtained from the roots of *Althaea officinalis* is partly soluble in water, insoluble in chloral hydrate or ammoniacal cuprous oxide solution, and dissolves almost entirely in boiling acids. The mucilage contains pentosans (identified by the formation of furfuraldehyde), yields mucic acid and a very little saccharic acid by oxidation with nitric acid, and is converted by hydrolysis with dilute sulphuric acid mainly into dextrose, galactose and a small quantity of a pentose also being formed.

The mucilage obtained from the bark of *Ulmus fulva* is insoluble in most solvents, but dissolves partly in dilute acids. It contains about 60% of pentosans, methylpentosans, and hexosans, the last yielding galactose, lævulose, and dextrose by hydrolysis. C. S.

**Preparation of Large Crystals of Betaine Periodide.** VLADIMIR STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1912, 36, 577).—A betaine salt is kept in a loosely-closed vessel containing 10% potassium iodide in 10% sulphuric acid, potassium iodide being run in as long as the precipitate first formed dissolves again. In the course of a week, oxidation has been brought about by the atmosphere, and very large crystals of the betaine periodide separate out. E. F. A.

**Compounds of Alkali and Alkali-earth Salts with Organic Bases.** FILIPPO CALZOLARI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 563—569. Compare Barbieri and Calzolari, *Abstr.*, 1911, i, 184, 266, 268).—The following compounds of salts, mostly hydrated, with hexamethylenetetramine have been prepared:  $\text{LiI} \cdot 4\text{H}_2\text{O} \cdot \text{C}_6\text{H}_{12}\text{N}_4$ ;  $\text{NaCNS} \cdot 4\text{H}_2\text{O} \cdot \text{C}_6\text{H}_{12}\text{N}_4$ ;  $\text{NaClO}_4 \cdot \text{H}_2\text{O} \cdot \text{C}_6\text{H}_{12}\text{N}_4$ ;  $2\text{NH}_4\text{CNS} \cdot \text{C}_6\text{H}_{12}\text{N}_4$ ;

$2\text{KCNS}, \text{C}_6\text{H}_{12}\text{N}_4$ ;  $\text{CaCl}_2, 10\text{H}_2\text{O}, \text{C}_6\text{H}_{12}\text{N}_4$ ;  $\text{CaBr}_2, 10\text{H}_2\text{O}, 2\text{C}_6\text{H}_{12}\text{N}_4$ ;  $\text{CaI}_2, 10\text{H}_2\text{O}, 2\text{C}_6\text{H}_{12}\text{N}_4$ ;  $\text{Ca}(\text{NO}_3)_2, 3\text{H}_2\text{O}, \text{C}_6\text{H}_{12}\text{N}_4$ ;  $\text{SrCl}_2, 10\text{H}_2\text{O}, 2\text{C}_6\text{H}_{12}\text{N}_4$ ;  $\text{SrBr}_2, 10\text{H}_2\text{O}, 2\text{C}_6\text{H}_{12}\text{N}_4$ ;  $\text{SrI}_2, 10\text{H}_2\text{O}, 2\text{C}_6\text{H}_{12}\text{N}_4$ ;  $\text{SrI}_2, 12\text{H}_2\text{O}, 4\text{C}_6\text{H}_{12}\text{N}_4$ , and  $\text{Ba}(\text{CNS})_2, 6\text{H}_2\text{O}, 2\text{C}_6\text{H}_{12}\text{N}_4$ . All of these salts are crystalline, and do not deliquesce in air. The following compounds with caffeine have also been prepared:  $\text{SrI}_2, \text{H}_2\text{O}, 2\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ ;  $\text{NaClO}_4, \text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ ;  $2\text{KCNS}, \text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ .  
C. H. D.

**Compound Obtained by Treating Carbamide with Formaldehyde.** STEFANO DI PALMA (*Boll. Chim. Farm.*, 1912, 51, 78—79).—The interaction of carbamide and formaldehyde in aqueous solution yields the *compound*,  $\text{C}_2\text{H}_6\text{O}_3\text{N}_2$  or  $\text{CO}(\text{NH}_2)_2 \cdot \text{CH}_2\text{O}$ , as a white, amorphous, odourless, and tasteless powder, which decomposes at  $245^\circ$ . With boiling concentrated sodium hydroxide solution, it yields ammonia, and concentrated sulphuric acid in the hot dissolves it with formation of a red coloration and evolution of gas; with hot dilute hydrogen chloride, it yields aldehyde vapour. When suspended in water and distilled in a current of steam, it is decomposed into its constituents.  
T. H. P.

**Cyanamide. I. Cyanamide and Ethyl Acetoacetate.** ADOLF SONN (*Ber.*, 1912, 45, 1958—1960. Compare Brigl, this vol., i, 533).—Ethyl  $\beta$ -cyanoaminocrotonate has been obtained by the interaction of sodium cyanamide and ethyl acetoacetate; it is unstable, decomposing to a pale yellow oil.

With mercuric chloride, a *compound*,  $(\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2)_2 \cdot \text{HgCl}_2$ , is obtained in slender, lustrous needles, m. p.  $101^\circ$ .

Disodium cyanamide and ethyl diethylacetoacetate interact to form ethyl isocarbopyrotritarate.

Monosodium cyanamide and ethyl diethylacetoacetate yield *ethyl 1-cyano-2:5-dimethylpyrrole-3:4-dicarboxylate*,  $\text{CN} \cdot \text{N} < \begin{matrix} \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ \text{CMe} \cdot \text{C} \cdot \text{CO}_2\text{Et} \end{matrix}$ ; it forms crystals, m. p.  $166^\circ$ .

Cyanamide salts readily interact with compounds containing acid methylene hydrogen.  
E. F. A.

**Preparation of Ammonia and Formic Acid from Calcium Cyanamide.** H. SULZER (*Zeitsch. angew. Chem.*, 1912, 25, 1268—1273).—Calcium cyanamide reacts with carbon according to the equation  $\text{CaCN}_2 + \text{C} \rightleftharpoons \text{Ca}(\text{CN})_2$ , but at the high temperature required for fusion, very little cyanide is formed. The melting point may be lowered by addition of alkali salts, when the reaction becomes  $\text{CaCN}_2 + \text{C} + 2\text{NaCl} = \text{CaCl}_2 + 2\text{NaCN}$  or  $\text{CaCN}_2 + \text{C} + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{NaCN}$ . The best results are obtained by mixing one hundred parts of calcium cyanamide, twenty parts of wood charcoal, and seventy-five to ninety parts of anhydrous sodium carbonate, and heating to whiteness in a closed iron crucible for fifteen to twenty minutes.

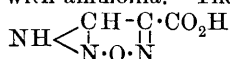
The hydrolysis of hydrogen cyanide to ammonia and formic acid may be utilised technically in the following manner. The ground product obtained as above is mixed with fifty to sixty times its quantity of water, and heated to  $170^\circ$  in an enamelled iron autoclave. The temperature is then raised to  $190^\circ$  for ten minutes, after which

the product is distilled. Ammonia is recovered from the distillate, and the residue contains sodium formate.

Formic acid is most conveniently detected in presence of hydrochloric acid by its reaction with a mixture of potassium dichromate solution and concentrated sulphuric acid, when reduction occurs, yielding a green solution. C. H. D.

**The Constitution of the Fulminuric Acids. V. Breaking Down of Furoxandicarboxylamide.** CELSO ULPANI (*Gazzetta*, 1912, 42, i, 375—390).—The amide obtained by the action of ammonia on the product of nitration of ethyl acetoacetate (Ulpiani and Bernardini, *Abstr.*, 1904, i, 971; 1905, i, 750; Wahl, *Abstr.*, 1908, i, 140) is boiled with an excess of water, and is converted into  $\beta$ -fulminuramide,  $\gamma$ - and ordinary fulminuric acids, and carbamide.

$\beta$ -Fulminuramide,  $C_3H_4O_2N_4$ , crystallises from water in plates, m. p.  $175^\circ$ , and is not decomposed by dilute acids. It does not react with ferric chloride. It is hydrolysed by barium hydroxide, yielding  $\beta$ -fulminuric acid,  $C_3H_3O_3N_3$ , which is also stable, and has m. p.  $196^\circ$ . The ethyl ester has m. p.  $103$ — $104^\circ$ . The nitroso-derivative,  $C_3H_2O_3N_3 \cdot H_2O$ , explodes at  $123^\circ$ , and yields the ammonium salt of oximinocynoacetic acid with ammonia. The formula

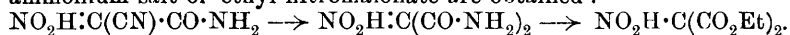


is assigned to the acid.

$\gamma$ -Fulminuric acid crystallises from water, m. p.  $247^\circ$ , and does not form a nitroso-compound. The silver salt has been analysed. Barium hydroxide removes ammonia, and a barium salt,  $C_3O_4N_2Ba \cdot 3H_2O$ , is formed, from which 4-nitro-5-hydroxyisooxazole,  $N \leq \begin{array}{c} CH \cdot C \cdot NO_2 \\ | \quad | \\ O - C \cdot OH \end{array}$ , m. p.  $125^\circ$ , is obtained by means of acids. This acid crystallises with  $H_2O$ , and yields a diammonium salt,  $C_3H_8O_4N_4$ .

$\gamma$ -Fulminuric acid is thus regarded as 4-nitro-5-aminoisooxazole,  $N \leq \begin{array}{c} CH \cdot C \cdot NO_2 \\ | \quad | \\ O - C \cdot NH_2 \end{array}$ , and a scheme is then given for the breaking down of the original amide. C. H. D.

**The Constitution of the Fulminuric Acids. VI. Liebig's Fulminuric Acid.** CELSO ULPANI (*Gazzetta*, 1912, 42, i, 390—408).—The constitution of Liebig's fulminuric acid is discussed. If ammonium fulminurate is suspended in alcohol, and a stream of dry hydrogen chloride passed through it, nitromalonamide and the ammonium salt of ethyl nitromalonate are obtained:



[With LUIGI BERNARDINI].—Determinations of the electrical conductivity of fulminuric acid in aqueous solution show that the strength of the acid approaches that of nitric acid, whilst the replacement of the cyano-group by the group  $-CO \cdot NH_2$ , in nitromalonamide, greatly diminishes the strength. The conductivity of the ammonium salts increases in the order of the substituting groups:  $(CO_2Et)_2$ ,  $(CO \cdot NH_2)_2$ ,  $(CN)(CO_2Et)$ ,  $(CN)(CO \cdot NH_2)$ .

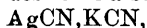
Alcoholic ammonia reacts with ethyl nitrocyanoacetate in a sealed tube at  $140^{\circ}$ , yielding a crystalline compound,  $C_5H_{10}O_3N_4 \cdot \frac{1}{2}H_2O$ , which has a low conductivity, and evolves ammonia when warmed with sodium carbonate. The constitution is uncertain. C. H. D.

The Binary Systems of Potassium and Sodium Cyanides with the Corresponding Salts of Silver, Copper, and Zinc, and with Potassium and Sodium Chlorides. WILHELM TRUTHE (*Zeitsch. anorg. Chem.*, 1912, **76**, 129—160).—The cyanides are fused in an atmosphere of nitrogen, dried and freed from oxygen, and the thermocouple is protected by means of a glass capillary.

Potassium cyanide has m. p.  $622^{\circ}$ , and sodium cyanide, m. p.  $561.7^{\circ}$ , both salts being previously dried in nitrogen at  $150^{\circ}$ . The absorption of oxygen, forming cyanates, lowers the m. p. The two salts form a continuous series of solid solutions, the freezing-point curve passing through a minimum at  $502^{\circ}$ . A transformation takes place in the solid crystals at  $260^{\circ}$ , reaching a maximum at about the ratio 1:1. As a similar transformation has been observed in the pairs  $NaBO_2$ – $KBO_2$ ,  $NaCl$ – $KCl$ , and  $NaCl$ – $LiCl$ , it is probable that a compound is formed. The change takes place on cooling with development of heat and contraction of volume.

Potassium cyanide and potassium chloride form a continuous series of solid solutions, and the crystals become turbid in course of time, although a thermal effect cannot be detected. Sodium cyanide and sodium chloride form an exactly similar series.

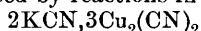
Potassium and silver cyanides form a stable double salt,



giving rise to a maximum on the freezing-point curve at  $370^{\circ}$ . As silver cyanide melts with decomposition at  $320$ – $350^{\circ}$ , the mixtures are best studied by preparing the double salt in the wet way, and then melting it with excess of the one or the other salt. Decomposition is thus avoided. The curve has two eutectic points, both at about  $290^{\circ}$ , and the form of the maximum indicates that the double salt is very little dissociated on fusion. Solid solutions are not formed. Microscopical examination confirms the thermal results.

The compound  $AgCN, NaCN$ , prepared in the wet way, has m. p.  $471^{\circ}$ , with some decomposition. Mixtures richer in silver cyanide decompose readily, and the freezing-point curve is incomplete on that side. There is a eutectic point at  $422^{\circ}$ , and two series of solid solutions are formed.

Cuprous cyanide melts without much decomposition at  $473^{\circ}$ , and forms a complex system with potassium cyanide. Three compounds are formed from the liquid:  $KCN, Cu_2(CN)_2$ , which gives a maximum at  $327^{\circ}$ ;  $2KCN, Cu_2(CN)_2$ , giving a flat maximum at  $327^{\circ}$ , and  $6KCN, Cu_2(CN)_2$ , which is indicated by a break in the freezing-point curve at  $400^{\circ}$ . Solid solutions are not formed. In addition to these, two compounds are produced by reactions in the solid state:



at  $230^{\circ}$ , and  $3KCN, Cu_2(CN)_2$  at about the same temperature.

Cuprous cyanide and sodium cyanide form a system of unusual type. There are four compounds, of which two,  $4NaCN, Cu_2(CN)_2$  and

$6\text{NaCN}, \text{Cu}_2(\text{CN})_2$ , form a continuous series of solid solutions with both components. The third,  $2\text{NaCN}, \text{Cu}_2(\text{CN})_2$ , has m. p.  $398^\circ$ , and occurs as a maximum on the curve, whilst the fourth,

$3\text{NaCN}, \text{Cu}_2(\text{CN})_2$ ,  
is formed in the solid state at  $318^\circ$ .

Zinc cyanide is infusible, and only decomposes slowly at  $1000^\circ$ . The compound  $2\text{KCN}, \text{Zn}(\text{CN})_2$  has a maximum m. p.  $538^\circ$ . Solid solutions are not formed, but the system has not been completely investigated, owing to extensive decomposition. This is still more marked in mixtures of sodium and zinc cyanides, and in mixtures of zinc and cuprous cyanides.

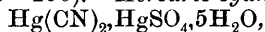
There is no necessary relation between the compounds which separate from molten mixtures and those which crystallise from aqueous solution, but the formulæ are in most cases the same.

C. H. D.

**Influence of Oxidising Agents on the Rate of Solution of Gold in Potassium Cyanide.** JAKOV I. MICHAILENKO and M. I. MESHTSCHERJAKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 567—570).—The dissolution of gold by potassium cyanide solution requires the presence of an oxidising agent, and is retarded or entirely prevented by the introduction of hydrogen ions into the solution. Hydroxyl ions do not favour the dissolution, and in excess may exert a retarding influence. In a neutral medium (that is, one to which neither acid nor alkali has been added) the rate of solution of the metal is not appreciably affected by the following oxidising agents: quinone,  $\text{Na}_2\text{SnO}_3 + 3\text{H}_2\text{O}$ ,  $\text{KBrO}_3$ ,  $\text{KIO}_3$ ,  $\text{KClO}_3$ ,  $\text{Hg}(\text{CN})_2$ ,  $\text{CuCl}_2 + 2\text{H}_2\text{O}$ ; it is, however, accelerated by  $\text{KClO}_4$ ,  $\text{KMnO}_4$ ,  $\text{KIO}_4$ ,  $\text{NH}_4\text{SO}_4$ ,  $\text{Na}_2\text{O}_2$ ,  $\text{KSO}_4$ ,  $\text{NaSO}_4$ ,  $\text{Br}$ ,  $\text{K}_3\text{Fe}(\text{CN})_6$ , or  $\text{KCO}_3$ . The relative accelerations produced by these oxidising agents in centinormal concentration are as follows:  $\text{KClO}_4$ , 1;  $\text{KIO}_4$ , 2;  $\text{KCO}_3$ , 2;  $\text{NH}_4\text{SO}_4$ , 3;  $\text{KSO}_4$ , 4;  $\text{NaSO}_4$ , 4;  $\text{Na}_2\text{O}_2$ , 4, and  $\text{K}_3\text{Fe}(\text{CN})_6$ , 5. The velocity of solution of the gold is increased by increase of the concentration of the oxidising agent to a certain limit, and may be diminished by further addition. The combined action of two oxidising agent present together is less than that of the more effective of them. The addition to potassium cyanide of  $\text{NaCl}$ ,  $\text{Hg}(\text{CN})_2$ ,  $\text{CuCl}_2$ , or  $\text{CoCl}_2$  has either no influence or a retarding one on the rate of solution of gold.

T. H. P.

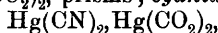
**Mercuric Oxycyanide.** III. ERWIN RUPP and S. GOY (*Arch. Pharm.*, 1912, 250, 280—290).—*Mercuric cyanide sulphate*,



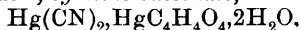
stout needles, is obtained by evaporating a solution of mercuric oxycyanide or of equal molecular quantities of mercuric cyanide and sulphate in dilute sulphuric acid. It is decomposed by water into mercuric cyanide and basic mercuric sulphate.

The following double salts have been prepared by dissolving mercuric oxycyanide in the requisite acid—in the case of the organic acids, in the absence of water: *cyanide nitrate*,  $\text{Hg}(\text{CN})_2, \text{Hg}(\text{NO}_3)_2$ , colourless plates; *cyanide acetate*,  $\text{Hg}(\text{CN})_2, \text{Hg}(\text{OAc})_2$ , slender needles; *cya ide*

formate,  $\text{Hg}(\text{CN})_2 \cdot \text{Hg}(\text{HCO}_2)_2$ , prisms; cyanide oxalate,



microcrystalline powder; cyanide succinate,



long prisms; cyanide benzoate,  $\text{Hg}(\text{CN})_2 \cdot \text{Hg}(\text{OBz})_2 \cdot \text{H}_2\text{O}$ , long prisms, all of which are decomposed by water.

Whilst mercuric cyanide forms clear solutions with aqueous ammonia and ammoniacal compounds, mercuric oxycyanide yields precipitates. The oxycyanide behaves like a mixture of mercuric cyanide and mercuric oxide, so that in the reaction with ammoniacal compounds the solutions contain mercuric cyanide, whilst the precipitates consist of mercuriammonium compounds.

The whole behaviour of solid mercuric oxycyanide is expressed by the formula  $\text{Hg}(\text{CN})_2 \cdot \text{HgO}$ . Its molecular weight in solution (and also that of the cyanideacetate), determined by the cryoscopic method, corresponds with the formula  $\text{OH} \cdot \text{Hg} \cdot \text{CN}$  (or  $\text{OAc} \cdot \text{Hg} \cdot \text{CN}$ ), but this is probably due to dissociation; evidence for the existence of an ion,  $\cdot \text{Hg} \cdot \text{CN}$ , has not been obtained. C. S.

**Transformation of Ferricyanic Acid into Ferrocyanic Acid and the Hydrolysis of Ferric, Zinc, and Aluminium Chlorides.** CAM. GILLET (*Bull. Soc. chim. Belg.*, 1912, 26, 236—238).—The reaction  $2\text{H}_4\text{Fe}(\text{CN})_6 + \text{Cl}_2 + \text{aq} \rightleftharpoons 2\text{H}_3\text{Fe}(\text{CN})_6 + 2\text{HCl} + \text{aq}$  is shown to be reversible. Hydrochloric or hydrobromic acids convert ferricyanic acid into ferrocyanic acid with the liberation of chlorine or bromine. When the acid is neutralised by a strong base there is complete conversion from ferrocyanide into ferricyanide. When the chlorine is removed as it is formed, complete conversion into ferrocyanic acid is effected. This may be done with reduced silver for the chlorine, or phenol or chloroform for the bromine. Instead of the acids, the chlorides or bromides of iron, zinc, or aluminium may be used with the same result; this indicates that these chlorides are hydrolysed in solution.

The chlorine liberated in the interaction between potassium ferricyanide and ferric chloride is not produced by the dissociation of the latter into ferrous chloride and chlorine, but it is due to the oxidation of the hydrochloric acid of the ferric oxide contained in the ferricyanic acid. E. F. A.

**Copper Salts of Hydroferrocyanic and Hydroferricyanic Acids.** ERICH MÜLLER, GUSTAV WEGELIN, and E. KELLERHOFF (*J. pr. Chem.*, 1912, 86, [ii], 82—111).—The authors have investigated the composition of the precipitates formed by the interaction of cupric sulphate and cuprous chloride with potassium ferrocyanide, potassium ferricyanide, hydroferrocyanic acid, and hydroferricyanic acid in various proportions in 0.1 molar aqueous solution. The composition of the precipitates was deduced by determining the amounts of  $\text{Cu}''$ ,  $\text{Cu}'$ ,  $\text{Fe}''(\text{CN})_6$ , and  $\text{Fe}'(\text{CN})_6$  remaining in the solution.

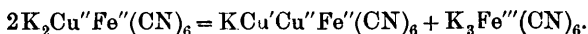
From theoretical considerations it is shown that the precipitate formed by mixing solutions containing equivalent amounts of cupric and ferrocyanogen ions should have the same composition

as that obtained from solutions containing the same equivalent amounts of cuprous and ferricyanogen ions, and this conclusion is confirmed by the authors' experimental results.

The greenish-brown precipitate formed from cupric sulphate and potassium ferricyanide has the same composition,  $\text{Cu}_3''[\text{Fe}'''(\text{CN})_6]_2$ , for all values of the ratio  $\text{CuSO}_4/\text{K}_3\text{Fe}'''(\text{CN})_6$ .

With cupric sulphate and potassium ferrocyanide, the precipitate has a constant composition only when one of the two components is in great excess; for values of the ratio  $\text{CuSO}_4/\text{K}_4\text{Fe}''(\text{CN})_6 (=w)$  in the neighbourhood of 0.1, a brown precipitate which changes to yellow and has the composition  $\text{K}_2\text{Cu}''\text{Fe}''(\text{CN})_6$  is produced, whilst if  $w > 2.5$  a brown precipitate of  $\text{Cu}_2''\text{Fe}''(\text{CN})_6$  is obtained. When  $w = 1.5$  the precipitate consists of  $\text{K}_2\text{Cu}_3''[\text{Fe}''(\text{CN})_6]_2$ . For values of  $w = 0.1-1.5$  a mixture of  $\text{K}_2\text{Cu}''\text{Fe}''(\text{CN})_6$  and  $\text{K}_2\text{Cu}_3''[\text{Fe}''(\text{CN})_6]_2$  is formed, whilst for values  $= 1.5-2.5$  the precipitate consists of a mixture of the latter compound with  $\text{Cu}_2''\text{Fe}''(\text{CN})_6$ .

When  $w < 1.5$  the solution contains a small amount of ferricyanide, probably produced as follows:



Similar results were obtained with solutions of sodium ferrocyanide and cupric sulphate.

In the case of cupric sulphate and hydroferrocyanic acid the brown precipitate has the composition  $\text{Cu}_2''\text{Fe}''(\text{CN})_6$  for all values of the ratio  $\text{CuSO}_4/\text{H}_4\text{Fe}''(\text{CN})_6 (=x)$  above 2; when  $x$  is approximately 0.5 the precipitate consists of  $\text{H}_2\text{Cu}_3''[\text{Fe}''(\text{CN})_6]_2$ , whilst for values of  $x = 0.5-2$  a mixture of the latter compound with  $\text{Cu}_2''\text{Fe}''(\text{CN})_6$  is produced.

With solutions of potassium ferrocyanide and cuprous chloride dissolved in aqueous sodium chloride, the white precipitate has the composition  $\text{K}_2\text{Cu}_2'\text{Fe}''(\text{CN})_6$  when the ratio  $\text{CuCl}/\text{K}_4\text{Fe}''(\text{CN})_6 (=y) < 2$ . For values of  $y > 3.5$  the precipitate consists of  $\text{KCu}_3'\text{Fe}''(\text{CN})_6$ , whilst for intermediate values (2—3.5) a mixture of these two substances is formed.

Similar results were obtained with solutions of hydroferrocyanic acid and cuprous chloride dissolved in hydrochloric acid.

The precipitates formed by mixing solutions of cuprous chloride and potassium ferricyanide consist of ferrocyanides and not ferricyanides. For values of the ratio  $\text{CuCl}/\text{K}_3\text{Fe}'''(\text{CN})_6 (=z) < 1$ , a mixture of  $\text{K}_2\text{Cu}_3''[\text{Fe}''(\text{CN})_6]_2$  and  $\text{K}_2\text{Cu}''\text{Fe}''(\text{CN})_6$  is produced. As  $z$  becomes  $> 1$ , the latter compound is gradually replaced by  $\text{K}_2\text{Cu}_2'\text{Fe}''(\text{CN})_6$ , until  $z = 1.75$ , when the precipitate consists only of  $\text{K}_2\text{Cu}_2'\text{Fe}''(\text{CN})_6$  and  $\text{K}_2\text{Cu}_3''[\text{Fe}''(\text{CN})_6]_2$ .

As  $z$  increases from 1.75 to 2, the two last-mentioned compounds are accompanied by  $\text{KCuCu}_3''[\text{Fe}''(\text{CN})_6]_2$ . For still greater values of  $z$  the precipitate consists of a mixture of  $\text{KCu}_3'\text{Fe}''(\text{CN})_6$ ,  $\text{K}_2\text{Cu}_2'\text{Fe}''(\text{CN})_6$ , and  $\text{KCuCu}_3''[\text{Fe}''(\text{CN})_6]_2$ . Only when the cuprous chloride is in great excess ( $z > 10$ ) has the precipitate a definite composition, namely,  $\text{KCu}_3'\text{Fe}''(\text{CN})_6$ . The latter compound is obtained as a white precipitate by dropping aqueous potassium ferrocyanide into the cuprous chloride solution.

F. B.

**Stereochemistry of the Aromatic Series.** ROMÁN CASARES (*Anal. Fis. Quim.*, 1912, 10, 150—152).—Polemical against Lozano (compare this vol., i, 430). G. D. L.

**The Study of Hydro-aromatic Substances.** EDWARD DIVERS, ARTHUR W. CROSSLEY, WILLIAM H. PERKIN, MARTIN O. FORSTER, and HENRY R. LE SUEUR (*Brit. Assoc. Report*, 1911, 99—101).—An account of the synthesis of 1:1:3-trimethylcyclohexene (*Trans.*, 1910, 97, 2218) and 1:1:2-trimethylcyclohexan-3-one (*Trans.*, 1911, 99, 1101). C. H. D.

**Possible Existence of Cyclic Hydrocarbons Containing Nuclear Triple Linkings.** ALEXEI E. FAWORSKY and W. BOSHOWSKY (*Annalen*, 1912, 390, 122—129).—The authors have unsuccessfully attempted to prepare a cyclic hydrocarbon containing a nuclear triple linking.

By bromination in cold chloroform, chloro- $\Delta^1$ -cyclohexene yields 1-chloro-1:2-dibromocyclohexane,  $C_6H_9ClBr_2$ , m. p. 43—44°, which is converted by alcoholic potassium hydroxide into chloro- $\Delta^1$ -cyclohexene and 1:2-dibromo- $\Delta^1$ -cyclohexene,  $C_6H_8Br_2$ , m. p. 39—40°, b. p. 90—92°/6 mm. The latter, the constitution of which is proved by its oxidation to adipic acid, is unattacked by zinc dust, copper, silver, calcium, or amalgamated zinc and aluminium, but in ethereal solution is converted by sodium into a mixture of dodecahydrotriphenylene (Mannich, *Abstr.*, 1907, i, 205) and a viscous substance which is not attacked by potassium permanganate. So far as the six-membered ring is concerned, therefore, the existence of a hydrocarbon containing a nuclear triple linking has been disproved. C. S.

**The Study of Isomorphous Sulphonic Derivatives of Benzene.** HENRY A. MIERS, HENRY E. ARMSTRONG, WILLIAM J. POPE, and WILLIAM P. WYNNE (*Brit. Assoc. Report*, 1911, 82—83. Compare Colgate and Rodd, *Trans.*, 1910, 97, 1585). C. H. D.

**Conversion of Carbazole into Dimethyl-di-cyclopentyl, a Hydrocarbon Present in Petroleum.** JULIUS SCHMIDT and AUGUST SIGWART (*Ber.*, 1912, 45, 1779—1787).—When carbazole is heated at 130° with hydrogen iodide and phosphorus, hexahydrocarbazole is obtained in almost theoretical proportion. At 200—240°, the main product is a hydrocarbon,  $C_{12}H_{22}$  (compare Graebe and Glaser, *Abstr.*, 1872, 302). On oxidation with nitric acid, butyric acid is obtained, and the compound is regarded as 3:3'-dimethyldicyclopentyl. It has b. p. 213—214°/738 mm.,  $D^{20}_D$  0.8784,  $n^{25}_D$  1.4730, figures which are in close agreement with those given by a hydrocarbon,  $C_{12}H_{22}$ , obtained from Louisiana petroleum by Coates (*Abstr.*, 1906, i, 329).

Hexahydrocarbazole forms colourless, silky, lustrous needles, m. p. 99°.

9-Methylhexahydrocarbazole methiodide, obtained on heating the carbazole with methyl iodide and methyl alcohol, crystallises in octahedral or cubic crystals, m. p. 194—195° (decomp.). On heating it, 9-methylhexahydrocarbazole is obtained as a mobile, colourless liquid,

b. p. 294—295°/748 mm,  $D_4^{20}$  1.035,  $n_D^{20}$  1.6248. The *picrate* forms pale yellow platelets, m. p. 143—144° (decomp.); the *picrolonate* separates in pale yellow, silky needles, m. p. 174—175°.

*Dimethyldicyclopentyl* is a transparent, mobile liquid, with a marked odour of petroleum. E. F. A.

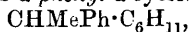
**Colloidal Palladium. Partial and Total Hydrogenation of Phenylacetylene, Tolane, and Diphenyldiacetylene.** CHR. KELBER and ANTON SCHWARZ (*Ber.*, 1912, 45, 1946—1952).—Colloidal palladium, which is active in glacial acetic acid and is not destroyed by dilute mineral acids, is prepared as follows. Gluten is heated with acetic acid, and to the solution is added palladous chloride dissolved in a little water. The clear, dark brown solution is faintly basified with ammonia, and then slowly treated with hydrazine hydrate. After the completion of the reaction, the deep, brownish-black liquid is dialysed until free from chlorine, and is then carefully evaporated, finally to dryness in a vacuum. The product forms black, glistening lamellæ, and is easily soluble in water or glacial acetic acid; the solutions are not rendered flocculent by dilute mineral acids. The substance contains about 17.2% of palladium.

By passing the calculated amounts of hydrogen through their solutions in glacial acetic acid containing 0.1 gram of the colloidal palladium, phenylacetylene has been reduced to styrene or ethylbenzene, tolane to stilbene and *isostilbene* or dibenzyl, and diphenyldiacetylene to *cis-cis-* and *cis-trans-* $\alpha\delta$ -diphenyl- $\Delta^{\gamma}$ -butadiene or  $\alpha\delta$ -diphenylbutane. C. S.

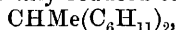
**Direct Hydrogenation of Diphenylethanes. Preparation of Dicyclohexylethanes** PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1912, 154, 1771—1773).—Diphenyl and diphenylmethane have both been reduced by direct hydrogenation to the corresponding dicyclohexyl and dicyclohexylmethane (compare this vol., i, 547, and Eykman, *Abstr.*, 1904, i, 26). The authors have extended the reaction to the next higher homologues.

$\alpha\beta$ -Diphenylethane when passed with excess of hydrogen over reduced nickel at 160—170° is transformed completely into  $\alpha\beta$ -dicyclohexylethane,  $C_6H_{11}\cdot CH_2\cdot CH_2\cdot C_6H_{11}$ , a colourless liquid, b. p. 270—271° (corr.);  $D_4^{18}$  0.8838;  $n_D^{18}$  1.480. It is not attacked by a mixture of nitric and sulphuric acids.

$\alpha\alpha$ -Diphenylethane is much more difficult to reduce. When its vapour is passed with excess of hydrogen over reduced nickel at 170°, the product formed is *a-phenyl-a-cyclohexylethane*,



a colourless liquid with an odour of citron, b. p. 264—266° (corr.),  $D_4^{17}$  0.9773,  $n_D^{17}$  1.549. It is violently attacked in the cold by the nitro-sulphuric mixture. This substance when submitted to three successive hydrogenations at 170° is finally reduced to *aa-dicyclohexylethane*,



a colourless liquid, b. p. 256—257° (corr.);  $D_4^{20}$  0.9271;  $n_D^{20}$  1.511. It is not acted on by a mixture of nitric and sulphuric acids.

W. G.

**Reaction Differences of Stereoisomeric Ethylene Halides. I.** PAUL PFEIFFER (*Ber.*, 1912, 45, 1810—1819).—It is found that certain stereoisomeric ethylene halides show greater differences in chemical behaviour than would be expected from the ordinary structural conception of the asymmetric carbon atom.

2:4-Dinitrostilbene gives two isomeric additive compounds with chlorine; the  $\alpha$ -chloride (yellow leaflets, m. p. 167°) is obtained by the action of chlorine on the chloroform solution, whilst the  $\beta$ -chloride is the main product when the reaction is carried out in carbon disulphide. When heated on the water-bath with pyridine, both these chlorides yield  $\alpha$ -chloro-2:4-dinitrostilbene,  $C_6H_3(NO_2)_2 \cdot CCl:CHPh$ , prismatic needles, m. p. 104°; when exposed to light the crystals are reddened, whilst the solution in pyridine gives a nitrophenylisatogen (see next abstract).

The 2:4-dinitrostilbene bromides are obtained by the action of bromine on the parent substance in glacial acetic acid, and can be separated by means of alcohol. The  $\alpha$ -isomeride forms colourless needles from acetic acid, m. p. 185° (compare Thiele and Escales, *Abstr.*, 1901, i, 689); the  $\beta$ -isomeride forms pale yellow leaflets, m. p. 145—146°. Whereas the  $\beta$ -bromide on warming in pyridine solution yields  $\alpha$ -bromo-2:4-dinitrostilbene, yellow tablets, m. p. 98—99°, reddened by light and converted by an aqueous alcoholic solution of sodium hydroxide into dinitrotolane, the  $\alpha$ -isomeride under similar treatment with pyridine gives 2:4-dinitrostilbene (m. p. 140°).

Stilbene when treated in ethereal solution with chlorine gives a mixture of the  $\alpha$ - and  $\beta$ -isomeric chlorides. The  $\alpha$ -chloride (needles, m. p. 191—193°) is surprisingly stable, and resists the action of pyridine, even at 200° in a sealed tube, whereas the  $\beta$ -compound (m. p. 93—94°), although more stable than the corresponding dinitrostilbene derivative, gives monochlorostilbene (prismatic needles, m. p. 52—54°).

The stilbene dibromides (compare Wislicenus and Seeler, *Abstr.*, 1896, i, 98) was prepared by the action of bromine on a cold carbon disulphide solution of stilbene. The  $\alpha$ -isomeride (m. p. 236°) on treatment with pyridine gives stilbene, whilst the  $\beta$ -compound (m. p. 111°) gives as chief product monobromostilbene. D. F. T.

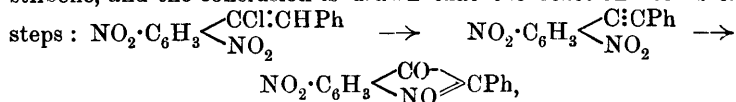
**Rearrangements in Light.** PAUL PFEIFFER (*Ber.*, 1912, 45, 1819—1830).—A pyridine solution of  $\alpha$ -chloro-2:4-dinitrostilbene,  $C_6H_3(NO_2)_2 \cdot CCl:CHPh$  (compare preceding abstract), on exposure to sunlight soon becomes coloured, due to the formation of an easily isolable red substance.

[With A. FORNET, E. KRAMER, FR. MATZKE, and L. SPIRO.]—In order to discover which of the nitro-groups is affected,  $\alpha$ -chloro-4-nitro-2-cyanostilbene (yellow, silky needles, m. p. 134°) and  $\alpha$ -chloro-2-nitro-4-cyanostilbene (yellow leaflets, m. p. 162—163°) were prepared by the action of pyridine at 150—170° on the two corresponding nitrocyano-stilbene chlorides,  $NO_2 \cdot C_6H_3(CN) \cdot CHCl \cdot CPhCl$  (the 4:2-compound, colourless needles, m. p. 118—119°; the 2:4-compound, colourless leaflets, m. p. 196—197°), which are easily obtained by the action of chlorine on chloroform solutions of the two nitrocyano-stilbenes (Ullmann and Gschwind, *Abstr.*, 1908, i, 623). The chloro-2-nitro-

4-cyanostilbene, unlike the isomeride, in pyridine solution is readily affected by light with the formation of an orange-red substance.

2 : 2'-Dinitrostilbene chloride,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CHCl} \cdot \text{CHCl} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , was obtained by the action of chlorine on a chloroform solution of *oo'*-dinitrostilbene (Bischoff, Abstr., 1888, 1094); it forms yellow needles, m. p. 152—153°, and when heated with pyridine at 160—170°, gives *α*-chloro-2 : 2'-dinitrostilbene, yellow needles or leaflets, m. p. 124°. The pyridine solution of this last substance is turned orange-red by light. Treatment with alcoholic potash, on the other hand, removes the elements of hydrogen chloride with the formation of *oo'*-dinitrotolane (yellow needles, m. p. 192—193° to a deep red liquid; compare Kliegl and Haas, Abstr., 1911, i, 433). The action of bromine in sunlight on an ethereal solution of dinitrotolane produces a yellow, crystalline dibromide, m. p. 217°, which, when crystallised from cold benzene, gives tablets of an unstable additive compound with benzene. Dinitrotolane, unlike dinitrostilbene, is readily affected when its pyridine solution is exposed to light.

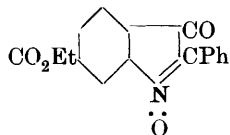
From the above experimental results, it is probable that the nitro-group in the ortho-position and also the carbon-carbon bond are both implicated in the change produced by light on *α*-chloro-2 : 4-dinitrostilbene, and the conclusion is drawn that the reaction occurs in the



the final product belonging to the isatogen class (Baeyer, Abstr., 1882, 620, etc.), being probably 6-nitro-2-phenylisatogen (formula annexed; compare Angeli and Angelico, Abstr., 1907, i, 153); it separates from the pyridine solution in red leaflets, m. p. 206°. Sulphur dioxide acting on the acetic acid solution gives a brownish-black substance (leaflets), and also yellow leaflets of a substance, m. p. 257—258°, probably 6-nitro-

2-phenylindoxyl.

*α*-Chloro-2-nitro-4-cyanostilbene can be hydrolysed by hydrogen chloride in alcoholic solution to ethyl *α*-chloro-2-nitrostilbene-4-carboxylate,  $\text{CO}_2\text{Et} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CCl} \cdot \text{CHPh}$ , yellow leaflets, m. p. 98°; this can be hydrolysed by sulphuric acid in 50% acetic acid solution to the free acid, *α*-chloro-2-nitrostilbene-4-carboxylic acid,



$\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{CCl} \cdot \text{CHPh}$ , bright yellow needles, m. p. 186°; sodium salt, yellow needles. The ester when exposed in pyridine solution to sunlight gives ethyl-2-phenylisatogen-6-carboxylate (formula annexed), orange needles, m. p. 138°.

D. F. T.

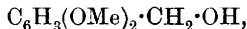
The Transformation of Aromatic Nitroamines and Allied Substances, and its Relation to Substitution in Benzene Derivatives. F. STANLEY KIPPING, KENNEDY J. P. ORTON, SIEGFRIED RUHEMANN, ARTHUR LAPWORTH, and JOHN T. HEWITT (*Brit. Assoc.*

*Report*, 1911, 94—98).—A series of quantitative studies of chlorination of anilides, and of the formation of nitroamines (*Trans.*, 1911, **99**, 1185, 1369, 1377). C. H. D.

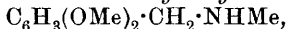
**Action of Aniline on Uranyl Salts. II.** GIUSEPPE INGHILLERI (*Atti R. Accad. Fisicocritici, Siena*, 1911).—Uranylaniline salts exhibit characteristics similar to those of the corresponding quinoline compounds (see this vol., i, 650). The following were prepared:

The action of aniline on uranyl nitrate yields *uranylaniline* or *phenyluranylamine*,  $\text{NPh}\cdot\text{UO}_2 + 6\text{H}_2\text{O}$ , which crystallises also with  $2\text{H}_2\text{O}$ , and when heated with concentrated acetic acid gives a bright red solution and a precipitate of the black oxide,  $\text{U}_2\text{O}_5$ . The *sulphate*,  $(\text{NPh})_2\text{UO}_2\text{SO}_4 + 3\text{H}_2\text{O}$ ; *acetate*,  $(\text{NPh})_2\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$ , and *oxalate*,  $(\text{NPh})_2\text{UO}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$ , were prepared. T. H. P.

**2:3-Dihydroxybenzylmethylamine and 2:3-Dihydroxybenzyl dimethylamine.** RENÉ DOUETTEAU (*Bull. Soc. chim.*, 1912, [iv], 11, (13), 652—656. Compare Tiffeneau, *Abstr.*, 1911, i, 972).—The starting point for the preparation of these substances was 2-hydroxy-3-methoxybenzaldehyde ("orthovanillin"), which can be methylated (compare Douetteau, *Abstr.*, 1911, i, 973) to 2:3-dimethoxybenzaldehyde; by the action of alcoholic potassium hydroxide, this is converted into 2:3-dimethoxybenzyl alcohol,



(m. p.  $48^\circ$ , b. p.  $257\text{—}258^\circ/761\text{ mm.}$ ), and 2:3-dimethoxybenzoic acid (m. p.  $116^\circ$ ; methyl ester, m. p.  $46.5^\circ$ ). The alcohol gives a *phenylurethane*, m. p.  $94^\circ$ , and an *acetate*, b. p.  $158\text{—}160^\circ/16\text{ mm.}$ ,  $278\text{—}279^\circ/754\text{ mm.}$ ,  $D_4^{20} 1.1621$ . The *chloride* of the alcohol could not be obtained in a higher degree of purity than 70% (b. p.  $133\text{—}137^\circ/13\text{ mm.}$ ,  $D_4^{20} 1.1958$ ), but when heated with a benzene solution of methylamine in a sealed tube, it gave 2:3-dimethoxybenzylmethylamine,



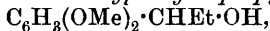
b. p.  $149^\circ/19\text{ mm.}$ ,  $D_4^{20} 1.0699$ ; *picrate*, m. p.  $170^\circ$ ; *methiodide*, m. p.  $181^\circ$ . Attempts to prepare the *hydrochloride* of 2:3-dihydroxybenzylamine by demethylation yielded only a syrupy product.

2:3-Dimethoxybenzyl dimethylamine,  $\text{C}_6\text{H}_3(\text{OMe})_2\cdot\text{CH}_2\cdot\text{NMe}_2$ , was obtained by the action of dimethylamine on 2:3-dimethoxybenzyl chloride; it has b. p.  $128\text{—}129^\circ/14\text{ mm.}$ ,  $D_4^{20} 1.0461$ ; *methiodide*, m. p.  $179^\circ$ . When heated with an equimolecular quantity of acetic anhydride, it undergoes scission into acetodimethylamide and 2:3-dimethoxybenzyl acetate (compare Tiffeneau, *Abstr.*, 1911, i, 779). When heated with hydriodic acid at  $130\text{—}140^\circ$  it gives 2:3-dihydroxybenzyl dimethylamine,  $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}_2\cdot\text{NMe}_2$ ; *hydrochloride*, m. p.  $165^\circ$ .

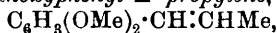
The effect of the Grignard reagent on the two substituted benzaldehydes used in the course of the preceding work was investigated.

2-Hydroxy-3-methoxybenzaldehyde reacts with magnesium ethyl bromide with the formation of 2-hydroxy-3-methoxyphenyl- $\Delta^1$ -propylene,  $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}:\text{CHMe}$ , m. p.  $74\text{—}75^\circ$ , b. p.  $147\text{—}148^\circ/16\text{ mm.}$  (compare Pauly, *Abstr.*, 1911, i, 785). Magnesium ethyl iodide gives a mixture of this substance with  $\alpha$ -2-hydroxy-3-methoxyphenyl-n-propyl alcohol,  $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CHEt}\cdot\text{OH}$ , b. p.  $165\text{—}170^\circ/16\text{ mm.}$

2:3-Dimethoxybenzaldehyde on treatment with magnesium ethyl bromide produces  $\alpha$ -2:3-dimethoxyphenyl-n-propyl alcohol,



a viscous liquid, b. p. 156—157°/14 mm.,  $D_0^{20}$  1.1212, which on distillation under ordinary pressure loses the elements of water with the formation of 2:3-dimethoxyphenyl- $\Delta^1$ -propylene,



b. p. 248—250°,  $D_0^{20}$  1.0612.

D. F. T.

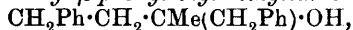
**Some Ethers of Cinnamyl Alcohol.** HENRI BEAUFOR (*Bull. Soc. chim.*, 1912, [iv], 11, 648—652).—A preliminary account of an investigation of the behaviour of various ethylenic substances towards treatment with iodine and yellow mercuric oxide.

Cinnamyl alcohol is converted into its sodium derivative by the action of sodamide, and then on careful treatment with methyl iodide, cinnamyl methyl ether,  $\text{CHPh} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OMe}$ , is obtained, b. p. 227°, 117°/16 mm.,  $D_0^{20}$  1.0037 (compare Pschorr and Dickhauser, *Abstr.*, 1911, i, 908). It gives a *dibromide*, m. p. 50.5°, and on treatment in ethereal solution with iodine and yellow mercuric oxide it gives the *iodohydrin*,  $\text{OH} \cdot \text{CHPh} \cdot \text{CHI} \cdot \text{CH}_2 \cdot \text{OMe}$ , which can be converted into the corresponding *oxide*, and also be caused to undergo rearrangement into a branched aldehyde (compare Bougault, *Abstr.*, 1902, i, 452). The action of iodine and mercuric oxide on the methyl and ethyl alcoholic solutions, however, yields the *methyl-iodohydrin* (b. p. 160—161°/15 mm.) and *ethyl-iodohydrin* (b. p. 164—165°/15 mm.) respectively.

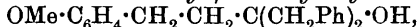
*Cinnamyl ethyl ether*,  $\text{CHPh} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OEt}$ , is obtained similarly to the methyl ether above; it is a colourless liquid, b. p. 238—239°/752 mm., 127—129°/17 mm.  $D_0^{20}$  0.9938; *dibromide*, m. p. 72°.

D. F. T.

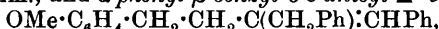
**Unsaturated Compounds. II. Elimination of Hydrogen Chloride from Unsymmetrical Carbonyl Chlorides.** ALEX. ORECHOFF and S. MEERSON (*Ber.*, 1912, 45, 1926—1930. Compare this vol., i, 436).—*Benzyl- $\beta$ -phenylethylmethylcarbinol*,



m. p. 50—51°, obtained in the usual manner from magnesium benzyl chloride and benzylacetone, is converted in ethereal solution by hydrogen chloride or hydrochloric acid,  $D$  1.19, into the *chloride*,  $\text{C}_{17}\text{H}_{19}\text{Cl}$ , m. p. 61—62°. *Dibenzyl  $\beta$ -o-anisylethylcarbinol*,



m. p. 72—73°, obtained in a similar manner from ethyl *o*-methoxydihydrocinnamate, forms a *chloride*,  $\text{C}_{24}\text{H}_{25}\text{OCl}$ , m. p. 90—91°. When boiled with pyridine, these two chlorides are converted into  *$\alpha\delta$ -diphenyl- $\beta$ -methyl- $\Delta^a$ -butylene*,  $\text{CH}_2\text{Ph} \cdot \text{CH}_2 \cdot \text{CMe} : \text{CHPh}$ , b. p. 205—206°/40 mm., and  *$\alpha$ -phenyl- $\beta$ -benzyl- $\delta$ -o-anisyl- $\Delta^a$ -butylene*,



m. p. 56—57°, b. p. 266—267°/19 mm., respectively, the constitutions of the two hydrocarbons being proved by oxidation with ozone, whereby the former yields benzaldehyde and benzylacetone, whilst the

latter is converted into benzaldehyde and a ketone which probably has the formula  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2\text{Ph}$ .

It is thus shown that, as in the case previously examined (*loc. cit.*), the nearest phenyl group has the strongest displacing influence on the hydrogen of the methylene group of the chloride. C. S.

**Mechanism of the Grignard Reaction.** ALEXANDER I. GORSKY (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 581—585).—The author discusses the work of von Baeyer and Villiger (Abstr., 1902, i, 355), Grignard (Abstr., 1903, i, 552), Schmidlin (Abstr., 1906, i, 392; 1907, i, 26), Tschitschibabin (Abstr., 1907, i, 1022), and Stadnikoff (Abstr., 1911, i, 435).

The reaction between triphenylmethyl ethyl ether, propyl iodide, and magnesium takes place most probably according to the equations:  $\text{CPh}_3 \cdot \text{OEt} + \text{MgPrI} = \text{CPh}_3\text{I} + \text{Pr} \cdot \text{Mg} \cdot \text{OEt}$  and  $\text{CPh}_3\text{I} + \text{MgPrI} = \text{MgI}_2 + \text{CHPh}_3 + \text{C}_2\text{H}_6$ . It is found that, under the conditions employed by Stadnikoff (*loc. cit.*), the reaction proceeds only in presence of alkyl iodide (perhaps also of bromide), whilst *iso*amyl chloride or iodobenzene does not react with magnesium and triphenylmethyl ethyl ether. This observation is explained by the fact that alkyl chlorides dissociate into alkylene and hydrogen chloride only with difficulty, and aromatic halogen derivatives exhibit no dissociation in this direction.

If, however, equimolecular proportions of *iso*amyl chloride and iodobenzene are taken together, the reaction proceeds energetically with formation of chlorobenzene and *iso*amyl iodide, the latter then dissociating into amylene and hydrogen iodide, and so giving the conditions for the reaction. The final products are the same as when propyl iodide is used, namely, triphenylmethane and the excess of triphenylmethyl ethyl ether does not take part in the reaction. The formation of amylene supports the scheme of the reaction given above.

With diphenylmethyl propyl ether and butyl iodide, the formation of tetraphenylethane probably results from the reactions:  $\text{CHPh}_2 \cdot \text{OPr} + \text{C}_4\text{H}_9 \cdot \text{MgI} = \text{CHPh}_2\text{I} + \text{C}_4\text{H}_9 \cdot \text{Mg} \cdot \text{OPr}$  and  $2\text{CHPh}_2\text{I} + 2\text{C}_4\text{H}_9 \cdot \text{MgI} = \text{CHPh}_2 \cdot \text{CHPh}_2 + \text{MgI}_2 + 2\text{C}_4\text{H}_8$ . T. H. P.

**Ambrein.** JOSEPH RIBAN (*Compt. rend.*, 1912, 154, 1729—1732\*).—Pelletier and Caventou in 1820 extracted from ambergris by means of alcohol a substance which they called ambrein. Having obtained a few grams of this substance accumulated in the course of years in a perfumery, the author has made a number of experiments in an attempt to elucidate its constitution.

Ambrein,  $\text{C}_{23}\text{H}_{40}\text{O}$ , purified by repeated crystallisations from alcohol is a white solid, separating in slender needles, m. p.  $82^\circ$ , which exhibit the phenomenon of superfusion for a long time even if sown with crystals. When warm and dry, it becomes highly electrified on slight rubbing. It has no optical activity, and is a neutral substance, insoluble in water, but soluble in most organic solvents, from which it does not crystallise out at all readily. When acted on by bromine in carbon tetrachloride solution, it gives an *octobromo*-derivative,  $\text{C}_{23}\text{H}_{32}\text{OBr}_8$ , a

\* and *Bull. Soc. chim.*, 1912, [iv], 11, 754—757.

white, vitreous solid. Chlorine under similar conditions decomposes it. On warming ambrein with phosphorus pentachloride, a white, amorphous mass of *pentachloroambrein*,  $C_{23}H_{35}OCl_5$ , is obtained. W. G.

**Syntheses of Nitriles in the Cyclic Series.** VICTOR GRIGNARD and E. BELLET (*Compt. rend.*, 1912, 155, 44—46).—Alkyl cyclic nitriles can be prepared by adding the corresponding magnesium alkyl bromide drop by drop to a cold ethereal solution of cyanogen, and subsequent hydrolysis. In this way the authors have prepared cyano-hexamethylene [*cyclohexanecarboxylonitrile*], b. p. 75—77°/16 mm. (compare Demjanoff, *Abstr.*, 1904, i, 410), and *o*-, *m*-, and *p*-methylcyclohexanecarboxylonitriles, colourless liquids, having respectively b. p. 79—81°/16 mm., 86—87°/16 mm., 85—87°/18 mm. All these nitriles possess a strong, disagreeable odour, and are hydrolysed by alcoholic potassium hydroxide to the corresponding acid, without the formation of the intermediate amide. On reduction with sodium and alcohol, they yield the corresponding methylhexahydrobenzylamines, which are colourless liquids with a slightly fruity odour, of which the *meta*-compound has b. p. 114—116°/80 mm., and the *para*-, b. p. 113—115°/80 mm.

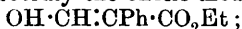
*l*-Pinene hydrochloride when slowly added to an ethereal solution of cyanogen gives *d*-hydro-pinene-carboxylonitrile, m. p. 157—158°,  $\alpha_D + 1.0^\circ$  (compare Houben and Doescher, *Abstr.*, 1911, i, 61). This

nitrile on saponification yields the *l*-acid,  $\begin{array}{c} \text{CH}_2\text{CH} \text{---} \text{CH}_2 \\ | \qquad \qquad \qquad | \\ \text{CH}_2\text{CMc} \text{---} \text{CH}\cdot\text{CO}_2\text{H} \end{array}$ , m. p. 88—89°. W. G.

**Synthesis of  $\alpha$ -Phenyl  $\alpha\beta$ -dimethylhydrocinnamic Acid [ $\alpha\beta$ -Diphenyl- $\alpha$ -methylbutyric Acid].** (Mme.) PAULINE RAMART-LUCAS (*Compt. rend.*, 1912, 155, 39—42).—An endeavour to elucidate the constitution of an acid, m. p. 173°, obtained on oxidising a hydrocarbon resulting from the dehydration of diphenyl- $\psi$ -butylcarbinol (compare this vol., i, 449).

$\alpha\beta$ -Diphenyl  $\alpha$ -methylbutyronitrile can be prepared from  $\alpha\beta$ -diphenylacrylonitrile by addition of magnesium methyl iodide followed by methyl iodide (compare Kohler, *Abstr.*, 1906, i, 427), or by the action of sodamide followed by methyl iodide on  $\alpha\beta$ -diphenylbutyronitrile. The nitrile, so obtained, can be hydrolysed by heating with a mixture of hydrochloric and acetic acids in sealed tubes at 180°, giving  $\alpha\beta$ -diphenyl- $\alpha$ -methylbutyric acid,  $\text{CHMePh}\cdot\text{CMcPh}\cdot\text{CO}_2\text{H}$ , m. p. 181—182°; thus the original acid is still unorientated. W. G.

**Isomerism of Ethyl Formylphenylacetate.** III. WILHELM WISLICENUS (*Annalen*, 1912, 389, 265—292. Compare *Abstr.*, 1900, i, 9, 597).—Four modifications of ethyl formylphenylacetate are known: (i) the liquid  $\alpha$ -form, which develops an intense bluish-violet coloration with ferric chloride, is simply related genetically to the metallic derivatives, and is undoubtedly the enolic modification,



(ii)  $\beta$ -modification, m. p. about 70°, which has hitherto been regarded as the aldo-form; (iii) Michael's modification, m. p. about 50° (*Abstr.*,

1906, i, 179), and (iv)  $\gamma$ -modification, m. p. about  $100^{\circ}$  (Wislicenus and Börner, Abstr., 1900, i, 597).

The author is of opinion that the  $\alpha$ - and the  $\gamma$ -modifications are the only forms which are chemically individual; the other solid forms are mixtures of the  $\alpha$ - and the  $\gamma$ -modifications.

The evidence on which this opinion is based is the following. The  $\beta$ -modification, m. p. about  $70^{\circ}$ , has been assumed to be the aldo-form, because it does not give a coloration with ferric chloride in dilute alcoholic solution. Against this view, however, is the fact that the  $\beta$ -modification is as easily soluble as the  $\alpha$  in alkali hydroxides, and both solutions behave alike on acidification. A dilute methyl-alcoholic solution of the  $\alpha$ -modification slowly, but almost entirely, loses its property of developing colour with ferric chloride, indicating the attainment of a state of equilibrium between the enolic and an aldo-modification. The same state is reached when the  $\beta$ -modification is kept in dilute methyl-alcoholic solution. The aldo-form in the solution, however, cannot be the  $\beta$ -modification, since the latter cannot be obtained directly from the solution either by evaporation or by precipitation with water. The true aldo-modification,  $\text{CHO}\cdot\text{CHPh}\cdot\text{CO}_2\text{Et}$ , of ethyl formylphenylacetate, therefore, has not been isolated; it exists only in dilute, alcoholic solution.

The  $\gamma$ -modification is obtained best by adding slowly a slightly alkaline 10% solution of the sodium derivative of ethyl formylphenylacetate to an excess of 25% sulphuric acid at  $0^{\circ}$ ; it has m. p.  $103\text{--}105^{\circ}$ , which is raised to about  $110^{\circ}$  after keeping for some time. It has previously been regarded as a geometrical isomeride of the  $\alpha$ -modification (*loc. cit.*). It is now shown to be the enol-aldo-form,  $\text{CHO}\cdot\text{CPh}\cdot\text{C}(\text{OH})\cdot\text{OEt}$ , since it can under suitable conditions develop a transient, pure blue coloration with ferric chloride, restores the colour of decolorised magenta solution, and contains, by optical evidence, an ethylenic linking. The two remaining solid forms, Michael's and the  $\beta$ -modifications, are simply mixtures of the  $\alpha$ - and the  $\gamma$ -modifications. This is proved as follows: It is known that the  $\alpha$ -modification changes almost completely into the  $\beta$  by keeping. When a solution of ethyl sodioformylphenylacetate is acidified, the m. p. of the solid obtained varies between  $50^{\circ}$  and  $105^{\circ}$  according to the concentration of the hydrogen ions; the greater the concentration, the higher is the m. p. of the solid. Mixtures of the liquid  $\alpha$ - and the solid  $\gamma$ -modifications yield solids of varying m. p. resembling the  $\beta$ - and Michael's modifications. Moreover, the lower is the m. p. of a solid mixture the greater is its solubility in petroleum, and the more intense is its colour reaction with ferric chloride. (The  $\alpha$ -modification is easily soluble in petroleum, whilst the  $\gamma$ -modification is almost insoluble.) The  $\alpha$ -modification when impure is unchanged by acids, but the quite pure substance is converted into solid mixtures of m. p. about  $70\text{--}75^{\circ}$ . Chloroform containing a little hydrogen chloride converts the solids of lower m. p. into the  $\gamma$ -modification; this in turn is converted slowly, but completely, into the  $\alpha$ -modification in indifferent solvents.

The colour of decolorised magenta solution is restored by all the solid modifications; the  $\alpha$ -modification does not do so except after long keeping (that is, after conversion into the  $\beta$ -form).

The metallic derivatives of ethyl formylphenylacetate are of the enol type. The copper derivative of the  $\beta$ -modification (Abstr., 1896, i, 552) is now shown to be the  $\alpha$ -copper derivative mixed with basic copper sulphate and the  $\beta$ - or  $\gamma$ -modification of the ester.

Whilst the enolic constituent of a desmotropic combination can be detected by ferric chloride, the aldo-form can be identified by decolorised magenta solution. Also copper acetate or silver acetate can be used to detect the existence of aldo-enol equilibrium. By shaking a benzene solution of ethyl formylphenylacetate with aqueous copper acetate, the benzene acquires an intense green colour or remains colourless according as the solution contains much or little of the enolic form. Again, by shaking a methyl-alcoholic solution of the ester covered with benzene with ammoniacal silver nitrate, the deposition of black silver occurs first in the benzene layer and subsequently in the alcoholic liquid. C. S.

**The Resolution of Racemic Cyanohydrins by means of an Optically Active Base.** MARIO BETTI and JAN VAN GIFFEN (*Gazzetta*, 1912, 42, i, 316—320).— $\beta$ -Hydroxynaphthylbenzylamine reacts with cyanohydrins, thus:  $C_{17}H_{15}ON + OH \cdot CHR \cdot CN = C_{17}H_{13}ON : CHR + H_2O + HCN$ , and it is suggested that racemic cyanohydrins may be resolved by using the *d*-base.

Anisylidenecyanohydrin combines with the *d*-base, yielding a crystalline compound,  $[\alpha]_D = +314^\circ$ . From the filtrate, a small quantity of levorotatory cyanohydrin is obtained, together with a larger quantity of the inactive compound. Methylsalicylidenecyanohydrin behaves similarly, yielding a crystalline compound,  $[\alpha]_D = +243^\circ$ , whilst only a small quantity of a levorotatory product, yielding an inactive acid on saponification, is obtained from the filtrate. *o*-Nitrobenzylidenecyanohydrin reacts with the base, forming an insoluble compound of unknown constitution. C. H. D.

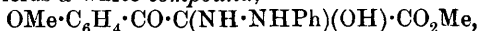
**Dimorphism and Crystalline Form of Diphenylmaleic Anhydride.** JULIEN DRUGMAN (*Zeitsch. Kryst. Min.*, 1912, 50, 576—581).—Two modifications of this substance are described. The  $\alpha$ -modification crystallises from acetone, etc., as large, pale greenish-yellow crystals with a slight bluish fluorescence, m. p.  $155^\circ$ ,  $D^{15} 1.340$ ;  $a:b:c = 0.5176:1:0.7024$ . The habit of the orthorhombic crystals varies widely according to whether they are grown from acetone or from toluene, whilst crystals grown from alcohol and from xylene are apparently hemimorphic. The  $\beta$ -modification crystallises, together with the  $\alpha$ -modification, from acetone or from toluene in the presence of water. It forms small, almost colourless, monoclinic crystals with a strong blue fluorescence, m. p.  $146^\circ$ ,  $D^{15} 1.345$ ;  $a:b:c = 2.561(5):1:2.327(5)$ ;  $\beta = 101^\circ 33'$ . The  $\beta$ -modification is a labile form; when heated, or when in contact with the  $\alpha$ -modification, it passes over into the latter. L. J. S.

***o*- and *p*-Methoxybenzoylglyoxylic Esters.** ANDRÉ WAHL and M. DOLL (*Compt. rend.*, 1912, 155, 49—51).—Ethylacetoacetate and its homologues are converted into  $\alpha\beta$ -diketonic esters by the action

of nitrous fumes. The authors are extending the reaction to the aromatic series.

Methyl *o*-methoxybenzoylacetate was not transformed into a diketonic ester by the above reaction, but yielded a white, crystalline compound, m. p. 141—142°, which was insoluble in the usual solvents, soluble in alkalis, but not reprecipitated by acids. Its analysis corresponds with methyl oximinomethoxybenzoylacetate, but it differs from it in its properties.

Methyl *p*-methoxybenzoylacetate when treated with nitrous fumes yields methyl anisoylgyoxylate,  $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CO} \cdot \text{CO} \cdot \text{CO}_2\text{Me}$ , an orange-yellow, mobile liquid, b. p. 185—192°/10 mm., which reduces Fehling's solution and silver nitrate. It is insoluble in water, but combines with it giving a hydrate, colourless needles, m. p. 109—110°. It gives additive products with a number of reagents, and with others condenses normally. With hydroxylamine it yields a monoxime, m. p. 153—154°, identical with methyl oximinoanisoylacetate (compare Wahl and Silberzweig, *Compt. rend.*, 1910, 150, 538). With phenylhydrazine it yields a white compound,



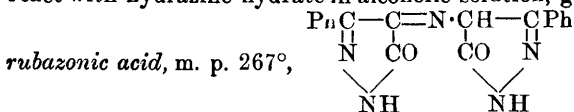
m. p. 193°, which on heating passes into the monophenylhydrazone, m. p. 121—122°, identical with methyl benzeneazoisoylacetate (*loc. cit.*), and phenylhydrazopyrazolone, m. p. 177°.

With *p*-nitrophenylhydrazine the product is either the *mono-p*-nitrophenylhydrazone, m. p. 175°, or *p*-nitrophenylhydrazopyrazolone, m. p. 340°, according to the temperature and proportion of the reagents used.

Hydrazine (1 mol.) in acetic acid solution gives a yellow, crystalline compound, m. p. 165°, and semicarbazide (1 mol.) gives a white, crystalline compound, m. p. 210°.

An anilide, m. p. 157—158°, and a toluidide, m. p. 152°, have been prepared from methyl anisoylgyoxylate. It condenses with *o*-phenylenediamine, giving a white, crystalline compound (annexed formula), m. p. 122°.

The authors have also prepared methyl, propyl, and isobutyl benzoylgyoxylates, which have respectively b. p. 146—149°/12 mm., 155—158°/12 mm., 161—164°/12 mm., and  $D_4^{20}$  1.233, 1.159, 1.124. They are all yellow, mobile liquids, and will be dealt with further in a later paper. They react with hydrazine hydrate in alcoholic solution, giving 3:3'-diphenyl-



rubazonic acid, m. p. 267°,

W. G.

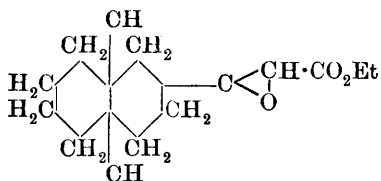
**Angeli-Rimini Reaction [of Aldehydes].** ANGELO ANGELI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 622—627).—The author replies to Balbiano's criticisms (this vol., i, 474) and gives the results of the application of the reaction to deoxybenzoin, piperylacetone, and benzyl methyl ketone.

Desoxylbenzoin yields benzhydroxamic acid, and piperylacetone, piperonalhydroxamic acid (compare Rimini, Abstr., 1901, i, 450).

With benzyl methyl ketone, a copper salt is obtained, which, on decomposition with dilute sulphuric acid, gives varying proportions of benzhydroxamic acid, acetylbenzylhydroxylamine, and a compound, m. p.  $232^{\circ}$ , containing sulphur and nitrogen. The second of these products is derived from acetylhydroxylamine isomeric with the hydroxamic acid which should be formed if the initial compound were an aldehyde instead of a ketone, and, like the hydroxamic acids, it is coloured red by ferric chloride; its copper salt is formed only when concentrated solution of acetylphenylhydroxylamine and copper acetate are employed, and, as only one hydrogen atom replaceable by metals is present, has the composition  $(C_9H_{10}O_2N)_2Cu$ .

This aldehyde reaction:  $(\alpha) R \cdot CHO + NH(OH)_2 = R \cdot C(OH) : NOH + H_2O$ , takes place in an alkaline medium, but excess of alkali may prevent the formation of hydroxamic acids. If the decomposition of dihydroxyammonia, according to the equation:  $(\beta) 2NH(OH)_2 = N_2O + 3H_2O$ , is more rapid than the reaction  $(\alpha)$ , the hydroxamic acids will be obtained in small amount or not at all. But it is found that the reaction  $(\alpha)$  may be activated by adding the calculated quantity of alkali in small portions and at wide intervals. If the concentrations of aldehyde and dihydroxyammonia (which is proportional to the alkali added) are indicated by  $C_a$  and  $C_b$ , the velocities of  $(\alpha)$  and  $(\beta)$  are given by  $dx/dt = K_1(C_a - x)(C_b - x)$  and  $dx/dt = K_2(C_b - x)^2$ , where  $K_1$  and  $K_2$  denote the respective velocity constants. The ratio of the velocities of  $(\alpha)$  and  $(\beta)$  will be  $K_1 \cdot C_a \cdot C_b / K_2 \cdot C_b^2$  or  $KC_a / C_b$ , and this can be made greater than unity either by increasing  $C_a$  or by diminishing  $C_b$ .  $C_a$  cannot, however, be greatly increased, since concentrated solutions are already used, whereas  $C_b$  can always be made as small as desired, and reaction  $(\beta)$  hence rendered negligible. This conclusion is found to be confirmed experimentally, and it is only by such an artifice that salicylaldehyde and *m*-hydroxybenzaldehyde can be transformed into the corresponding hydroxamic acids. T. H. P.

**Glycidic Esters of Decahydro- $\beta$ -naphthyl Ketone, Decahydro- $\beta$ -naphthaldehyde, and Methyldecahydro- $\beta$ -naphthyl Ketone.** GEORGES DARZENS and HENRI LEROUX (*Compt. rend.*, 1912, 154, 1812—1814. Compare Abstr., 1905, i, 116, 601).—Decahydro- $\beta$ -naphthyl ketone readily condenses with ethyl chloro-



acetate, giving the *glycidic ester* (annexed formula), a colourless, slightly viscous liquid, b. p.  $148-150^{\circ}/4$  mm. It is readily saponified to the *acid*, a very viscous liquid, which on distillation under reduced pressure is decomposed, giving *decahydro- $\beta$ -naphthaldehyde*, a colourless, mobile

liquid, b. p.  $95-96^{\circ}/3$  mm., which gives a *semicarbazone*, m. p.  $178-179^{\circ}$ .

Condensation of decahydro- $\beta$ -naphthyl ketone with ethyl chloro-

propionate yields *ethyl decahydro-β-naphthylmethylglycidate*, a colourless, mobile liquid, b. p. 155—156°/4 mm. On saponification, it yields the *acid*, crystallising in fine needles, m. p. 149—150°. This acid is much less readily decomposed than its lower homologue, but on distillation it yields *decahydro-β-naphthyl methyl ketone*, a mobile liquid with a camphor-like odour, b. p. 94—95°/3 mm., which gives a *semicarbazone*, m. p. 240—241°. W. G.

**A New Compound Occurring in Wood Vinegar (Methylcyclopentenolone).** JULIUS MEYERFELD (*Chem. Zeit.*, 1912, 36, 549—552).—Several alicyclic ketones are already known to exist in the products of distillation of wood.

*Methylcyclopentenolone*,  $C_6H_8O_2$ , is colourless, and has m. p. 106° and b. p. 210°, with slight decomposition. It crystallises well from organic solvents, and from hot water with  $H_2O$ . Its solution is slightly acid, and gives a violet coloration with ferric chloride. It reduces an alkaline solution of permanganate, yielding acetic and oxalic acids. It also reduces Fehling's solution and ammoniacal silver nitrate. It yields a monoacetyl derivative, and an osazone not containing oxygen, proving the presence of the group  $-CO\cdot CH(OH)-$ . On reduction, a mixture of the two 1-methylcyclopentanol, b. p. 146°, is obtained, whilst on removal of water a methylcyclopentene is obtained. The constitution has not been further determined, as six isomerides are possible.

The *osazone*,  $C_{18}H_{18}N_4$ , crystallises from alcohol, and has m. p. 140° (decomp.). The *acetyl* derivative forms colourless crystals, m. p. 65° and b. p. 129—130°/12 mm. The *phenylhydrazone* of the acetyl compound forms yellow needles, m. p. 170°. Hydroxylamine yields a *compound*,  $C_6H_{10}O_2N_2$ , probably containing the groups  $\cdot NH\cdot OH$  and  $\cdot NOH$ , as it forms a *diacetyl* derivative, m. p. 76°, exploding at 110°.

The ketone-alcohol forms metallic salts, of which the *zinc*,  $(C_6H_7O_2)_2Zn, H_2O$ , the *magnesium*,  $(C_6H_7O_2)_2Mg, H_2O$ , and *sodium*,  $C_6H_7O_2Na$ , salts have been analysed. C. H. D.

**Action of Hydrazine on Ethylenic β-Substituted Amino-ketones.** EMILE ANDRÉ (*Compt. rend.*, 1912, 155, 52—54).—Ethylenic β-substituted aminoketones of the types  $NR^{II}R^{III}\cdot CR\cdot CH\cdot COR^I$  and  $NHR^{II}\cdot CR\cdot CH\cdot COR^I$  readily condense with hydrazine with the elimination of the amines  $NHR^{II}R^{III}$  or  $NH_2R^{II}$  and the formation of 3:5-disubstituted pyrazoles, which are also obtained by the same reaction from the corresponding acetylenic ketones or the ethylenic β-alkoxy- or phenoxy-ketones (compare Moureu and Brachin, *Abstr.*, 1903, i, 581; 1904, i, 824). The author has applied the reaction to dipropylaminoacetylstyrene, diethylaminopropionylstyrolene, *cyclohexylaminobutylstyrene*, and diethylaminobenzoylstyrene.

W. G.

**Catalytic Hydrogenation of Benzylideneacetone [Styryl Methyl Ketone].** GUSTAVE VAVON (*Compt. rend.*, 1912, 154, 1705—1706).—Styryl methyl ketone, when dissolved in ether, is

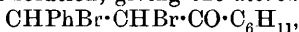
readily reduced by hydrogen in the presence of platinum-black. By stopping the action at the required stages, three successive products can be obtained (compare Abstr., 1911, i, 657, 730).

*α-Phenylbutan-γ-one*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{COMe}$ , the first product, is a colourless liquid, b. p.  $110\text{--}112^\circ/12\text{ mm.}$ ;  $D_4^{17}$  0.992;  $n_D^{17}$  1.514. It gives an *oxime*, fine needles, m. p.  $87^\circ$ . The next stage in the reduction gives *α-phenylbutan-γ-ol*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$ , a colourless liquid with a pleasant odour, b. p.  $115\text{--}116^\circ/12\text{ mm.}$ ;  $D_4^{17}$  0.976;  $n_D^{17}$  1.513. It forms an *acetate*, b. p.  $123\text{--}124^\circ/13\text{ mm.}$ ;  $D_4^{16}$  0.991;  $n_D^{16}$  1.489; and a *benzoate*, b. p.  $195^\circ/12\text{ mm.}$ ;  $D_4^{15}$  1.058;  $n_D^{15}$  1.545.

The complete reduction of styryl methyl ketone gives *α-cyclohexylbutan-γ-ol*,  $\text{C}_6\text{H}_{11}\cdot[\text{CH}_2]_2\cdot\text{CHMe}\cdot\text{OH}$ , a colourless liquid with an agreeable odour, b. p.  $112^\circ/14\text{ mm.}$ ;  $D_4^{17}$  0.905;  $n_D^{17}$  1.467. It yields an *acetate*, b. p.  $115\text{--}116^\circ/12\text{ mm.}$ ;  $D_4^{14}$  0.932;  $n_D^{14}$  1.450; and a *benzoate*, b. p.  $190^\circ/12\text{ mm.}$ ;  $D_4^{14}$  1.009;  $n_D^{14}$  1.512. W. G.

**Derivatives of Hexahydrobenzaldehyde.** JULES FRÉZOULS (*Compt. rend.*, 1912, 154, 1707—1708. Compare Abstr., 1910, i, 480).

—Hexahydrobenzaldehyde does not condense with acetic anhydride or potassium cyanide, but under their influence, polymerises. On mixing it with acetophenone in the presence of sodium methoxide, immediate condensation takes place, giving *phenyl hexahydrostyryl ketone*,  $\text{C}_6\text{H}_{11}\cdot\text{CH}\cdot\text{CH}\cdot\text{COPh}$ , colourless needles, m. p.  $167\text{--}168^\circ$ . By the condensation of benzaldehyde and hexahydroacetophenone, the isomeride *cyclohexyl styryl ketone*,  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_{11}$ , is obtained as large, colourless plates, m. p.  $58\text{--}59^\circ$ , which is readily acted upon by bromine in chloroform solution, giving the *dibromide*,

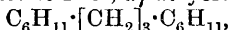


long needles, m. p.  $144\text{--}145^\circ$ .

The yield of both the ketones is very poor indeed. An attempt to condense hexahydrobenzaldehyde and hexahydroacetophenone only gave an oily product which would not crystallise. W. G.

**Catalytic Hydrogenation of Phenyl Styryl Ketone: Diphenylpropane and *syn*-Dicyclohexylpropane.** JULES FRÉZOULS (*Compt. rend.*, 1912, 155, 42—44. Compare previous abstract).—An endeavour to prepare hexahydrobenzylidenehexahydroacetophenone, which was, however, unsuccessful, the ketone group being reduced prior to this stage.

If the vapour of phenyl styryl ketone is passed with hydrogen over freshly reduced nickel at  $200^\circ$ , *α-dicyclohexylpropane*,



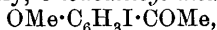
is produced as a colourless liquid, b. p.  $291\text{--}292^\circ$  (corr.);  $D_{21}^{24}$  0.8752;  $n_D^{24}$  1.4736. It solidifies at  $-30^\circ$  to fine needles, m. p.  $-17^\circ$ .

Under similar conditions, but using nickel that has already served for several days, the product is *α-diphenylpropane*,

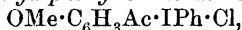


a colourless liquid, b. p.  $299\text{--}300^\circ$  (corr.);  $D_{19}^{19}$  0.9018;  $n_D^{19}$  1.5028 (compare Claus and Mercklin, Abstr., 1886, 143). W. G.

**Iodoketones and their Derivatives with Uni- and with Multi-valent Iodine.** CONRAD WILLGERODT and KARL BURKHARD (*Annalen*, 1912, **389**, 292—305).—*o*-Iodoanisole, acetyl chloride, and aluminium chloride react in carbon disulphide cooled by a freezing mixture to form, ultimately, *o*-iodoanisyl methyl ketone,



m. p. 103°, white needles. From this, *anisyl methyl ketone o*-iododichloride,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Ac}\cdot\text{ICl}_2$ , decomp. 128°, yellow leaflets, is obtained in the usual manner; the iodoso- and the iodoxy-compounds cannot be prepared. 5-Acetyl-2-methoxydiphenyliodinium chloride,



m. p. 198°, white leaflets, obtained by treating the preceding iododichloride and mercury diphenyl with water, yields an alkaline solution of the *iodinium hydroxide* with silver oxide and water, and the following salts by double decomposition: *bromide*, m. p. 190°; *iodide*, m. p. 169° (*periodide*,  $\text{C}_{15}\text{H}_{14}\text{O}_2\text{I}_4$ , m. p. 115°, garnet-red crystals); *dichromate*, decomp. 151°, yellow needles, and *platinichloride*, m. p. 161°.

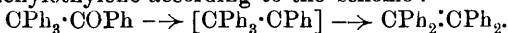
*o*-Iodoanisyl chloromethyl ketone,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{I}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , m. p. 134°, obtained by the action of chlorine on a not too strongly cooled solution of *o*-iodoanisyl methyl ketone in chloroform, yields *o*-iodo-*p*-anisic acid by oxidation with potassium permanganate, and the *iododichloride*,  $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{ICl}_2$ , yellow leaflets, by passing chlorine into its cooled solution in a little chloroform.

By methods similar to the preceding, *o*-iodophenetyl methyl ketone,  $\text{OEt}\cdot\text{C}_6\text{H}_3\text{I}\cdot\text{COMe}$ , m. p. 81°, and the following derivatives have been prepared: *phenetyl methyl ketone o*-iododichloride, decomp. 103°; 5-acetyl-2-ethoxydiphenyliodinium chloride, m. p. 192°, and the corresponding *platinichloride*, decomp. 172°; *bromide*, m. p. 191°; *iodide*, m. p. 164°; *periodide*, decomp. 125°, and *dichromate*, m. p. 157° (decomp.).

The reaction between *o*-iodoanisole and benzoyl chloride in cold carbon disulphide with aluminium chloride leads to the formation of 3-iodo-4-methoxybenzophenone,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{I}\cdot\text{COPh}$ , m. p. 80°, from which the following have been prepared: 4-methoxybenzophenone 3-iododichloride, decomp. 123°; 3-iodoso-4-methoxybenzophenone, decomp. 108° (*acetate*, decomp. 163°); 3-iodoxy-4-methoxybenzophenone, decomp. 190°, and 5-benzoyl-2-methoxydiphenyliodinium chloride,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{Bz}\cdot\text{IPh}\cdot\text{Cl}$ , m. p. 181°, and its corresponding *platinichloride*, decomp. 194°, *bromide*, m. p. 179°, *iodide*, m. p. 156°, and *dichromate*, decomp. 167°.

C. S.

**Action of Phosphorus Tribromide and Phosphorus on  $\beta$ -Benzopinacolin.** P. J. MONTAGNE (*Chem. Weekblad*, 1912, **9**, 468—470. Compare Stoermer, *Abstr.*, 1904, i, 181; Stoermer and Martinsen, *Abstr.*, 1907, i, 446).—Stoermer's work on the interaction of phosphorus tribromide and phosphorus with compounds containing the carbonyl group renders it probable that  $\beta$ -benzopinacolin would yield tetraphenylethylene according to the scheme:



At 200—210° there is no action; at 240—250°, triphenylmethane (m. p. 93·5°) is formed, the necessary hydrogen being derived from

decomposition of part of the molecule. A small proportion of anthracene is also formed.

A. J. W.

**Number of Isomerides of Merotropic and Desmotropic Compounds.** ARTHUR MICHAEL (*Annalen*, 1912, 390, 30—46).—Previously it has been shown (Abstr., 1906, i, 179) that the three forms of ethyl formylphenylacetate are enolic, the two forms of oxalacetic acid are ketonic, and that dibenzoylacetylmethane exists in one enolic and two ketonic modifications. Now it is shown (following abstracts) that dibenzoylpropionylmethane also exists in two ketonic modifications. Contrary to the expectation that these two forms would resemble closely the two ketonic forms of dibenzoylacetylmethane, it has been found that the presence of the propionyl in place of the acetyl group materially alters the ease of the keto-enolic transformation.

The existence of the preceding two dibenzoylacylmethanes, each in two ketonic modifications, is specially important in that it shows that the structures of such modifications cannot be those corresponding with racemic and with meso-configurations, as has previously been assumed in the case of alkyl diacylsuccinates and other substances which contain two equally asymmetric carbon atoms and exist in two ketonic modifications.

The cause of the preceding cases of isomerism undoubtedly is to be found in the spatial arrangement of the atoms in the molecule. A conception of stereochemical formulæ is given, based on the law of entropy and bearing special reference to the possible number of isomerides, as conditioned by the free and the bound chemical energies of the atoms.

Not only the structural formula, but also the stability, of an organic compound is determined by these factors. If it is assumed that the bound energy of two singly linked carbon atoms is insufficient to prevent rotation, then for a certain configuration the maximum entropy of the system will be attained, or, in other words, the free chemical energy of atoms which are not directly united will be as fully as possible transformed into bound energy and heat. When this favoured configuration has been attained, oscillatory motion may occur, but not free rotation, because this would necessitate a spontaneous transformation of bound into free chemical energy, that is, a degradation of the entropy. The fact that a saturated organic compound, which theoretically can exist in several different modifications, actually occurs only in one or in stereoisomeric forms, must depend on the change of entropy accompanying the conversion of one form into another. If the change is considerable, only one form is stable; if it is relatively small, several forms may exist; whilst if the change is small enough, the several forms are interconvertible by very feeble physical or chemical agencies.

C. S.

**Isomeric Ketonic Modifications of Dibenzoylacetylmethane.** ARTHUR MICHAEL (*Annalen*, 1912, 390, 46—48).—The known ketonic modification, the  $\beta$ -form, of dibenzoylacetylmethane, is converted by boiling for one-half to three-quarters of an hour with acetyl chloride into

x x 2

a new ketonic modification,  $\gamma$ -dibenzoylacetylmethane, m. p. 146—149°, which is unimolecular, does not develop a coloration with alcoholic ferric chloride except after some time, and can be crystallised only from acetyl chloride without undergoing a partial change into one of the other modifications. The m. p. depends largely on the duration of the heating, since the  $\gamma$ -form changes by heating into the  $\beta$ -ketonic and the enolic modifications.

Comparative experiments on the behaviour of the  $\beta$ - and the  $\gamma$ -modifications in various solvents, such as acetyl chloride, acetic anhydride, methyl iodide, carbon tetrachloride, ethylene dibromide, etc., show that usually the  $\gamma$ -form changes to the  $\beta$ -form, and that enolisation does not occur to any great extent, as a rule; in chloroform, however, the  $\gamma$ -modification is almost completely, the  $\beta$ -modification to the extent of one-third, changed to the enolic form. In benzene solution, in the presence of 1% aqueous sodium carbonate, the  $\beta$ -form is enolised thrice as rapidly as the  $\gamma$ -form. C. S.

**Isomeric Ketonic Modifications of Dibenzoylpropionylmethane.** ARTHUR MICHAEL and HAROLD HIBBERT (*Annalen*, 1912, 390, 68—88).—The reaction between benzoylpropionylmethane and anhydrous sodium carbonate and benzoyl chloride in ether in the presence of two to three drops of water leads to the formation of the enolic modification of dibenzoylpropionylmethane,  $C_{18}H_{16}O_3$ , a heavy, viscous liquid, which develops a deep red coloration with alcoholic ferric chloride, easily changes to the  $\beta$ -ketonic modification, and dissolves readily and completely in aqueous sodium carbonate. The ketonisation of the enolic modification is greatly retarded by certain solvents, particularly chloroform.

The  $\beta$ -ketonic modification, m. p. 122—123°, is obtained by keeping the liquid form for five days and washing the resulting solid with petroleum to remove traces of the unchanged enolic modification. It crystallises unchanged, in prisms or needles, from glacial acetic acid, but is enolised by other solvents. It dissolves slowly in aqueous sodium carbonate, and develops a coloration with ferric chloride only after about thirty seconds, both reactions being preceded by enolisation. Unlike  $\beta$ -dibenzoylacetylmethane,  $\beta$ -dibenzoylpropionylmethane is enolised by acetyl chloride, not converted directly into the  $\gamma$ -ketonic modification. However, it crystallises from hot 50% alcohol as a mixture, m. p. 125—133°, which, after being heated at 100—102° for two to three hours, is converted by boiling acetyl chloride into the  $\gamma$ -ketonic form, m. p. 151—153°.  $\gamma$ -Dibenzoylpropionylmethane, like the  $\beta$ -form, is unimolecular, and behaves in a similar manner towards aqueous sodium carbonate and towards alcoholic ferric chloride. In most solvents it changes to the  $\beta$ -form or to a mixture of the  $\beta$ - and the  $\gamma$ -forms; from glacial acetic acid, dichloroethylene, or chloroform, however, it can be recovered almost unchanged.

The  $\beta$ - and the  $\gamma$ -forms behave alike towards fatty tertiary amines (compare Michael and Smith, *Abstr.*, 1908, i, 943). C. S.

**Constitution of Natural Chrysazin Derivatives.** OTTO A. OESTERLE (*Arch. Pharm.*, 1912 250, 301—306).—Chrysophanic acid,

aloe-emodin, and rhein are anthraquinone derivatives, each containing a side-chain in the  $\beta$ -position, but whether this position is 2 or 3 is still an open question. Fischer, Falco, and Gross regard the side-chains are being in position 3 (Abstr., 1911, i, 309). The author at one time believed them to be in position 2, but since rhein is converted through its amide and amine into a trihydroxyanthraquinone which is not identical with 1:2:8-trihydroxyanthraquinone, he is now of opinion that the carboxyl group in rhein occupies position 3 and consequently the side-chains in chrysophanic acid and in aloe-emodin also occupy the same position.

The 1:3:8-trihydroxyanthraquinone obtained from rhein has m. p. 277—278°, forms an acetate, m. p. 197—198°, dissolves in dilute alkalis with a violet-red colour, and develops an orange coloration in concentrated sulphuric acid.

C. S.

**Oxidation of Unsaturated Compounds with Organic Peroxides.** III. **Oxidation of Derivatives of Unsaturated Compounds with Two Double Linkings.** NIKOLAUS PRIELESCHAEFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 613—647. Compare Abstr., 1911, i, 604).—The present paper deals with the oxidation, by means of benzoylhydroperoxide, of compounds containing two double linkings. In these cases the reaction proceeds in the normal way, and, in dependence on the proportion of active oxygen employed, either one or both of the double linkings may be oxidised, the less hydrogenated of the two linkings being oxidised first.

The velocity of the reaction and the properties of the oxide obtained depend, not only on the distribution of the oxygen groups with reference to the double linkings, but also on their character—whether aldehydic, alcoholic, etc. In the case of unsaturated alcohols, if the oxygen ring is in the  $\alpha\beta$ -position as regards the hydroxyl group, it exhibits considerable stability and inertness, being incapable of hydration. In compounds containing either an esterified alcohol group, such as acetyl-linalool, or a carboxyl group, oxidation of an  $\alpha\beta$ -double linking is so slow that it may be regarded as virtually absent. When aldehydes and ketones with conjugated systems of double linkings are oxidised, the oxide formed is so unstable that it undergoes decomposition with formation of an aldehyde with a carbon atom chain containing one less member than that of the original compound. With ketoxides, the decomposition occurs at the double linking and yields two aldehyde molecules.

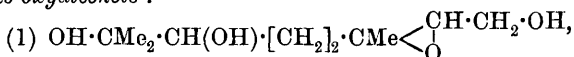
*Geraniol monoxide*,  $\text{CMe}_2 \begin{array}{c} \diagup \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{OH} \\ \diagdown \text{O} \end{array}$ , ob-

tained by employing 1 atom of active oxygen per mol. of the alcohol, is a colourless, viscous liquid, b. p. 157—158°/25 mm.,  $D_4^{16}$  0.9716,  $D_{16}^{16}$  0.9610  $n_D^{16}$  1.4681. In presence of traces of acid, it combines energetically with water, giving the *trihydric alcohol*,  $\text{C}_{10}\text{H}_{17}(\text{OH})_3$ , which is a faintly yellow, viscous liquid, b. p. 204—206°/19 mm.,  $D_4^{16}$  1.0606,  $D_{16}^{16}$  1.0486,  $n_D^{16}$  1.4935, and yields a *triacetyl* derivative,  $\text{C}_{10}\text{H}_{17}\text{O}_3\text{Ac}_3$ , b. p. 208°/25 mm.,  $D_4^{16}$  1.0756,  $D_{16}^{16}$  1.0619 (compare Markownikoff and Reformatsky, Abstr., 1893, i, 662; Wagner, *Proc. Warsaw Soc. Nat.*, 1896). The oxidation of one ethylene linking of

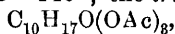
geraniol by the hydroperoxide is accompanied by attack of the hydroxyl group, a small proportion being obtained of a compound, b. p. 119—120°/25 mm., having aldehydic properties; the products of the reaction contain also a higher fraction, consisting of a mixture of the dioxide (see below) with condensation products.

*Geraniol dioxide*,  $\text{CMe}_2 \begin{array}{c} \diagup \\ \text{O} \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe} \begin{array}{c} \diagdown \\ \text{O} \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{OH}$ , ob-

tained by employing 2 atoms of active oxygen per mol. of geraniol, is a colourless, mobile liquid, b. p. 180—183°/25 mm.,  $D_0^{16}$  1.0587,  $D_{16}^{16}$  1.0472,  $n_D^{16}$  1.4653, and on hydration gives two isomeric, crystalline *trihydric oxyalcohols*:



monoclinic prisms, m. p. 145—146°; the *triacetyl* derivative,



is a colourless, viscous liquid, b. p. 189.5—190°/14 mm.,  $D_0^{16}$  1.1396,  $D_{16}^{16}$  1.1253; (2) m. p. 163—164°. These two isomerides are optically inactive and are hence derived from the limonene and terpinolene forms of geraniol; they are accompanied by an isomeric liquid product, which is probably a mixture of the two crystalline compounds, but no pentahydric alcohol could be isolated (compare Wagner, *loc. cit.*).

*Linalool monoxide*,  $\text{CMe}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe}(\text{OH}) \cdot \text{CH} \begin{array}{c} \diagdown \\ \text{O} \end{array} \text{CH}_2$ , is a

colourless, mobile liquid, b. p. 197—198°/758 mm.,  $D_0^{16}$  0.9660,  $D_{16}^{16}$  0.9520,  $n_D^{16}$  1.45567,  $[\alpha]_D -5^\circ$ , and forms an *acetyl* derivative,  $\text{C}_{10}\text{H}_{17}\text{O}_2\text{Ac}$ , b. p. 118—119°/25 mm.,  $D_0^{16}$  0.9901,  $D_{16}^{16}$  0.9770,  $n_D^{16}$  1.44972,  $[\alpha]_D -4.83^\circ$ , which does not undergo hydration in presence of acid. Attempts to hydrate the monoxide were unsuccessful, the reaction being accompanied by condensation and, apparently, dehydration; the resulting product is an *aldehyde*,  $\text{C}_{10}\text{H}_{16}$ (<sup>1</sup>), b. p. 120—122°/25 mm.,  $D_0^{16}$  0.8706,  $D_{16}^{16}$  0.8576,  $n_D^{16}$  1.5038.

*Linalool dioxide*,  $\text{CMe}_2 \begin{array}{c} \diagup \\ \text{O} \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe}(\text{OH}) \cdot \text{CH} \begin{array}{c} \diagdown \\ \text{O} \end{array} \text{CH}_2$ , is a

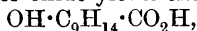
colourless liquid, b. p. 131—133°/25 mm.,  $D_0^{16}$  1.0552,  $D_{16}^{16}$  1.0440,  $n_D^{16}$  1.46170,  $[\alpha]_D +5.3^\circ$ . On hydration it yields the *trihydric oxyalcohol*,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe}(\text{OH}) \cdot \text{CH} \begin{array}{c} \diagdown \\ \text{O} \end{array} \text{CH}_2$ , as a viscous liquid, b. p. 207—212°/26 mm.; with acetic anhydride, this compound yields the *tetra-acetyl* derivative,  $\text{C}_{10}\text{H}_{17}(\text{OH})(\text{OAc})_4$ , b. p. 207—209°/20 mm.,  $D_0^{16}$  1.1249,  $D_{16}^{16}$  1.1114,  $n_D^{16}$  1.4531.

*Acetyl-linalool monoxide*,  $\text{CMe}_2 \begin{array}{c} \diagup \\ \text{O} \end{array} \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe}(\text{OAc}) \cdot \text{CH} \cdot \text{CH}_2$ ,

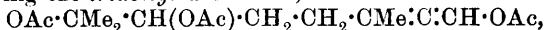
is a colourless, mobile liquid, b. p. 138—139°/25 mm.,  $D_0^{16}$  0.9879,  $D_{16}^{16}$  0.9742,  $n_D^{16}$  1.44847,  $[\alpha]_D -2.58^\circ$ . On hydration, it gives a mixture of the *trihydric alcohol*,  $\text{C}_{10}\text{H}_{17}(\text{OH})_3$ , and its monoacetyl derivative,  $\text{C}_{10}\text{H}_{17}(\text{OH})_2 \cdot \text{OAc}$ ; the latter could not be isolated, but the former is a colourless, viscous liquid, b. p. 177—180°/15 mm., which gradually deposits crystals, m. p. 54—55°.

Acetyl-linalool dioxide could not be obtained, benzoylhydroperoxide oxidising the double linking in the  $\alpha\beta$ -position to the acetyl group only with great difficulty.

*Citral monooxide*,  $\begin{array}{c} \text{CMe}_2 \\ | \\ \text{O} \end{array} \text{---} \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CH} \cdot \text{CHO}$ , is a mobile liquid which rapidly turns yellow in the air, b. p. 144.5—145.5°/20 mm.,  $D_4^{16}$  0.9679,  $n_D^{16}$  1.47848; it gives all the reactions of aldehydes, its oxime and semicarbazone being non-crystalline. With water it gives the *glycol*,  $\text{OH} \cdot \text{CMe}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CMe} \cdot \text{CH} \cdot \text{CHO}$ , which is a mobile liquid, b. p. 141—142°/24 mm.,  $D_0^0$  1.0584,  $D_{16}^{16}$  1.0335, and forms a non-crystalline oxime and semicarbazone. Oxidation of the glycol with moist silver oxide yields the unsaturated *acid*,

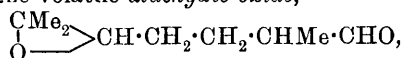


b. p. 176—180°/19 mm., which could not be obtained quite pure. When heated in a sealed tube with active anhydride, the glycol reacts in the enolic form (compare Semmler and Schossberger, Abstr., 1911, i, 475), giving the *triacetyl* derivative,



b. p. 205—207°/15 mm.

In the preparation of citral dioxide, the latter decomposes, yielding formic acid and the volatile *aldehydic oxide*,



b. p. 114—115°/25 mm.,  $D_0^0$  0.9724,  $D_4^{16}$  0.9419,  $n_D^{16}$  1.43728, which gives a non-crystalline oxime and semicarbazone. This compound is readily hydrated to the *aldehydic glycol*,  $\text{C}_9\text{H}_{16}\text{O}(\text{OH})_2$ , b. p. 161—162°/25 mm.,  $D_0^0$  1.0690,  $D_{16}^{16}$  1.0573,  $n_D^{16}$  1.4710.

*Benzylideneacetone oxide*,  $\begin{array}{c} \text{CHPh} \\ | \\ \text{O} \end{array} \text{---} \text{CHAc}$ , is a mobile, golden-yellow liquid, b. p. 123—125°/11 mm.,  $D_0^0$  1.0835,  $D_{16}^{16}$  1.0694, which, in presence of water, undergoes gradual decomposition into benzaldehyde and probably methylglyoxal; the same decomposition occurs on keeping or distilling the oxide.

With increase of the number of oxygen atoms united to the carbon in the  $\alpha\beta$ -position with respect to the double linking, oxidation by means of benzoylhydroperoxide no longer occurs. Attempts to oxidise cinnamic acid in this way were unsuccessful. T. H. P.

**The Isomeric Tanacetyl Alcohols.** VINCENZO PAOLINI and BIANCA DIVIZIA (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 570—574).—It has been shown (Paolini, Abstr., 1911, i, 730) that tanacetyl alcohol (thujol) is a mixture of two isomerides. A dextrorotatory tanacetone, distinct from  $\beta$ -tanacetone, has now been isolated from thuja oil, and yields on reduction a mixture of alcohols quite similar to the ordinary tanacetyl alcohol, in which  $\beta$ -thujyl alcohol predominates. Similarly, a mixture has been isolated from the products of reduction of oil of absinthe, the fraction of b. p. 208—210° being used. From this, a phthalate with  $[\alpha]_D + 2^\circ 28'$  and m. p. 95—96° has been obtained, yielding on hydrolysis the alcohol, with  $[\alpha]_D + 50^\circ 01'$ . It is proposed

to term this alcohol *δ-thujyl alcohol*, reserving  $\gamma$  for the alcohol accompanying it in oil of absinthe. C. H. D.

**The Density of Camphor as Deduced from the Densities of its Solutions in Different Solvents.** H. MALOSSE (*Compt. rend.*, 1912, 154, 1697—1698).—The densities at 20° of solutions of camphor in the following solvents have been determined: 99% alcohol, 90% alcohol, acetone, methyl alcohol, benzene, ethyl acetate, olive oil, dimethylaniline, acetic acid, and carbon tetrachloride; the concentrations of the solutions varied from 10 to 60 grams of camphor per 100 grams of solution. Graphs of the results were then drawn, and extrapolated to a solution containing 100 grams of camphor, that is, pure camphor. The mean density thus obtained is 0.963, the greatest deviations from the mean being  $\pm 0.002$ . T. S. P.

**Essential Oils. IV. Essence of Mespilodaphne pretiosa.** GUSTAVE LALOUÉ (*Bull. Soc. chim.*, 1912, [iv], 11, 602—606. Compare Abstr., 1911, i, 138).—The author has studied the essential oils obtainable from the branches and wood of the *Mespilodaphne pretiosa*, belonging to the Lauracea family. The branches on distillation with steam yield 0.5% of a very mobile, pale yellow oil,  $D_4^{15}$  0.8912;  $a_D$  7°20';  $n_D^{20}$  1.469; acid number, 1.4; acetyl number, 165.2. It has a smell closely resembling that of linalool, and is chiefly composed of that alcohol. The wood on similar treatment yields a mixture of a light and a heavy oil, the total yield being 0.69%. The lighter oil, which constitutes five-sevenths of the mixture, is greenish-yellow, with an odour of rosewood. Its constants are:  $D_4^{15}$  0.9539;  $a_D$  +8°48';  $n_D^{20}$  1.501; acid number, 0.7; saponification number, 100.8; acetyl number, 205.1. The heavy fraction is a light brown oil with an odour of cinnamon,  $D_4^{15}$  1.0551;  $a_D$  +3°8';  $n_D^{20}$  1.545; acid number, 3.5; saponification number, 203.7; acetyl number, 247.8. It consists, for the greater part, of a benzoate, which is probably that of linalool or geraniol. W. G.

**Constituents of Oil of Savin.** J. WATSON AGNEW and ROBIN B. CROAD (*Analyst*, 1912 37, 295—298).—The oil was first hydrolysed with potassium hydroxide, then distilled with steam, and the distillate, after being dried over anhydrous sodium sulphate, submitted to fractional distillation. The following yields were obtained: First runnings (pinene), b. p. 150—160°, 1.7%; sabinene, b. p. 162—166°, 16.0%; terpinene fraction, b. p. 175—185°, 5.3%; sabinol, b. p. 208—209°, 17.0%; residue, b. p. above 210°, 16.0%; resin from steam-distillation, 31.0%; acids (acetic, formic, and another acid, m. p. 85°), 7.0%. Certain samples examined yielded large quantities of pinene, and had evidently been mixed with oil of turpentine. W. P. S.

**Production and Polymerisation of Butadiene, Isoprene, and their Homologues.** WILLIAM H. PERKIN (*J. Soc. Chem. Ind.*, 1912, 31, 616—624).—Despite frequently recurring statements to the contrary, there can now be no doubt that caoutchouc may actually be obtained synthetically by the polymerisation of isoprene and its homologues, and that the synthetic product is really caoutchouc and strictly comparable with natural caoutchoucs.

The raw material for the synthetic production of caoutchouc must be available in large quantities, and the only materials fulfilling the necessary conditions seem to be wood, starch, sugar, petroleum, and coal.

Much work has been done on the halogenation of hydrocarbons, such as pentane and isopentane and the elimination of halogen hydride from the products, and the conversion of lactic acid into dimethylallene and isoprene by a somewhat complicated process has been investigated, but the important method whereby isoprene may be obtained readily and in quantity requires *isoamyl* alcohol as the initial material. *isoAmyl* chloride, obtained by the action of hydrogen chloride on the fraction, b. p. 128—131°, of commercial fusel oil, is chlorinated in the vaporous state in sunlight or the light of a mercury lamp, in a specially constructed apparatus, whereby the formation of more highly halogenated substances than dichlorides is prevented. The chlorinated product can be separated by careful fractionation into  $\gamma\delta$ -dichloro- $\beta$ -methylbutane, b. p. 142°,  $\beta\delta$ -dichloro- $\beta$ -methylbutane, b. p. 152—155°, and  $\alpha\delta$ -dichloro- $\beta$ -methylbutane, b. p. 170—172°, the constitution of the last being proved by its conversion ultimately into  $\beta$ -methyladipic acid. All three dichlorides yield isoprene when passed over hot soda-lime, so that in the preparation of the hydrocarbon the fraction, b. p. 140—180°, of the chlorinated products is passed directly over soda-lime in an iron tube at about 470°; the yield of isoprene is about 40% of that theoretically possible.

The polymerisation of isoprene to caoutchouc is effected by Matthews' sodium process, which has the important advantages over other methods that it is practically quantitative, can be performed in the cold or at a very moderate heat, and is not seriously affected by the presence of impurities, such as  $\beta$ -methyl- $\Delta^2$ -butylene or other hydrocarbons which are not capable of polymerisation to caoutchouc. The isoprene is sealed up with about 3% of thin sodium wire, and is heated at about 60° for several days; the dark brown product may be treated with acetone, and the precipitated caoutchouc may be washed with alcohol or heated with steam to remove acetone and any unpolymerised hydrocarbon.

There is every reason to believe that this process may be developed into an actual process for the manufacture of rubber provided that some cheap means of obtaining fusel oil in quantity is discovered.

Reference is made to Fernbach's fermentative processes, whereby starch is converted into acetone, on the one hand, and fusel oil on the other. The fusel oil thus produced contains a high percentage of butyl alcohol. Since Harries has shown that the rubber obtained by the polymerisation of  $\Delta^{\alpha\gamma}$ -butadiene is of better quality than that obtained from isoprene (Abstr., 1911, i, 798), butyl alcohol has been converted into butyl chloride, and this, by chlorination in the apparatus previously mentioned, into a mixture of  $\alpha\beta$ -,  $\alpha\gamma$ -, and  $\alpha\delta$ -dichlorobutanes. All of these yield  $\Delta^{\alpha\gamma}$ -butadiene when passed over hot soda-lime.

$\alpha\gamma$ -Dichlorobutane has also been obtained by the following method. Acetaldehyde is converted by very dilute potassium carbonate into aldol, which is then reduced, electrolytically or by neutral reducing

agents, to  $\alpha\gamma$ -butylene glycol; the latter is converted by hydrochloric acid into  $\alpha\gamma$ -dichlorobutane, from which the butadiene is produced by the soda-lime method. The butadiene is polymerised to butadiene rubber by the sodium process. The author does not go so far as to say that synthetic rubber is identical with natural caoutchouc, but states that it is comparable with ordinary caoutchouc in that it can be vulcanised and answers all the other tests to which caoutchouc must be put by the manufacturer. C. S.

**Chemistry of Caoutchouc.** IV. DAVID SPENCE (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 299—306).—The effect of temperature on the vulcanisation of caoutchouc has been investigated. Practically no vulcanisation takes place in good specimens heated to 40°; the change is not appreciably accelerated on exposure to sunlight. On the other hand, partly decomposed caoutchouc undergoes considerable vulcanisation under the same conditions. Even at temperatures just below 60°, vulcanisation is very slow; above that temperature it is much more rapid. The widely accepted view that it is impossible to vulcanise caoutchouc so that all the free sulphur disappears is erroneous. G. S.

**Occurrence and Method of Formation of Resin-Acids.** II. JOHN KÖHLER (*J. pr. Chem.*, 1912, 85, [ii], 523—534. Compare Abstr., 1906, i, 100).—It has been shown previously that a white, crystalline resin, consisting essentially of sapinic acids, is occasionally found in winter under the bark of Swedish pines and firs. This particular variety of resin (winter-resin) is also met with during other seasons, but then invariably contains turpentine. The more frequent occurrence of this resin in winter is referred to the sensitiveness of the sapinic acids towards heat and atmospheric oxygen.

Whilst making observations on the occurrence of winter-resin in the neighbourhood of Wengen in the Bernese Oberland, the author came across two instances in which the winter-resin (of red firs) was associated with a pale yellow liquid, which is considered to be the parent substance of the resin acids.

The liquid is acid in character and rapidly becomes partly crystalline, owing to transformation into resin acids, but whether this change is due to atmospheric oxidation could not be determined. From experiments on the molecular weight of the liquid in glacial acetic acid before and after transformation, and allowing for the resin acids and turpentine present in the liquid, the molecular weight of the substance is estimated at 154.

The author inclines to the view that the parent substance consists of an aldehyde or camphor-like compound,  $C_{10}H_{16}O$ , from which the resin acids are formed by oxidation as follows:  $2C_9H_{15}\cdot CHO + O = C_{19}H_{29}\cdot CO_2H + H_2O$ .

The crystalline resin associated with the above-mentioned liquid contained in one instance 25% of *l*-pimaric acid, whilst the crystalline substance deposited from the liquid itself consisted almost entirely of sapinic acids. In the other case the resin was composed of almost pure *l*-pimaric acid. F. B.

**Chemical Examination of Pine-resin (from *Picea excelsa*).**  
 III. JOHN KÖHLER (*J. pr. Chem.*, 1912, 85, [ii], 534—564).—The author finds that *l*-pimaric acid, which, hitherto, has been isolated only in an impure condition from galipot, is a common constituent of the resin of the red fir (*Picea excelsa*).

It is occasionally found in fairly well-developed crystals in the winter-resin obtained from the upper portion of the stem, but is generally accompanied by more readily soluble acids (probably sapinic acids) of a less rotatory power. It has the formula  $C_{20}H_{30}O_2$  and  $[\alpha]_D^{20} - 280.5^\circ$ . The m. p. is indefinite ( $134-152^\circ$ ), owing to partial transformation into colophonic acids.

When heated, it yields a mixture of *l*-colophonic acids, identical with the  $\alpha$ -colophonic acids obtained from sapinic acid, together with *i*-colophonic acid.

The active colophonic acids crystallise in the monoclinic system, and cannot be separated by fractional crystallisation.

*i*-Colophonic acid crystallises in prisms belonging to the rhombic system:  $[a : b : c = 0.47698 : 1 : c]$ .

The colophonic acids are distinguished from the naturally occurring resin acids in that they gelatinise when dissolved in alcohol and dilute aqueous ammonia and the resulting solution diluted with water.

F. B.

**Resins Employed in Embalming in Egypt and Carthage during the First Millenium B.C.** ALEXANDER TSCHIRCH and LOUIS REUTTER (*Arch. Pharm.*, 1912, 250, 170—185).—Copious references to the literature of the processes of embalming and the materials used by the ancients are given. Previous investigators have examined the materials employed by their appearance, odour, volatility, solubility, etc., but their deductions are untrustworthy, because, owing to the fact that the ancients frequently employed mixtures of resinous materials, the only certain method of examination is to isolate and analyse individual chemical substances.

Using this process, the authors have examined the resins obtained from embalmed Egyptian mummies, and have recognised storax (probably *Storax officinalis* or *Liquidambar orientalis*) by the isolation of cinnamic and benzoic acids, vanillin, and gum mastic by the isolation of  $\beta$ -masticic acid,  $\beta$ -masticonic acid, and resen, and Aleppo resin by the isolation of alepopinic acid, and asphalt, although the presence of the last cannot be proved definitely. Natron and sugar have also been identified, the latter probably being derived from the wine in which the corpses have been washed.

The same substances have been found in the materials used for embalming in Carthage. In addition, sandarac has also been (somewhat doubtfully) identified. One substance found in the embalming materials of Carthaginian, but never of Egyptian, mummies is incense. Amber has been found in the embalming material of a Phœnician mummy. The authors note with interest that the m. p.'s of the cinnamic acid, benzoic acid, and vanillin, and the rotatory and reducing powers of the sugar are the same as at the present time, although some of these substances are 3000 years old.

C. S.

[The Glucoside of *Aralia japonica*.] LUCIEN DANZEL (*J. Pharm. Chim.*, 1912, [vii], 5, 530—534. Compare Houdas, Abstr., 1899, i, 772).—The leaves of *Aralia japonica* on extraction with alcohol and precipitation with water yield a glucoside *aralin*, which, after extraction with ether and several crystallisations from alcohol, is obtained in colourless, transparent crystals, m. p.  $260^{\circ}$ ,  $[\alpha]_D^{20} + 52.5^{\circ}$ . It is insoluble in water, contains no nitrogen, and is unacted on by nitric or hydrochloric acids. It does not reduce Fehling's solution. It is hydrolysed by dilute sulphuric acid, yielding dextrose and *aralidin*, a white, crystalline solid, m. p.  $246-248^{\circ}$ , insoluble in water and having an acid reaction to bases. It has no action on Fehling's solution.

W. G.

Distribution of Amygdalin. LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1912, 250, 298—301).—In order to ascertain whether amygdalins from different sources are stereoisomeric, the author has determined the m. p., specific rotation, molecular weight, percentage of nitrogen, and rotation of the mandelic acid obtained after hydrolysis, of the amygdalins obtained from the kernels of the apricot, peach, plum, cherry, and from the apple and the quince. The results show that all these amygdalins are identical with that from the bitter almond.

C. S.

The Glucosidic Acids of Convolvulin and the Composition of Crude *iso*Rhodeose. EMIL VOTOČEK (*Zeitsch. Zuckerind. Böhm.*, 1912, 36, 577—584).—Rhamnose has been identified among the products of acid hydrolysis of convolvulinic acid. Convolvulin on alkaline hydrolysis yields  $\alpha$ -methylbutyric acid and two glucosidic acids, crystalline convolvulinic acid and amorphous purgic acid. The former yields dextrose, rhodose, and rhamnose and hydroxypentadecic acid on hydrolysis; the latter gives rise to decic acid, hydroxylauric acid, and syrupy *isorhodeose*.

The hydrogen cyanide addition product of *isorhodeose* when oxidised with nitric acid does not form mucic acid.

E. F. A.

Saponin of the White Soapwort. II. LEOPOLD ROSENTHALER and KNUT T. STRÖM (*Arch. Pharm.*, 1912, 250, 290—297. Compare Abstr., 1906, i, 32).—When heated with dilute sulphuric acid, gypsophila-saponin yields, in addition to sugars, a substance which ordinarily is called sapogenin; the authors, however, prefer the name *prosapogenin*. It has m. p.  $207^{\circ}$  (decomp.), crystallises in needles or prisms, has  $[\alpha]_D^{18} + 11.92^{\circ}$ , forms a *semicarbazone*, m. p.  $241^{\circ}$ , and is converted by 2% sulphuric acid under pressure into *sapogenin*,  $C_{24}H_{34}O_5$ , m. p.  $267-268^{\circ}$ , crystalline rosettes. Sapogenin has  $[\alpha]_D^{18} + 90.86^{\circ}$ , is a monobasic acid, forms a *methyl ester*, m. p.  $192^{\circ}$ , *diacetyl derivative*, m. p.  $164-165^{\circ}$ , and *semicarbazone*, m. p.  $259-260^{\circ}$  (decomp.), and yields, by oxidation with alkaline potassium permanganate at  $60-70^{\circ}$ , *as*-dimethylsuccinic acid and a small quantity of a volatile (fatty?) acid.

C. S.

**Preparation of Chlorophyll.** VLADIMIR STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1912, 36, 574—576).—Ether does not extract chlorophyll from undamaged leaves, but from finely divided leaves the chlorophyll is extracted completely without difficulty.

Fresh leaves full of sap may be deprived of 70% of this by exposure for a short time in a tall, closed vessel to ether vapour. When pressed, without cutting up the leaves, the sap is removed as a brown fluid, the chlorophyll remaining in the residue.

Very little lecithin is extracted by ether in this way, whereas extraction with alcohol and shaking of this extract with benzene causes a good deal of lecithin to accompany the chlorophyll.

E. F. A.

**The Chlorophyll Group. XVI. Anhydro- $\beta$ -phyllotaonin** HENRYK MALARSKI and LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1912 42, 219—234).—According to Kózniewski and Marchlewski, the product obtained by the action of hydrochloric acid on alkachlorophyll, which was discovered by Schunck and called phyllotaonin, is a mixture containing an anhydride of lactam character which cannot be extracted from its ethereal solution by 15% hydrochloric acid, and a corresponding hydrated derivative which can be extracted by 4% hydrochloric acid. On these differences of properties, a method of separation of the two substances is founded. The lactam can be converted into the hydrated derivative by treatment with sodium hydroxide, and this substance on heating in solution can be reconverted into the anhydride. This anhydride is designated anhydro- $\beta$ -phyllotaonin, and the authors give an account of their experiments for obtaining this substance pure. The chief operations are as follows: The chlorophyll is treated with 2% alcoholic potassium hydroxide. From the filtered clear solution the alkaneo-chlorophyll is precipitated by barium or calcium chloride. The precipitate, after extraction with ether, is treated with concentrated hydrochloric acid, in which it almost entirely dissolves. The filtered solution in acid is then diluted with water and neutralised with sodium carbonate, and the precipitate after drying is dissolved in chloroform. The chloroform solution is diluted with a large amount of ether; the solution thus obtained is extracted with 15% hydrochloric acid, and then with concentrated acid. The latter solution is then diluted with water and immediately extracted with ether. The residue from the last extract is then recrystallised from alcohol. The spectrum of the anhydrophyllotaonin is described in some detail, and a preliminary account is given of some of its chemical reactions.

S. B. S.

**Tannin.** JOSEF HERZIG (*Ber.*, 1912, 45, 1986).—The fact that dextrose was not obtained by Herzig and Renner (*Abstr.*, 1909, i, 713) on hydrolysis of methylotannin with potassium hydroxide is not regarded as contrary to the possibility that tannin is a glucoside (compare Manning and Nierenstein, this vol., i, 566).

E. F. A.

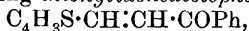
**Transformations of Thiophen-2-aldehyde.** E. GRISHKEWITSCH-TROCHIMOWSKY and IPPOLYT MATSCHUREVITSCH (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 570—581. Compare *Abstr.*, 1911, i, 481).—Thiophen-

2-aldehyde readily forms a *sodium hydrogen sulphite* compound,  $C_4H_3S \cdot CH(OH) \cdot O \cdot SO_3Na$ .

The *semicarbazone*,  $C_4H_3S \cdot CH:N \cdot NH \cdot CO \cdot NH_2$ , forms white, silvery scales, m. p.  $213^\circ$  (decomp.).

The *azine*,  $C_4H_3S \cdot CH:N \cdot N:CH \cdot C_4H_3S$ , crystallises in yellow needles, m. p.  $151-152^\circ$ .

With acetophenone in presence of sodium methoxide, thiophen-2-aldehyde condenses, giving *thienylideneacetophenone*,



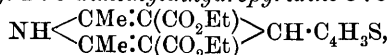
which forms yellowish-green crystals, m. p.  $59^\circ$ . With bromine this compound yields the *dibromide*,  $C_4H_3S \cdot CHBr \cdot CHBr \cdot C(=O)Ph$ , in colourless needles, m. p.  $113^\circ$  (decomp.).

*Thienylideneacetone*,  $C_4H_3S \cdot CH:CH \cdot COMe$ , m. p.  $30-35^\circ$ , forms a *dibromide*,  $C_8H_8OBr_2S$ , m. p. about  $60^\circ$  (decomp.).

*Dithienylideneacetone*,  $C_4H_3S \cdot CH:CH \cdot CO \cdot CH:CH \cdot C_4H_3S$ , obtained by the condensation of thienylideneacetone with thiophen-2-aldehyde in presence of sodium hydroxide, forms bright yellow plates, m. p.  $119-120^\circ$ , and yields a *tetrabromide*,  $C_{13}H_{10}OBr_4S_2$ , m. p. about  $105^\circ$  (decomp.).

*Benzylidenethienylideneacetone*,  $C_4H_3S \cdot CH:CH \cdot CO \cdot CH:CHPh$ , forms pale yellow needles, m. p.  $100^\circ$ , and gives a *tetrabromide*,  $C_{15}H_{12}OBr_4S$ , m. p. about  $105^\circ$  (decomp.).

*Ethyl 4-thienyl-2 : 6-dimethyldihydropyridine-3 : 5-dicarboxylate*,



obtained by the condensation of thiophen-2-aldehyde, ethyl acetate, and ammonia in alcoholic solution, forms blue needles, m. p.  $169-170^\circ$ .

Oxidation of the preceding compound yields *ethyl 4-thienyl-2 : 6-dimethylpyridine-3 : 5-dicarboxylate*,  $N \begin{array}{c} \diagup CMe:C(CO_2Et) \\ \diagdown CMe:C(CO_2Et) \end{array} > C \cdot C_4H_3S$ ,

which forms faintly yellow, shining needles, m. p.  $76.5-77.5^\circ$ , and gives a *hydriodide*,  $C_{17}H_{19}O_4NS \cdot HI$ , m. p. about  $160^\circ$  (decomp.), and a *platinichloride*,  $(C_{17}H_{19}O_4NS)_2 \cdot H_2PtCl_6$ , decomposing at about  $120^\circ$ . From *silver 4-thienyl-2 : 6-dimethylpyridine-3 : 5-dicarboxylate*, the *hydrochloride* of 4-thienyl-2 : 6-dimethylpyridine-3 : 5-dicarboxylic acid,  $N \begin{array}{c} \diagup CMe:C(CO_2H) \\ \diagdown CMe:C(CO_2H) \end{array} > C \cdot C_4H_3S \cdot HCl$ , was prepared. The attempted preparation of 4-thienyl-2 : 6-dimethylpyridine by dry distillation of the potassium salt of the dicarboxylic acid with lime resulted in decomposition of the acid into hydrogen sulphide, carbon dioxide, and 2 : 6-dimethylpyridine.

The thiophen ring is found to be unstable towards potassium cyanide, attempts to prepare a compound analogous to benzoin by the condensation of thiophen-2-aldehyde with potassium cyanide being hence unsuccessful.

T. H. P.

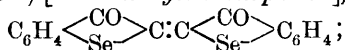
"Selenindigo" ("Bis-selenonaphthenindigo") and Aromatic Selenium Compounds. I. RUDOLF LESSER and R. WEISS (*Ber.*, 1912, 45, 1835-1841).—A preliminary account of the results of successful endeavours to prepare compounds containing a selenium

atom in place of a sulphur atom. The products show, in general, similar chemical properties to the corresponding sulphur compounds, but differ from them in physiological effect.

A solution of potassium hydroselenide is treated with a diazotised solution of anthranilic acid, and the resultant diazo-compound decomposed by warming; on acidifying the hot solution there separates *diphenyldiselenide-di-o-carboxylic acid* ("diselenodisalicylic acid"),  $\text{Se}_2(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$ , a pale yellow, crystalline substance, m. p. 296—297° (decomp.). The mother liquors contain *diphenylselenide-di-o-carboxylic acid*,  $\text{Se}(\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H})_2$ , pale yellow, microscopic needles, m. p. 228—229°. The diseleno-acid is reduced in alkaline solution by zinc dust to "*selenosalicylic acid* [*o-selenobenzoic acid*],  $\text{SeH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , which is stable only as the salt, and on acidification the diseleno acid is re-obtained. If the reduced alkaline solution is introduced into a solution of the theoretical quantity of a salt of chloroacetic acid, the mixture warmed, and then precipitated by mineral acid, there is obtained a quantitative yield of *o-carboxyphenylselenolacetic acid*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{Se}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , microscopic needles, m. p. 233—234° (decomp.). Chlorosulphonic acid dissolves this substance to a red solution, which on treating with water precipitates a red substance, soluble in alkalis to a violet-blue solution.

When *o*-carboxyphenylselenolacetic acid is boiled with excess of acetic anhydride and some anhydrous potassium acetate, and the excess of acetic anhydride subsequently removed by distillation or by the addition of water, an *acetyl* compound is obtained, which by hydrolysis with sodium hydroxide solution yields *3-hydroxyselenonaphthen*,  $\text{C}_6\text{H}_4\langle\text{C}(\text{OH})\rangle\text{CH}$ , colourless, silky needles, m. p. 76—77°.

This resembles the analogous hydroxythionaphthen in its main properties; by dissolving in alkali solution and oxidation with potassium ferricyanide, it is converted into "*selenindigo*" ("*2:2-bis-selenonaphthenindigo*") [*2:2'-bisoxyselenonaphthen*],



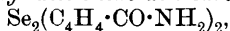
compare Friedländer, Abstr., 1908, i, 371, 372, 673, 674); this is sparingly soluble in ordinary solvents, but separates from xylene in reddish-brown needles, which sublime undecomposed at 270° approx. and have m. p. 330—335°. It is reduced by alkali and hyposulphite to a yellow vat which dyes cotton and wool violet-red.

Hydroxyselenonaphthen condenses likewise with isatin, and red silky needles of "*2-selenonaphthen-3-indole-indigo*" [*3'-indoxyl-2-selenonaphthen-3-one*],  $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{C}:\text{C}\langle\text{CO}\rangle\text{C}_6\text{H}_4\text{NH}$  (which sublime undecomposed at approx. 250°, and have m. p. about 350°), separate immediately on warming an alcoholic solution of the two substances with a drop of piperidine. It gives a yellow vat with alkali and hyposulphite, which dyes a bluer shade than thioindigo scarlet.

"*Acenaphtheneselenonaphthenindigo*" [*8-oxo-7-oxyselenonaphthenyl-acenaphthene*],  $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{C}:\text{C}\langle\text{C}_{10}\text{H}_6\rangle\text{CO}$ , prepared analogously to the

above, forms yellowish-red needles, which sublime at  $220^{\circ}$  approx., and have m. p.  $272^{\circ}$ ; it gives, on reduction, a yellow vat.

If an intimate mixture of diphenyl-diselenide-di-o-carboxylic acid with phosphorus pentachloride is heated to melting and the benzene extract of the product saturated with ammonia, there is obtained a precipitate of *diphenyl-diselenide-di-o-carboxylamide*,



yellow needles, m. p.  $265\text{--}266^{\circ}$ . On boiling with a solution of potassium permanganate, this is oxidised to "*selenosaccharin*"

(*benzoic selenonimide*),  $\text{C}_6\text{H}_4\langle\text{CO}\rangle_{\text{SeO}_2}\text{NH}$ , colourless needles, m. p.

$227\text{--}228^{\circ}$  (decomp.), which are sparingly soluble in water; the sweet taste of the sulphur analogue is entirely lacking. The imino-hydrogen is replaceable by metals, the salts with the alkalis being very soluble.

Oxidation of diphenyl-diselenide-di-o-carboxylic acid gives the parent substance of "*selenosaccharin*," *o-selenolbenzoic acid*, which is very easily soluble in water. D. F. T.

**Compounds of Chloral Hydrate with Urotropine and Caffeine.** ALBERT LEULIER (*J. Pharm. Chim.*, 1912, [vii], 6, 18—21).—Chloral hydrate in saturated aqueous solution combines with urotropine and caffeine, forming in each case two compounds according to the proportions of the reagents employed.

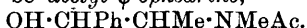
*Monochloralurotropine*,  $\text{C}_6\text{H}_{10}\text{N}_4\cdot\text{C}_2\text{HOCl}_3\cdot\text{H}_2\text{O}$ , crystallising in rhombohedra, and *dichloralurotropine*,  $\text{C}_6\text{H}_{12}\text{N}_4\cdot(\text{C}_2\text{HOCl}_3\cdot\text{H}_2\text{O})_2$ , crystallising in needles, resemble one another in their properties. They are colourless and odourless, and very soluble in alcohol and water. They volatilise at about  $100^{\circ}$  without melting. They are both neutral substances, which reduce copper solutions and ammoniacal silver nitrate. With mineral acids they yield formaldehyde, and with alkalis the chloral is attacked, giving chloroform in the cold and carbylamine on heating.

*Dichloralcaffeine*,  $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\cdot\text{H}_2\text{O}\cdot(\text{C}_2\text{HOCl}_3\cdot\text{H}_2\text{O})_2$ , m. p.  $72\text{--}73^{\circ}$ , on remaining loses 1 mol. of chloral and passes into *monochloralcaffeine*,  $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\cdot\text{H}_2\text{O}\cdot\text{C}_2\text{HOCl}_3\cdot\text{H}_2\text{O}$ , m. p.  $92\text{--}93^{\circ}$ . The latter compound dissolves in water, and in solution slowly dissociates on remaining, the caffeine separating out. In hot alcoholic solution it is completely dissociated. When heated at  $100^{\circ}$  all the chloral is driven off, leaving pure caffeine. W. G.

**Ephedrine and  $\psi$ -Ephedrine.** ERNST SCHMIDT and FRANZ W. CALLIESS (*Arch. Pharm.*, 1912, 250, 154—170).—The following results have been obtained during the course of unsuccessful experiments for the syntheses of ephedrine and  $\psi$ -ephedrine.

As the result of attempts to racemise the active bases, it has been found that ephedrine is almost unattacked by aqueous barium hydroxide at  $210^{\circ}$ , whilst  $\psi$ -ephedrine is converted by intramolecular change into ephedrine; the results are the same when alcoholic potassium hydroxide at  $100\text{--}110^{\circ}$  is employed. On the contrary, ephedrine is converted by concentrated sulphuric acid on the water-bath into  $\psi$ -ephedrine, whilst at the ordinary temperature ephedrine

and  $\psi$ -ephedrine are both converted by the acid in seventy-two hours into a substance (or substances) of the same rotatory power. By heating with acetic anhydride, ephedrine and  $\psi$ -ephedrine yield identical *acetyl* derivatives, m. p.  $101^\circ$  (*hydrochloride*, m. p.  $176^\circ$ ,  $[\alpha]_D^{20}$   $96.8^\circ$ ; *platinichloride*, m. p.  $184^\circ$ ; *aurichloride*, m. p.  $165^\circ$ ), which are shown to be *acetyl- $\psi$ -ephedrine*,



During the acetylation, therefore, the ephedrine has changed to  $\psi$ -ephedrine.

The same change is effected by nitrous acid. The hydrochloride of either base reacts with sodium nitrite to form the same *nitroso*-compound, m. p.  $80^\circ$ , colourless needles, from which  $\psi$ -ephedrine hydrochloride is obtained by hydrolysis with 25% hydrochloric acid.

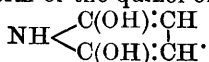
C. S.

**Harmaline Derivatives.** OTTO FISCHER and WALTER BOESLER (*Ber.*, 1912, 45, 1930—1934).—By the successive addition of pyridine and sodium acetate to a dilute acetic acid solution of harmaline and *p*-toluenediazonium chloride, *bis-p-tolueneazoharmaline*,  $\text{C}_{27}\text{H}_{26}\text{ON}_6$ , m. p.  $182$ — $183^\circ$  (decomp.), reddish-brown needles, has been obtained. *Bisbenzeneazoharmaline*, decomp. about  $180^\circ$ , *bis-p-chlorobenzeneazoharmaline*, decomp.  $185^\circ$ , and *bis-p-bromobenzeneazoharmaline*, decomp.  $200$ — $203^\circ$ , have been prepared in a similar manner. Harmine, apoharmine, and harminic acid do not form similar compounds.

Harmaline in 80—90% sulphuric acid is converted, after two days in darkness or six to seven hours in sunlight, into a *sulphonic acid*,  $\text{C}_{13}\text{H}_{14}\text{O}_4\text{N}_2\text{S}$ , yellow needles. When shaken with nitric acid, D 1.15, at the ordinary temperature, harmaline is converted into nitro-harmaline (*acetyl* derivative,  $\text{C}_{15}\text{H}_{15}\text{O}_4\text{N}_3$ , m. p.  $181^\circ$  [decomp.], golden-yellow leaflets), *m*-nitroanisic acid, and nitroapoharminecarboxylic acid (*Abstr.*, 1905, i, 229). Nitroharmaline is converted into nitroharmine by boiling dilute nitric acid, or, better, by potassium permanganate and dilute sulphuric acid.

C. S.

**Chemical Action of Light.** XXIII. Autoxidations. II. GIACOMO L. CIAMICIAN and PAUL SILBER (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 619—621; *Ber.*, 1912, 45, 1842—1845. Compare this vol., i, 174).—On prolonged exposure to light, pyrrole undergoes complete decomposition into products which are largely tarry and from which the following compounds have been isolated: (1) a crystalline compound,  $\text{C}_{12}\text{H}_{14}\text{O}_5\text{N}_2$ , apparently derived from tripyrrole; (2) ammonium salts of undetermined composition, and (3) succinimide which has previously not been obtained from pyrrole and may be regarded as the ketonic form of the quinol of pyrrole,



In the dark, pyrrole undergoes slight resinification.

Ethyl dihydrocollidinedicarboxylate (Hantzsch's ester) also undergoes autoxidation in presence of oxygen and water, yielding ethyl collidine-dicarboxylate.

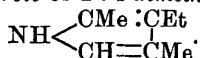
T. H. P.

**Hæmopyrrole.** LEON MARCHLEWSKI (*Zeitsch. physiol. Chem.*, 1912, 79, 351—352).—Polemical. Reply to Fischer and Bartholomäus (this vol., i, 580). W. D. H.

**The Solution of the Hæmopyrrole Question.** HANS FISCHER and ERICH BARTHOLOMÄUS (*Ber.*, 1912, 45, 1979—1986. Compare this vol., i, 297, 384, 493, 580).—The constitution of a 2:3-dimethyl-4-ethylpyrrole has been rendered probable for hæmopyrrole: this is now confirmed by the synthesis of 2:3-dimethyl-4:5-diethylpyrrole.

By condensation of dipropionylmethane with oximinomethyl ethyl ketone, a pyrrole of the constitution  $\text{NH} \begin{smallmatrix} \text{CMe}:\text{CMe} \\ \text{CEt}:\text{C}\cdot\text{COEt} \end{smallmatrix}$  is obtained, from which, by the action of concentrated sulphuric acid, the propionyl group is eliminated and 2:3-dimethyl-5-ethylpyrrole obtained. This is entirely different from hæmopyrrole. On introduction of a second ethyl group, a diethyl pyrrole identical with that obtained from hæmopyrrole is obtained.

In addition a new pyrrole has been obtained from the hæmopyrrole mixture, namely, *cryptopyrrole* or 2:4-dimethyl-3-ethylpyrrole,



*Cryptopyrrole picrate* has m. p. 137—138°.

*Dipropionylmethane* is a colourless oil, b. p. 172—173°/711 mm.,  $D_{20}^{20}$  0.9445; it gives a reddish-brown coloration with ferric chloride in alcoholic solution.

*4-Propionyl-2:3-dimethyl-5-ethylpyrrole* crystallises in colourless needles, m. p. 118—119°; the absorption spectrum shows a broad band in the green.

*2:3-Dimethyl-5-ethylpyrrole* is a yellow oil, characterised by yielding an azo-dye with diazobenzenesulphonic acid, which forms bronze-coloured crystals. It forms a dimethyldiethylpyrrole, m. p. 106—107°.

E. F. A.

**The Synthesis of Tetramethylpyrrole.** GIUSEPPE PLANCHER and T. ZAMBONINI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 598—600).—Two grams of acetyltrimethylpyrrole are heated to 220° in a sealed tube with a solution of 2 grams of sodium in 20 c.c. of absolute methyl alcohol. The product is precipitated with water, filtered in an atmosphere of nitrogen, dried in a vacuum, and crystallised from light petroleum; it then forms colourless crystals, m. p. 111°. This tetramethylpyrrole,  $\text{C}_8\text{H}_{13}\text{N}$ , has a faecal odour, and rapidly darkens in air. The *picrate* has m. p. 128° (decomp.). C. H. D.

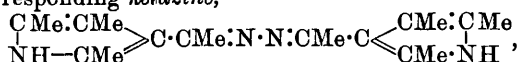
**Syntheses of Phyllopyrrole.** U. COLACICCHI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 489—493).—The acetyltrimethylpyrrole obtained by the action of heat on the dipyrrolylmethane formed by the condensation of paracetaldehyde with 3-acetyl-2:4-dimethylpyrrole (compare this vol., i, 491) is not identical with 3-acetyl-2:4:5-trimethylpyrrole prepared by Knorr and Lange's method (*Abstr.*, 1902, i, 821). When attempts were made to hydrolyse the latter compound with

alcoholic potassium hydroxide in a sealed tube, the products were found to contain phyllopyrrole (Willstätter and Asahina, this vol., i, 41), the acetyl group of the original derivative being replaced by ethyl. A similar replacement is effected by the action of sodium ethoxide on hydrazones (compare Knorr and Hess, Abstr., 1911, i, 1019) and on ketazines (compare Fischer and Bartholomäus, this vol., i, 50). The author has, indeed, obtained phyllopyrrole also from the ketazine corresponding with 3-acetyl-2:4:5-trimethylpyrrole.

3-Acetyl-2:4:5-trimethylpyrrole,  $\text{NH} \begin{smallmatrix} \text{CMe}:\text{CAc} \\ \text{CMe}:\text{CMe} \end{smallmatrix}$ , obtained by re-

ducing a mixture of molecular proportions of oximinomethyl ethyl ketone and acetylacetone with zinc dust in acetic acid solution, forms shining, colourless needles or prisms, m. p. 209—210°, and gives the characteristic pine splinter reaction.

The corresponding ketazine,



obtained by the action of hydrazine hydrate, forms prismatic crystals, m. p. about 305°.

Reduction by Knorr's method of a mixture of molecular proportions of oximinoacetylacetone and methyl ethyl ketone yields the diacetyl-dimethylpyrazine obtained by Wolff (Abstr., 1903, i, 203).

Phyllopyrrole is found to have m. p. 64—65°, and its picrate, 101—103°. T. H. P.

**Action of Sodium Alkoxides on Esters of Pyrrole-carboxylic Acids.** U. COLACICCHI and C. BERTONI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 653—656).—The authors find that, like acetyl, hydrazine, and ketazine residues in the pyrrole nucleus (preceding abstract), the carbethoxy-group can also be replaced by an alkyl group by the action of sodium alkoxide.

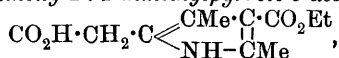
In this way they have succeeded in converting ethyl 2:3:5-trimethylpyrrole-4-carboxylate into either 2:3:5-trimethyl-4-ethylpyrrole (phyllopyrrole; compare Willstätter and Asahina, this vol., i, 41) or 2:3:4:5-tetramethylpyrrole, and in converting ethyl 2:4-dimethyl-3:5-dicarboxylate into 2:3:4:5-tetramethylpyrrole. T. H. P.

**New Pyrogenic Transposition in the Pyrrole Group: Relative Stability to Heat of Isomeric Derivatives.** U. COLACICCHI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 657—658).—When 3-acetyl-2:4-dimethylpyrrole is heated in a sealed tube at about 300°, it is transformed quantitatively into 5-acetyl-2:4-dimethylpyrrole. This is the first transference which has been observed of a group from one carbon atom to another of the pyrrole nucleus, and indicates that acyl derivatives of pyrrole with the acyl group in the 2 position are more stable than those with this group in the 1 or 3 position.

T. H. P.

**Synthesis of 2:4-Dimethylpyrrole-5-acetic Acid and 2:4-Dimethylpyrrole-5-propionic Acid.** HANS FISCHER and ERICH BARTHOLOMÄUS (*Ber.*, 1912, 45, 1919—1926).—The action of zinc dust

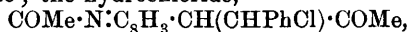
on a glacial acetic acid solution of  $\beta$ -oximinolævulic acid and ethyl acetoacetate, initially at  $0^\circ$  and finally on the water-bath, leads to the formation of 3-carbethoxy-2:4-dimethylpyrrole-5-acetic acid,



m. p.  $152-153^\circ$  (decomp.), slender needles. The substance yields ethyl 2:4:5-trimethylpyrrole-3-carboxylate by keeping in the fused state for some time, but is converted by hot moderately concentrated sulphuric acid into 2:4-dimethylpyrrole-5-acetic acid. This acid forms yellow, unstable crystals, and reacts with diazotised sulphanilic acid to form a well-crystallised, brown *azo*-compound,  $\text{C}_{14}\text{H}_{15}\text{O}_5\text{N}_3\text{S}$ , which exhibits the stability and the reactions characteristic of a member of the  $\beta$ -series.

$\beta$ -Oximino- $\gamma$ -acetylbutyric acid, ethyl acetoacetate, and zinc dust react in a similar manner to form 3-carbethoxy-2:4-dimethylpyrrole-5-propionic acid,  $\text{C}_{12}\text{H}_{17}\text{O}_4\text{N}$ , m. p.  $119-120^\circ$  (decomp.), white needles. The substance is converted by heating with moderately concentrated sulphuric acid into 2:4-dimethylpyrrole-5-propionic acid, which has not been obtained crystalline, but couples with diazobenzenesulphonic acid to form a crystalline *azo*-compound,  $\text{C}_{15}\text{H}_{17}\text{O}_5\text{N}_3\text{S}$ . This *azo*-dye is quite different from that obtained from phonopyrrolecarboxylic acid, which undoubtedly belongs to the  $\alpha$ -series. Since the phonopyrrole obtained by the distillation of phonopyrrolecarboxylic acid yields an *azo*-dye belonging to the  $\beta$ -series, a migration of a group from the  $\beta$ - to the  $\alpha$ -position must have occurred during the distillation (compare Piloty, Abstr., 1911, i, 92; Fischer and Bartholomäus, this vol., i, 384).  
C. S.

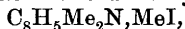
**Nature of Picolide and Pyrrocoline.** MAX SCHOLTZ (*Ber.*, 1912, 45, 1718—1725. Compare this vol., i, 385).—Picolide condenses with benzaldehyde in acetic acid solution in presence of hydrogen chloride; the hydrochloride,



is formed first, and yields monobenzylidene picolide when boiled with alcohol.

By the action of nitric acid on picolide, one or two acetyl groups are replaced by nitro-groups according to the concentration of the acid. Both are yellow, crystalline compounds; the dinitro-derivative is perhaps a dinitropyrrocoline. A second acetyl group could not be eliminated from the mononitro-compound so as to form mononitropyrrocoline.

When heated with methyl iodide and methyl alcohol at  $120^\circ$ , pyrrocoline forms the methiodide of dimethylpyrrocoline,



thus behaving similarly to 1-methylpyrrole.

When pyrrocoline reacts with isatin, in addition to the coloured compound previously described (*loc. cit.*), a colourless compound, derived from the interaction of two molecules of each component, is obtained.

Pyrrocoline condenses with simple ketones on warming in acetic

acid solution, yielding compounds composed of 2 mols. of pyrrocoline and 1 mol. ketone.

The pyrrole hydrogen in pyrrocoline can be replaced by acid radicles. Thus when boiled with acetic anhydride and sodium acetate, pyrrocolyl methyl ketone is formed, in which the position of the acetyl group is uncertain. It condenses with benzaldehyde to benzylideneacetylpyrrocoline.

*Benzylidenepicolide*,  $\text{NAc} \cdot \text{C}_8\text{H}_7(\text{:CHPh}) \cdot \text{CO} \cdot \text{CH}_3$ , forms greenish-yellow crystals, m. p.  $157^\circ$ , dissolving in concentrated sulphuric acid with a deep red coloration; the *hydrochloride* is a red, crystalline mass, decomp.  $125^\circ$ .

*Mononitropicolide*,  $\text{C}_{10}\text{H}_8\text{ON} \cdot \text{NO}_2$ , separates in yellow needles, m. p.  $196^\circ$ .

*Dinitropyrrocoline* (?),  $\text{C}_8\text{H}_5\text{N}(\text{NO}_2)_2$ , crystallises in large, yellow plates, m. p.  $229^\circ$ .

The *methiodide* of *dimethylpyrrocoline* crystallises in colourless platelets, m. p.  $180^\circ$ .

The colourless compound,  $\text{C}_{32}\text{H}_{22}\text{O}_3\text{N}_4$ , of pyrrocoline and isatin forms colourless platelets, which are not melted at  $300^\circ$ .

The compound,  $\text{CMe}_2(\text{C}_8\text{H}_6\text{N})_2$ , from pyrrocoline and acetone, is a yellow, crystalline powder, m. p.  $244\text{--}246^\circ$  to a black liquid.

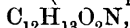
The corresponding compound,  $\text{CMePh}(\text{C}_8\text{H}_6\text{N})_2$ , from acetophenone, is a yellow microcrystalline powder, m. p.  $98^\circ$ .

*Acetylpyrrocoline*,  $\text{C}_8\text{H}_6\text{N} \cdot \text{COMe}$ , is a somewhat viscid, yellow oil, b. p.  $195^\circ/18\text{ mm.}$ ,  $288^\circ/760\text{ mm.}$

*Benzylideneacetylpyrrocoline* crystallises in yellow needles, m. p.  $127^\circ$ , and dissolves in concentrated sulphuric acid with a blood-red coloration.

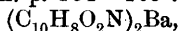
E. F. A.

**Syntheses in the Indole Group. III. Methylindole C- and N-Carboxylic Acids.** BERNARDO ODDO (*Gazzetta*, 1912, 42, i, 361—375).—3-Methylindole reacts with magnesium ethyl bromide without heating, and the product is converted by carbon dioxide into 3-methylindole-1-carboxylic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CMe} \\ \text{N}(\text{CO}_2\text{H}) \end{smallmatrix} \text{CH}$ , which forms a crystalline precipitate, m. p.  $129^\circ$  (decomp.). The *ethyl* ester,



prepared from the magnesium compound and ethyl chlorocarbonate, has b. p.  $288.5^\circ$  under atmospheric pressure, and  $215^\circ/11\text{ mm.}$  Prolonged heating converts it into the ester of the following acid.

3-Methylindole-2-carboxylic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CMe} \\ \text{NH} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$ , is prepared by heating the magnesium compound, obtained as above, in a stream of carbon dioxide, finally raising the temperature to  $315\text{--}320^\circ$ . The product is recrystallised from benzene containing a little ether, and then forms white needles, m. p.  $164\text{--}165^\circ$ . The *barium* salt,



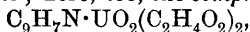
has been analysed.

2-Methylindole-3-carboxylic acid, obtained from 2-methylindole, the reaction with carbon dioxide being carried out in boiling toluene solution, crystallises from chloroform and has m. p.  $174^\circ$  (decomp.).

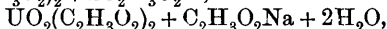
The *barium* salt has been analysed. The *ethyl* ester forms small needles, m. p. 135°. C. H. D.

**Complex Salts of Quinoline with Uranyl Salts.** GIUSEPPE INGILLERI and G. GORI (*Atti R. Accad. Fisocritici, Siena*, 1909).—These salts are of the type  $\text{UO}_2(\text{C}_9\text{H}_7\text{N})_2\text{X}_2$ , and are usually micro-crystalline and yellow, those with an inorganic acid radicle being dark yellow or orange. The following have been prepared :

(1) The *nitrate*; in addition to the complex salt of normal type, one having the formula  $\text{C}_9\text{H}_7\text{N}\cdot\text{UO}_2\cdot\text{NO}_3\cdot 5\text{H}_2\text{O}$ , was obtained. (2) The *sulphate*. (3) The *acetate*; here, too, the *complex* salt,



exists besides the normal one. Uranyl and potassium acetates form the double salt,  $(\text{C}_2\text{H}_3\text{O}_2)_2\text{UO}_2 + \text{C}_2\text{H}_3\text{O}_2\text{K} + 5\text{H}_2\text{O}$ ; the complexes,  $(\text{C}_9\text{H}_7\text{N})_2\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 + 2\text{C}_2\text{H}_3\text{O}_2\text{K}$ ,



and  $(\text{C}_9\text{H}_7\text{N})_2\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 + 2\text{C}_2\text{H}_3\text{O}_2\text{Na}$  have also been prepared.

(4) The *oxalates*,  $(\text{C}_9\text{H}_7\text{N})_2\text{UO}_2\cdot\text{C}_2\text{O}_4$ ,  $\text{C}_2\text{O}_4\text{UO}_2 + \text{Na}_2\text{C}_2\text{O}_4 + 3\text{H}_2\text{O}$ ,  $(\text{C}_9\text{H}_7\text{N})_2\text{UO}_2\cdot\text{C}_2\text{O}_4 + 2\text{Na}_2\text{C}_2\text{O}_4$ , and  $(\text{C}_9\text{H}_7\text{N})_2\text{UO}_2\cdot\text{C}_2\text{O}_4 + 2\text{K}_2\text{C}_2\text{O}_4$ . (5) The *tartrate*,  $(\text{C}_9\text{H}_7\text{N})_2\text{UO}_2\cdot\text{C}_4\text{H}_4\text{O}_6$ .

Calcium chloride forms with quinoline a crystalline compound,  $\text{CaCl}_2\cdot x\text{C}_9\text{H}_7\text{N}$ , similar to that formed with ammonia,  $\text{CaCl}_2\cdot 8\text{NH}_3$ .

T. H. P.

**Synthesis of Quininic Acid and of 6-Methoxy-4-methylquinoline.** AMÉ PICTET and R. R. MISNER (*Ber.*, 1912, 45, 1800—1804).—4-Methylquinoline was obtained by Beyer (*Abstr.*, 1886, 630) by the condensation of aniline with acetone and formaldehyde by means of concentrated hydrochloric acid. Attempts to improve the yield by the addition of oxidising agents, etc., have been unsuccessful.

By condensation in a similar manner of *p*-anisidine with acetone and formaldehyde, 6-methoxy-4-methylquinoline is obtained.

Quininic acid,  $\text{OMe}\cdot\text{C}_6\text{H}_3\text{<}\begin{array}{c} \text{C}(\text{CO}_2\text{H})\cdot\text{CH} \\ \text{N}=\text{CH} \end{array}$ , is prepared by condensing *p*-anisidine with formaldehyde and ethyl pyruvate, and subsequent hydrolysis of the ester formed.

When aniline is condensed with monochloroacetone and formaldehyde, 3-chloro-4-methylquinoline is obtained, and not the  $\omega$ -chloro-compound. E. F. A.

**Cyanocyclaminanes. V. Synthesis of Cinchonic and Quininic Acids.** ADOLF KAUFMANN, HEINRICH PEYER [and R. WIDMER] (*Ber.*, 1912, 45, 1805—1810. Compare Kaufmann and Widmer, *Abstr.*, 1911, i, 749, 750).—6-Methoxyquinoline methosulphate interacts with potassium cyanide to form a cyanoquinolan, which is converted by iodine into the methiodide of 4-cyano-6-methoxyquinoline. On distillation in a vacuum, quininonitrile is obtained, which can be hydrolysed either by acids or alkalis in presence of hydrogen peroxide to quininic acid. Cinchononitrile is hydrolysed by the same process by way of the

amide to cinchonic acid. The synthetic acids are in every way identical with those obtained from the alkaloids.

*4-Cyano-6-methoxy-1-methylquinolan* separates in well formed, yellow crystals, m. p. 80—81°, which soon become brown and black on exposure to air.

*4-Cyano-6-methoxyquinoline methiodide* forms slender, lustrous, orange needles or dark cherry-red, stunted prisms, m. p. 198° (decomp.).

*Quininonitrile* crystallises in yellow, woolly needles, m. p. 157°; it is readily hydrolysed by alcoholic potassium hydroxide and hydrogen peroxide to quinic acid, m. p. 280°. E. F. A.

**2:8-Diaminoacridine.** LUDWIG BENDA (*Ber.*, 1912, 45, 1787—1799).—Diaminoacridine is prepared in quantity by the following series of operations (compare Gram, *Diss.*, Jena, 1892). *p:p*-Diaminodiphenylmethane is nitrated to *p:p*-diamino-*o:o*-dinitrodiphenylmethane, and this reduced to *p:p:oo*-tetraminodiphenylmethane, which was not isolated, but the crude product containing tin was heated under pressure at 135—140°. A crystalline tin double salt of diaminoacridine was thus obtained.

2:8-Diaminoacridine behaves similarly to its homologue, the base of the acridine yellow dyes; the hydrochloride is, however, soluble in cold water. It can be diazotised, but on boiling, brown, amorphous, insoluble products are obtained. To prepare dihydroxyacridine the diaminoacridine is heated with 45% sulphuric acid in sealed tubes at 195°. The tetra-azoacridine prepared by means of nitrosylsulphuric acid can be degraded to acridine.

With formaldehyde and aromatic bases, diaminoacridine forms at first a sparingly soluble, orange condensation product of the acridine and formaldehyde alone; on warming, the amine enters into the reaction. The dyes have a deeper hue than the original diaminoacridine, and dye egg-yellow and orange to brown shades. The formula of these dyes is not yet established.

2:8-Diamino-10-methylacridinium chloride has a very intense trypanocidal action, being at least three times as effective as the homologue from acridine yellow. It has been tried on man in cases of sleeping sickness with good effect.

Diaminoacridine crystallises from water in very long, brownish-yellow needles or slender, matted needles, according to the rate of cooling. On heating, it begins to darken at 260°, m. p. 283° (decomp.). The sulphate forms red, matted needles.

2:8-Dihydroxyacridine crystallises in slender, orange needles with a bronze lustre, which becomes red at 275°, but have not melted at 300°. It dissolves in concentrated sulphuric acid with a bluish-green fluorescence.

2:8-Diamino-10-methylacridinium chloride forms long, red prisms dissolving in water to a yellow solution, which fluoresces green only when much diluted. It has a very bitter taste, about double that of 2:8-diaminoacridine. The *sulphate* crystallises in red needles.

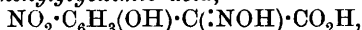
On heating with 45% sulphuric acid a *dihydroxy*-compound, crystallising as hydrochloride in orange-red, matted needles, is obtained. An

*anhydride*, composed of two molecules of the 2:8-dihydroxyacridinium base less a molecule of water, forms lustrous, orange-red needles, which become red at 245° and sinter at 260—265°, m. p. 275°.

E. F. A.

**Benzisooxazoles.** WALTHER BORSCHKE (*Annalen*, 1912, 390, 1—29).—The author has attempted to prepare from methyl 5-nitrobenzisooxazole-2-carboxylate (Abstr., 1909, i, 385) the first representative of a benzisooxazole unsubstituted in the heterocyclic nucleus, but unsuccessfully, since the hydrolysis of the ester, whether in acid, alkaline, or neutral solution, is always accompanied by fission of the heterocyclic ring.

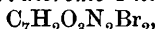
[With PAUL OPPENHEIMER.]—The hydrolysis of the ester by aqueous alcoholic 20% sodium hydroxide, followed by acidification, yields 4-nitro-2-hydroxyphenylglyoximic acid,



m. p. 166—167° (decomp.). The same substance is obtained by hydrolysing the ester with dilute sulphuric acid.

5-Nitrobenzisooxazole-2-carboxylamide,  $\text{C}_8\text{H}_5\text{O}_4\text{N}_3$ , m. p. 189—190°, obtained from the ester and alcoholic ammonia at 100°, is also converted into the nitrohydroxyphenylglyoximic acid by concentrated sulphuric acid and concentrated aqueous sodium nitrite.

4-Nitrosalicylonitrile,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CN} \cdot \text{H}_2\text{O}$ , m. p. 140—160° (decomp.), the preparation of which from methyl 5-nitrobenzisooxazole-2-carboxylate, from 4-nitro-2-hydroxyphenylglyoximic acid, from 2:4-dinitrotoluene, or from 2:4-dinitrobenzaldehyde is described, has been converted into the *acetyl* derivative, m. p. 100°, by boiling acetic anhydride, into the *benzoyl* derivative, m. p. 122°, by benzoyl chloride in pyridine, into 1:1-dibromo-4-nitrosalicylonitrile,

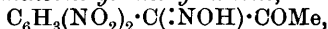


m. p. 193° (decomp.), by bromination in acetic acid and sodium acetate, and into 4:1-dinitrosalicylonitrile, m. p. 174°, by nitric acid, D 1.52, at 0°. 4-Aminosalicylonitrile,  $\text{NH}_2 \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CN}$ , m. p. 182°, yellowish-white needles, is obtained by reducing the nitro-compound by tin, alcohol, and concentrated hydrochloric acid; its *dibenzoyl* derivative has m. p. 198—199°.

4-Nitrosalicylic acid, m. p. 235° (decomp.), is obtained in about 80% yield by heating methyl 5-nitrobenzisooxazole-2-carboxylate with 5*N*-hydrochloric acid at 150°; it forms an *ethyl* ester, m. p. 87°, and an *amide*, m. p. 192—194°, and is converted by nitric acid, D 1.52, into trinitroresorcinol (styphnic acid).

When treated with sodium ethoxide, a well-cooled alcoholic solution of 2:4-dinitrobenzyl methyl ketone and *isoamyl* nitrite yields 5-nitro-2-acetylbenzisooxazole,  $\text{NO}_2 \cdot \text{C}_6\text{H}_3 \begin{smallmatrix} \text{CAc} \\ \text{O} \end{smallmatrix} \text{N}$ , m. p. 135—136°, together with 4-nitrosalicylonitrile as a by-product; the amount of the latter increases at higher temperatures.

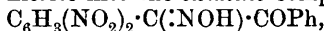
2:4-Dinitro- $\alpha$ -oximinobenzyl methyl ketone,



m. p. 156°, obtained by treating a benzene solution of 2:4-dinitrobenzyl methyl ketone at 0° with hydrogen chloride and *isoamyl* nitrite,

forms a *semicarbazone*, m. p. 226° (decomp.), and a *phenylhydrazone*, m. p. 197—198° (decomp.), red needles. It is converted by hot alcoholic sodium ethoxide into 5-nitro-2-acetylbenzisoxazole (*phenylhydrazone*, m. p. 192—193°), which is stable to boiling alcohol and 5*N*-hydrochloric acid, but is hydrolysed rapidly by 5% sodium hydroxide, yielding 4-nitrosalicylonitrile and acetic acid.

2 : 4-*Dinitrophenylacetyl chloride*,  $C_6H_3(NO_2)_2 \cdot CH_2 \cdot COCl$ , m. p. 77°, obtained from the acid and thionyl chloride in boiling benzene, is converted by ethereal ammonia into 2 : 4-*dinitrophenylacetamide*, m. p. 180°, and reacts in benzene with aluminium chloride to form, ultimately,  $\omega$ -2 : 4-*dinitrophenylacetophenone*,  $C_6H_3(NO_2)_2 \cdot CH_2 \cdot C(=O)Ph$ , m. p. 135—136°. The latter is converted, in benzene, by hydrogen chloride and *isoamyl nitrite* into the *oximino*-compound,



m. p. 174° (decomp.), which reacts with boiling alcoholic sodium ethoxide to form 5-*nitro-2-benzoylbenzisoxazole*, m. p. 157—158°, which partly decomposes during the reaction into ethyl benzoate and 4-nitrosalicylonitrile. C. S.

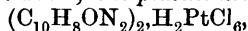
**The Action of Aldehydes on Pyrrole Compounds.** U. COLACICCHI and C. BERTONI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 600—604. Compare Colacicchi, *Abstr.*, 1911, i, 1030).—Phenylpyrrole condenses with paraldehyde, yielding a yellow powder,  $C_{12}H_{11}N$ , decomposing at 195—200°, together with a small quantity of a second substance, insoluble in light petroleum. The compound obtained from phenylpyrrole and formaldehyde,  $C_{11}H_9N$ , is amorphous, and decomposes at about 100°, whilst that from propaldehyde,  $C_{13}H_{13}N$ , decomposes at 145°.

*Bis-3-acetyl-2 : 4-dimethylpyrrolpropane*,  $(OAc \cdot C_4NHMe_2)_2CHEt$ , prepared from 3-acetyl-2 : 4-dimethylpyrrole and propaldehyde in presence of zinc chloride, crystallises from alcohol in small, white plates, m. p. 216—217°.

*Bis-3-acetyl-2-phenyl-4-methylpyrrolmethane*,  $(OAc \cdot C_4NHPhMe)_2CH_2$ , forms colourless prisms, m. p. 252—253°. *Bis-5-benzoyl-2 : 4-dimethylpyrrolpropane*,  $(OBz \cdot C_4NHMe_2)_2CHEt$ , crystallises from alcohol in glistening, yellow leaflets, m. p. 245—246°. C. H. D.

**Syntheses in the Pyrrole Group. IV. Pyridine-pyrrole Bases.** BERNARDO ODDO (*Gazzetta*, 1912, 42, i, 346—352. Compare *Abstr.*, 1910, i, 426).—Magnesium pyrrol iodide reacts with nicotinic chloride, suspended in ether. After remaining overnight, the pasty mass is mixed with ice and made alkaline with sodium hydrogen carbonate. The ether is then removed, and the residue extracted with boiling water.

3-*Pyridyl 2-pyrrol ketone*,  $C_5NH_4 \cdot CO \cdot C_4NH_4$ , crystallises from aqueous alcohol in white needles, m. p. 132°. The *aurichloride* is an orange precipitate, m. p. 165°; the *platinichloride*,



is granular, and decomposes at 235° without melting. The *picrate* crystallises from boiling water, and has m. p. 228—230° (decomp.). The *silver salt*,  $C_5NH_4 \cdot CO \cdot C_4H_3NAg$ , is a white precipitate.

A solution of the ketone in ether reacts with magnesium ethyl iodide, forming the *compound*,  $\text{MgEt} \cdot \text{C}_5\text{NH}_4\text{I} \cdot \text{CO} \cdot \text{C}_4\text{NH}_3 \cdot \text{MgI}, \text{Et}_2\text{O}$ .

2-Pyridyl 2-pyrryl ketone, prepared in the same manner from picolinic chloride, forms bright yellow crystals, m. p.  $74^\circ$ . The *picrate* forms yellow, silky needles, m. p.  $85^\circ$ , and the *platinichloride* a yellow precipitate, not melted at  $265^\circ$ . The *aurichloride* and the *silver* derivative have been prepared. C. H. D.

**Thiele's Theory and Indigotin.** M. TSCHILIKIN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 498—514).—The author shows by means of a number of examples that Thiele's theory of residual valency (*Abstr.*, 1899, i, 554) readily explains the transformations which indigotin and its derivatives undergo. T. H. P.

**Quinoline-indole Dyes.** WALTER KÖNIG (*J. pr. Chem.*, 1912, 85, [ii], 514—522).—2-Methylindole-3-aldehyde readily condenses with salts of the following bases, yielding yellow, red, bluish-red to blue basic dyes: 2-methylquinoline, 4-methylquinoline, 2-methylpyridine, 4-methylpyridine, 2:5-dimethylpyridine, and 5-methylacridine. The dyes form periodides, and on treatment with alkalis yield strongly coloured bases.

The present paper deals with the dyes derived from 2- and 4-methylquinoline methiodides and methoperchlorates.

The dye,  $\text{CH}=\text{CH} \begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{NMeI} \end{array} \begin{array}{c} \text{C} \cdot \text{CH} \cdot \text{CH} \cdot \text{C} \\ \text{C}_6\text{H}_4 \\ \text{CMe} \end{array} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{NH} \end{array}$ , obtained by condensing the aldehyde with 2-methylquinoline methiodide by means of piperidine in methyl alcoholic solution, forms small, brownish-red crystals, m. p.  $280^\circ$ , and is converted by aqueous sodium hydroxide into the corresponding *dye base*, which forms bluish-green needles of a golden lustre.

2-Methylquinoline methoperchlorate,  $\text{C}_{11}\text{H}_{12}\text{O}_4\text{NCl}$ , prepared from 2-methylquinoline methiodide and sodium perchlorate in aqueous solution, crystallises in almost colourless prisms, m. p.  $154^\circ$ , and condenses with 2-methylindole-3-aldehyde, yielding the *dye*,

$\text{C}_{21}\text{H}_{19}\text{O}_4\text{N}_2\text{Cl}$ , which forms microscopic, brownish-red needles, m. p. above  $300^\circ$  (decomp.). The *chloride*,  $\text{C}_{21}\text{H}_{19}\text{N}_2\text{Cl}$ , obtained by shaking a suspension of the preceding perchlorate in acetone with 20% aqueous sodium hydroxide, and subsequently treating the acetone solution of the dye base with hydrochloric acid and sodium chloride, is orange-red in colour, has m. p. above  $290^\circ$ , and forms a *mercurichloride*.

The condensation of 4-methylquinoline methiodide and 2-methylindole-3-aldehyde by means of piperidine in methyl-alcoholic solution yields the bluish-red dye,  $\text{NMeI} \cdot \text{C}_6\text{H}_4 \begin{array}{c} \text{CH} \\ | \end{array} \begin{array}{c} \text{CH} \\ | \end{array} \begin{array}{c} \text{C} \cdot \text{CH} \cdot \text{CH} \cdot \text{C} \\ \text{C}_6\text{H}_4 \\ \text{CMe} \end{array} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{NH} \end{array}$ , which has m. p. above  $300^\circ$ , and crystallises with methyl alcohol (1 mol.).

The corresponding *perchlorate* yields with sodium hydroxide the *dye base*,  $\text{NMe} \cdot \text{C}_6\text{H}_4 \begin{array}{c} \text{CH} \\ | \end{array} \begin{array}{c} \text{CH} \\ | \end{array} \begin{array}{c} \text{C} \cdot \text{CH} \cdot \text{CH} \cdot \text{C} \\ \text{C}_6\text{H}_4 \\ \text{CMe} \end{array} \begin{array}{c} \text{C}_6\text{H}_4 \\ \text{N} \end{array}$ . This crystallises in

lustrous, blue needles, m. p.  $240^{\circ}$  (decomp.), which lose their metallic lustre and become brown on exposure to air. From chloroform it separates in lustrous, green needles, containing 2 mols. of the solvent, which is removed at  $160^{\circ}$ . The colour of its solutions varies greatly with the nature of the solvent, being yellowish-red in water, reddish-violet in alcohol, bluish-violet in chloroform, and blue in pyridine and nitrobenzene. In aqueous solution, it undergoes partial transformation into a yellow substance, which crystallises in needles of a golden lustre, and is converted by acids into the original dye. F. B.

**A New Method of Preparing Cyclamine-aldehydes and -alcohols.** ADOLF KAUFMANN and LOUIS G. VALLETTE (*Ber.*, 1912, 40, 1736—1742).—Whereas 5-methylacridine readily reacts with nitrosodimethylaniline, the latter does not interact with quinaldine, lepidine, or  $\alpha$ -picoline. The quaternary salts of these bases, however, readily take part in the condensation. Abnormally here the reactivity of the methyl group is greatly increased by the saturation of the nitrogen; thus quinaldine ethiodide condenses with nitrosodimethylaniline, particularly in the presence of a few drops of piperidine, with the formation of a reddish-violet colour. The condensation product forms green needles, decomp.  $200^{\circ}$ ; it is decomposed by mineral acids into *as*-dimethyl-*p*-phenylenediamine and quinoline-2-aldehyde ethiodide.

Quinaldine ethiodide condenses with nitroso-naphthol, forming an intense olive-green solution, and also with nitrosoantipyrine.

The *methiodide* of  $\alpha$ -picoline crystallises in long, colourless needles, m. p.  $224^{\circ}$ ; it condenses with nitrosodimethylaniline to a red solution, from which the condensation product crystallises, + Et·OH, in green needles, m. p.  $185^{\circ}$  (decomp.). It becomes red on drying in the oven. Picoline ethiodide behaves similarly.

Lepidine methiodide condenses to a compound of coppery lustre, which dissolves in alcohol with an intense blue coloration.

The condensation product of nitrosodimethylaniline with 5-methylacridine forms coarse, orange-red crystals, m. p.  $234^{\circ}$ , and slender plates, m. p.  $210$ — $211^{\circ}$ . When decomposed by acids, acridine-5-aldehyde (Bernthsen and Muhlert, *Abstr.*, 1887, 850), m. p.  $148^{\circ}$ , is obtained. The *anil* crystallises in yellowish-brown platelets, m. p.  $163^{\circ}$ ; the *oxime* forms yellow needles, m. p.  $247^{\circ}$  (decomp.), and yields a *hydrochloride* crystallising in yellowish-red needles, m. p.  $252^{\circ}$  (decomp.).

The *aldehyde* from the quinaldine ethiodide condensation product was characterised as *phenylhydrazone*; this formed red, stunted needles, m. p.  $245^{\circ}$ .

The methiodide of the dimethylaminoanil of pyridine-2-aldehyde was hydrolysed in a similar manner; the *phenylhydrazone* obtained crystallised in orange-yellow needles with a blue reflex, m. p.  $244^{\circ}$  (decomp.). E. F. A.

**Diacetylfulrazan.** LUIGI ALESSANDRI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 659—666).—The author finds that when diacetylgyloxime (compare Thal, *Abstr.*, 1892, 1074) is fused, it loses water, yielding

diacetylfurazan,  $\begin{matrix} \text{CAc:N} \\ \text{CAc:N} \end{matrix} > \text{O}$ , which may also be obtained by dissolving glyoxime in acetic anhydride.

Schmidt and Widman (Abstr., 1909, i, 524) obtained from acetylacetone a compound which they described as diacetylfurazan, but which gives only a monophenylhydrazone and a monosemicarbazone. The author shows that this compound is identical with the one obtained by Angeli (Abstr., 1891, 890) by the action of concentrated nitric acid on acetylacetone; its constitution is not determined.

*Diacetylfurazandiphenylhydrazone*,  $\text{C}_{18}\text{H}_{18}\text{ON}_6$ , m. p.  $210^\circ$ , the *dioxime*,  $\text{C}_6\text{H}_8\text{O}_3\text{N}_4$ , m. p.  $128^\circ$ , and the *disemicarbazone*,  $\text{C}_8\text{H}_{12}\text{O}_3\text{N}_8$ , decomposing at  $239-240^\circ$ , were prepared. Oxidation of diacetylfurazan by means of permanganate yields the furazandicarboxylic acid described by Wolff (Abstr., 1895, i, 192). T. H. P.

**Dicyclic Compounds and their Comparison with Naphthalene.** KARL FRIES (*Annalen*, 1912, 389, 305—398).—Zincke has observed that derivatives of dicyclic compounds containing one benzenoid and one heterocyclic nucleus (1:2:3-benzotriazole, 2:1:3-benzotriazole, benziminoazole, and indazole) exhibit an astonishing similarity to the corresponding derivatives of naphthalene (Abstr., 1910, i, 140). With the object of seeing how extensive in reality is the agreement between such dicyclic systems and naphthalene, or whether the typical distinctions in behaviour between derivatives of benzene and the corresponding derivatives of naphthalene may not also be existent in such systems, the author has described in this communication the behaviour of derivatives of *N*-phenyl- $\psi$ -azoiminobenzene [2-phenyl-2:1:3-benzotriazole], *N*-phenylazoiminobenzene [1-phenyl-1:2:3-benzotriazole], 4:7-dimethyl-1:2:3-benzotriazole, and 3:3-diphenylcoumaranone.

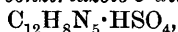
As criteria of difference of behaviour between a benzene derivative and the corresponding naphthalene compound, the author selects (i) the reduction of naphthalene, (ii) the action of chlorine, nitric acid, and diazonium salts on  $\alpha$ -halogenated or alkylated  $\beta$ -naphthols, (iii) the oxidation of 2:3-dihydroxynaphthalene and its derivatives. With regard to (ii), it is known that chlorine converts  $\beta$ -naphthol and 1-methyl- $\beta$ -naphthol respectively into 1:1-dichloro-2-ketodihydronaphthalene and 1-chloro-2-keto-1-methyldihydronaphthalene (Abstr., 1908, i, 730), that nitric acid converts 1-bromo- $\beta$ -naphthol into 1:2-bromonaphthaquinonitrole and 1-methyl- $\beta$ -naphthol into 1:2-methylnaphthaquinonitrole (Abstr., 1906, i, 190), and that  $\beta$ -naphthols with substituents in position 1 do not, as a rule, couple with diazonium salts. With regard to (iii), 2:3-dihydroxynaphthalene and its halogenated derivatives are, unlike the catechols, not directly oxidised to *o*-quinones (Zincke and Fries, Abstr., 1904, i, 1008). The author finds that the benzotriazoles exhibit the widest similarity in behaviour to the corresponding naphthalene derivatives, that the resemblance in properties of indazoles and naphthalene compounds is more superficial than real, and that coumaranones behave entirely like benzene derivatives.

1-Bromo-1-nitro-2-ketodihydronaphthalene,  $\text{C}_{10}\text{H}_6\text{O}_3\text{NBr}$ , m. p.  $74^\circ$ , is obtained by addition of nitric acid, D 1.52, to a chloroform solution

of 1-bromo- $\beta$ -naphthol at 0°. By heating its solution in an indifferent solvent,  $\beta$ -naphthaquinone is very conveniently obtained in good yield, but cannot be kept for many hours, owing to the presence of some impurity which causes it to become tarry. The bromonitro-ketone is converted into 1:6-dinitro- $\beta$ -naphthol by keeping its solution in glacial acetic acid, and into 1-nitro- $\beta$ -naphthol by treating its solution in acetone with aqueous sodium carbonate.

[With E. ROTH.]—4-Chloro-5-acetyl-amino-2-phenyl-2:1:3-benzotriazole,  $\text{NPh} \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_4\text{Cl} \cdot \text{NHAc}$ , m. p. 219°, leaflets, is obtained by passing chlorine into a hot solution of 5-acetyl-amino-2-phenyl-2:1:3-benzotriazole containing sodium acetate. By hydrolysis it yields 4-chloro-5-amino-2-phenyl-2:1:3-benzotriazole,  $\text{C}_{12}\text{H}_9\text{N}_4\text{Cl}$ , m. p. 153°, the solutions of which exhibit a greenish-blue fluorescence which disappears on the addition of acids or alkalis. By the reduction of 6-chloro-5-nitro-2-phenyl-2:1:3-benzotriazole by tin and hydrochloric acid, the authors obtain a dichloroaminophenylbenzotriazole,  $\text{C}_{12}\text{H}_8\text{N}_4\text{Cl}_2$ , m. p. 178°, not the 6-chloro-5-amino-2-phenyl-2:1:3-benzotriazole described by Zincke and Scharff (Abstr., 1910, i, 140). Zincke and Scharff's compound, m. p. 229°, not 221—222° as stated, is formed when the reducing agent is iron and acetic acid.

The diazotisation of 5-amino-2-phenyl-2:1:3-benzotriazole in concentrated sulphuric acid by sodium nitrite in concentrated sulphuric acid yields 2-phenyl-2:1:3-benzotriazole-5-diazonium sulphate,

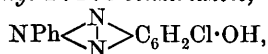


m. p. 142° (decomp.), which can be crystallised from 2*N*-sulphuric acid, and couples normally with dimethylaniline or R-salt. By treating a solution of the diazonium sulphate in 6 parts (by vol.) of concentrated sulphuric acid with 1.5 parts of ice and then heating, 5-hydroxy-

2-phenyl-2:1:3-benzotriazole,  $\text{NPh} \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{OH}$ , m. p. 177°, is

obtained in about 60% yield. The hydroxy-compound, which forms an acetyl derivative, m. p. 98°, is converted, by treating its solution in dilute sodium hydroxide with sodium nitrite and then with dilute sulphuric acid at 0°, into 4-nitroso-5-hydroxy-2-phenyl-2:1:3-benzotriazole, decomp. 185°, which forms metallic derivatives resembling those of nitroso- $\beta$ -naphthol in colour and behaviour.

By passing the calculated quantity of chlorine into its solution in glacial acetic acid, 5-hydroxy-2-phenyl-2:1:3-benzotriazole yields 4-chloro-5-hydroxy-2-phenyl-2:1:3-benzotriazole,

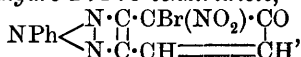


m. p. 149°, which is converted by further chlorination in the same solvent into 4:4-dichloro-5-keto-2-phenyl-4:5-dihydro-2:1:3-benz-

triazole,  $\text{NPh} \begin{smallmatrix} \text{N} \cdot \text{C} \cdot \text{CCl}_2 \cdot \text{CO} \\ | \quad | \\ \text{N} \cdot \text{C} \cdot \text{CH} = \text{CH} \end{smallmatrix}$ , m. p. 165°, yellow plates, which is

reconverted into the chlorohydroxyphenylbenzotriazole by reduction with stannous chloride. 4-Bromo-5-hydroxy-2-phenyl-2:1:3-benzotriazole,  $\text{C}_{12}\text{H}_8\text{ON}_3\text{Br}$ , m. p. 129° (acetyl derivative, m. p. 160°), obtained in a similar manner to the chloro-compound, is converted in

cold chloroform solution by nitric acid, D 1.52, into 4-bromo-4-nitro-5-keto-2-phenyl-4:5-dihydro-2:1:3-benztriazole,



m. p. about 150°, which is converted in cold acetone into 4-nitro-5-hydroxy-2-phenyl-2:1:3-benztriazole,  $\text{C}_{12}\text{H}_9\text{O}_3\text{N}_4$ , m. p. 145°, yellow needles, by aqueous sodium carbonate, and in boiling benzene into 4:5-diketo-2-phenyl-4:5-dihydro-2:1:3-benztriazole, orange-yellow crystals, which sinters at about 160°, but is not melted at 340°. This orthoquinone develops a dark green coloration with alkalis, yields the diazine,  $\text{C}_{18}\text{H}_{11}\text{N}_5$ , m. p. 225°, yellow needles, with *o*-phenylenediamine, and is reduced by acetic acid and zinc to 4:5-dihydroxy-2-phenyl-2:1:3-benztriazole, m. p. 189°, colourless needles (diacetyl derivative, m. p. 158°).

When an alcoholic solution of 5-chloro-2:4-dinitroacetanilide is boiled with phenylhydrazine and hydrated sodium acetate, the initially formed hydrazine is ultimately converted into 5-nitro-6-acetyl-amino-2-phenyl-2:1:3-benztriazole, m. p. 225°, orange needles, by the hydrolysis of which is produced 5-nitro-6-amino-2-phenyl-2:1:3-benztriazole,  $\text{NPh} \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{array} > \text{C}_6\text{H}_2(\text{NO}_2) \cdot \text{NH}_2$ , m. p. 236°, glistening black

prisms. Its reduction by hydrochloric acid and stannous chloride in excess yields 5:6-diamino-2-phenyl-2:1:3-benztriazole, m. p. 244°, colourless crystals, solutions of which exhibit a strong blue fluorescence which disappears on the addition of acids or alkalis. The diacetyl derivative, m. p. 286° (decomp.), is converted by boiling hydrochloric

acid into the iminazole,  $\text{NPh} \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{array} > \text{C}_6\text{H}_2 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} > \text{CMe}$ , m. p. 256°.

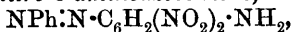
An alcoholic solution of the diamine is converted by sodium nitrite and acetic acid into the azoimide,  $\text{NPh} \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{array} > \text{C}_6\text{H}_2 \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{NH} \end{array} > \text{N}$ , m. p. about 280°, sintering at 250°, and by benzil into the compound,  $\text{NPh} \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{array} > \text{C}_6\text{H}_2 \begin{array}{c} \text{N} \cdot \text{CPh} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{CPh} \end{array}$ , m. p. above 300°, yellow needles.

4:4:7:7-Tetrachloro-5:6-diketo-2-chlorophenyl-4:5:6:7-tetrahydro-2:1:3-benztriazole,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{N} \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{array} > \text{C}_6\text{Cl}_4\text{O}_2 \cdot \frac{1}{2} \text{H}_2\text{O}$ , m. p. 155°

(decomp.), is obtained by exhaustively chlorinating an emulsion of the stannichloride of the preceding diamine in acetic and concentrated hydrochloric acids. It is reduced by stannous chloride and acetic and hydrochloric acids to 4:7-dichloro-5:6-dihydroxy-2-chlorophenyl-2:1:3-benztriazole,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{N} \begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{array} > \text{C}_6\text{Cl}_2(\text{OH})_2$ , m. p. 270°, long needles, which

is converted into, not an orthoquinone, but colourless products by many oxidising reagents. 5-Chloro-2:4-dinitroaniline, when boiled with phenylhydrazine under the conditions in which its acetyl derivative yields a phenyl-2:1:3-benztriazole, is converted into 4:6-dinitro-3-aminodiphenylhydrazine,  $\text{NHPh} \cdot \text{NH} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{NH}_2$ , m. p. 193°, orange needles or prisms (acetyl derivative, m. p. 194°

decomp.), which is oxidised by ferric chloride and boiling glacial acetic acid to 4:6-dinitro-3-aminoazobenzene,



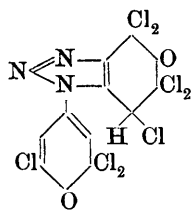
m. p. 200°, red needles (*acetyl* derivative, m. p. 175°).

3-Chloro-4:6-dinitrophenol, m. p. 92°, obtained by boiling 1:3-dichloro-4:6-dinitrobenzene with aqueous sodium carbonate, is unchanged by phenylhydrazine and sodium acetate in boiling alcohol, whilst its *acetyl* derivative, m. p. 69°, is simply hydrolysed under the same conditions.

[With J. Empson].—The nitration by sulphuric and nitric acids at 0° of 5-acetylamino-1-phenyl-1:2:3-benztriazole yields the *acetyl* derivative, m. p. above 300°, yellow needles, of 5-amino-1-p-nitrophenyl-1:2:3-benztriazole,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \begin{smallmatrix} \diagup \text{N} \diagdown \\ \diagdown \text{N} \diagup \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{NH}_2$ , m. p. above 300°, orange-yellow needles, the reduction of which by stannous chloride and acetic acid yields 5-amino-1-p-aminophenyl-1:2:3-benztriazole, colourless needles, m. p. about 60°, re-solidifying at about 90°, and melting again at 154°.

The nitration of 5-acetylamino-1-phenyl-1:2:3-benztriazole by nitric acid, D 1.52, alone yields a dinitro-compound, decomp. 175°, yellow needles, which appears to be 4-nitro-5-nitroamino-1-phenyl-1:2:3-benztriazole,  $\text{C}_{12}\text{H}_8\text{O}_4\text{N}_6$ .

By warming a solution of 5-amino-1-phenyl-1:2:3-benztriazole with acetic anhydride, adding aqueous sodium acetate, and passing chlorine into the boiling solution, 4-chloro-5-acetylamino-1-phenyl-1:2:3-benztriazole, m. p. 178°, is obtained; the base resulting from its hydrolysis has m. p. 151°. By treatment with nitric acid, D 1.52, the *acetyl* derivative yields 4-chloro-5-acetylamino-1-p-nitrophenyl-1:2:3-benztriazole, m. p. 265°. The corresponding base, m. p. above 300°, orange-yellow needles, is reduced by stannous chloride and acetic acid to 4-chloro-5-amino-1-p-aminophenyl-1:2:3-benztriazole, m. p. 234°, the exhaustive chlorination of which in acetic and concentrated hydrochloric acids yields a substance,  $\text{C}_{12}\text{H}_3\text{O}_2\text{N}_3\text{Cl}_8$ , m. p. 180° (decomp.), white prisms, which is also produced by the exhaustive chlorination of 5-amino-1-p-aminophenyl-1:2:3-benztriazole, and receives the annexed formula because it yields 4:6:3':5'-tetrachloro-5:4'-dihydroxy-1-phenyl-1:2:3-benztriazole,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{N} \begin{smallmatrix} \diagup \text{N} \diagdown \\ \diagdown \text{N} \diagup \end{smallmatrix} \text{C}_6\text{HCl}_2 \cdot \text{OH}$ , m. p. 234° (*acetyl* derivative, m. p. 260°), by reduction with stannous chloride and boiling glacial acetic acid.



By diazotising 5-amino-1-phenyl-1:2:3-benztriazole in concentrated sulphuric acid and heating the diluted solution, 5-hydroxy-1-phenyl-1:2:3-benztriazole,  $\text{C}_{12}\text{H}_9\text{ON}_2$ , m. p. 220° (*acetyl* derivative, m. p. 132°), is obtained. By chlorination in acetic acid, it yields, firstly 4-chloro-5-hydroxy-1-phenyl-1:2:3-benztriazole, m. p. 205° (*acetyl* derivative, m. p. 175°), and then 4:4-dichloro-5-keto-1-phenyl-4:5-dihydro-1:2:3-benztriazole,  $\text{N} \begin{smallmatrix} \diagup \text{N} \diagdown \\ \diagdown \text{N} \diagup \end{smallmatrix} \text{C}(\text{CO})\text{Cl}_2 \cdot \text{CH} \begin{smallmatrix} \diagup \text{N} \diagdown \\ \diagdown \text{N} \diagup \end{smallmatrix} \text{C}_6\text{H}_2\text{Cl}_2$ , m. p. 128° (rapidly

heated) or 187° (slowly heated); by reduction, the latter is converted into the former.

The bromination of 5-hydroxy-1-phenyl-1:2:3-benztriazole in glacial acetic acid yields 4-bromo-5-hydroxy-1-phenyl-1:2:3-benztriazole, m. p. 222° (decomp.), together with a small quantity of the keto-bromide.

4-Bromo-4-nitro-5-keto-1-phenyl-4:5-dihydro-1:2:3-benztriazole, obtained by shaking a chloroform solution of the preceding bromo-compound with nitric acid, D 1.52, decomposes at 100° or in boiling benzene, and yields 4:5-diketo-1-phenyl-4:5-dihydro-1:2:3-benztriazole,

$\text{NPh} \begin{smallmatrix} \text{N}^+ \text{N}^- \end{smallmatrix} \text{C}_6\text{H}_2\text{O}_2$ , decomp. 170°, orange-red needles, which is converted into the diazine,  $\text{C}_{13}\text{H}_{11}\text{N}_5$ , m. p. 250°, yellow needles, by *o*-phenylenediamine in glacial acetic acid, and into 4:5-dihydroxy-1-phenyl-1:2:3-benztriazole, m. p. 214°, by sodium hydrogen sulphite and acetic acid.

[With K. NOLL.]—3:5-Dinitro-*p*-xylene-2-diazoperbromide (Zincke and Ellenberger, Abstr., 1905, i, 486) is converted by sunlight, and more rapidly by heat, into 2-bromo-3:5-dinitro-*p*-xylene, m. p. 117°, and by aqueous ammonia at 0° into 3:5-dinitro-*p*-xyl-2-azoimide,  $\text{C}_6\text{HMe}_2(\text{NO}_2)_2 \cdot \text{N}_3$ , m. p. 71–73°, which yields 5-nitro-2:3-dinitroso-*p*-xylene, m. p. 81°, by heating at 105–130°, and 5-nitro-2:3-diamino-*p*-xylene, m. p. 169°, red needles, by reduction by alcoholic sodium sulphide. The diamine yields 6-nitro-4:7-dimethylbenzimidazole,  $\text{CH} \begin{smallmatrix} \text{NH} \\ \text{N} \end{smallmatrix} \text{C}_6\text{HMe}_2 \cdot \text{NO}_2$ , m. p. 221°, by boiling with formic acid, and

5-nitro-4:7-dimethyl-1:2:3-benztriazole,  $\text{N} \begin{smallmatrix} \text{N}^- \\ \text{NH} \end{smallmatrix} \text{C}_6\text{HMe}_2 \cdot \text{NO}_2$ , m. p.

above 300°, by treatment with sodium nitrite and hydrochloric acid in boiling alcoholic solution. The latter is reduced by tin and hydrochloric acid to 5-amino-4:7-dimethyl-1:2:3-benztriazole, m. p. 224° (acetyl derivative, m. p. above 300°), which yields, after diazotisation and heating of the solution, 5-hydroxy-4:7-dimethyl-1:2:3-benztriazole, m. p. 240°, which does not couple with diazonium salts, forms an acetyl derivative, m. p. 211°, and is converted by nitric acid, D 1.52, at 0° into 4-nitro-5-keto-4:7-dimethyl-4:5-dihydro-1:2:3-benztriazole,

$\text{N} \begin{smallmatrix} \text{N}^- \\ \text{NH} \end{smallmatrix} \begin{smallmatrix} \text{C} \cdot \text{CMe}(\text{NO}_2) \cdot \text{CO} \\ \text{C} \cdot \text{CMe} = \text{CH} \end{smallmatrix}$ , m. p. 138° (decomp.). This quinonitrole is converted by boiling glacial acetic acid into 4-hydroxy-5-keto-4:7-dimethyl-4:5-dihydro-1:2:3-benztriazole, m. p. 150° (decomp.). By chlorination in acetic acid, 5-hydroxy-4:7-dimethyl-1:2:3-benztriazole yields 4-chloro-5-keto-4:7-dimethyl-4:5-dihydro-1:2:3-benztriazole, m. p. 170° (decomp.).

4:6:6:7-Tetrachloro-5-keto-4:7-dimethyl-4:5:6:7-tetrahydro-1:2:3-benztriazole,  $\text{N} \begin{smallmatrix} \text{N}^- \\ \text{NH} \end{smallmatrix} \begin{smallmatrix} \text{C} \cdot \text{CMeCl} \cdot \text{CO} \\ \text{C} \cdot \text{CMeCl} \cdot \text{CCl}_2 \end{smallmatrix}$ , m. p. 175° (decomp.), obtained by saturating with chlorine a suspension of 5-amino-4:7-dimethyl-1:2:3-benztriazole in cold acetic and concentrated hydrochloric acids, is reduced by stannous chloride and hydrochloric acid to 6-chloro-5-hydroxy-4:7-dimethyl-1:2:3-benztriazole, m. p. 290° (decomp.) (acetyl derivative, m. p. 234°), which yields, not an ortho-

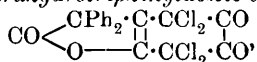
quinone, but an unexamined quinonitrole by oxidation with nitric acid.

[With J. KOHLHAAS.]—The following results show that coumaranone derivatives behave like benzenoid substances. The lactone of 2:4-dihydroxytriphenylacetic acid yields by chlorination or bromination in glacial acetic acid the *lactones* of 5-chloro-2:4-dihydroxytriphenylacetic acid,  $\text{OH} \cdot \text{C}_6\text{H}_2\text{Cl} \langle \text{CPh}_2 \rangle \text{CO}$ , m. p.  $147^\circ$ , of 3:5-dibromo-2:4-

dihydroxytriphenylacetic acid,  $\text{OH} \cdot \text{C}_6\text{HBr}_2 \langle \text{CPh}_2 \rangle \text{CO}$ , m. p.  $164^\circ$ , and of the corresponding bromo-compounds,  $\text{C}_{20}\text{H}_{13}\text{O}_3\text{Br}$ , m. p.  $186^\circ$ , and  $\text{C}_{20}\text{H}_{12}\text{O}_3\text{Br}_2$ , m. p.  $186^\circ$ . By exhaustive chlorination in glacial acetic acid, the lactone of 2:4-dihydroxytriphenylacetic acid yields the pentachloro-compound,  $\text{CO} \langle \text{CPh}_2 \cdot \underset{\text{O}}{\underset{\text{O}}{\text{C}}} \cdot \text{CHCl} \cdot \text{CCl}_2 \text{CO} \rangle$ , m. p.  $207\text{--}209^\circ$  (decomp.), which is converted into the preceding dichlorinated lactone by reduction with stannous chloride.

The nitration by acid, D 1·52, of the lactone of 2:4-dihydroxytriphenylacetic acid in cold glacial acetic acid yields the *lactones* of 5-nitro-2:4-dihydroxytriphenylacetic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_2(\text{OH}) \langle \text{CPh}_2 \rangle \text{CO}$ , m. p.  $183^\circ$  (acetyl derivative, m. p.  $159^\circ$ ), and of 3-nitro-2:4-dihydroxytriphenylacetic acid, m. p.  $147^\circ$  (acetyl derivative, m. p.  $190^\circ$ ). By nitration under similar conditions, the *lactones* of 5-chloro-3-nitro-2:4-dihydroxytriphenylacetic acid, m. p.  $196^\circ$  (decomp.), and of 5-bromo-3-nitro-2:4-dihydroxytriphenylacetic acid, m. p.  $192^\circ$ , have been obtained. The *lactones* of 5-amino-2:4-dihydroxytriphenylacetic acid, m. p.  $281^\circ$  (decomp.) (diacetyl derivative, m. p.  $215^\circ$  [decomp.]), of 3-amino-2:4-dihydroxytriphenylacetic acid, m. p.  $208^\circ$ , and of 5-chloro-3-amino-2:4-dihydroxytriphenylacetic acid, m. p.  $181^\circ$ , have been prepared by the reduction of the corresponding nitro-compounds.

The *lactone*, m. p.  $206^\circ$  (decomp.), of 3:3:6:6-tetrachloro-2-hydroxy-4:5-diketo-3:4:5:6-tetrahydrotriphenylacetic acid,



obtained by the thorough chlorination of a suspension of the lactone of 5-amino-2:4-dihydroxytriphenylacetic acid in acetic and hydrochloric acids, is reduced by stannous chloride and acetic acid to the *lactone*, m. p.  $220^\circ$  (decomp.), of 3:6-dichloro-2:4:5-trihydroxytriphenylacetic acid, which gives a blue coloration with alcoholic ferric chloride. The latter in cold acetic acid is converted by nitric acid,

D 1·4, into the *quinone*,  $\text{CO} \langle \text{CPh}_2 \cdot \underset{\text{O}}{\underset{\text{O}}{\text{C}}} \cdot \text{CCl} \cdot \text{CO} \rangle$ , m. p.  $245^\circ$  (decomp.), red crystals.

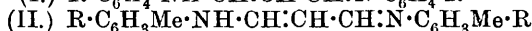
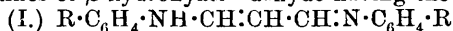
The chlorination of the lactone of 3-amino-2:4-dihydroxytriphenylacetic acid under the same conditions as the preceding isomeride yields an (unexamined) keto-chloride, which by reduction by stannous chloride is converted into the *lactone* of 5:6-dichloro-2:3:4-trihydroxytriphenylacetic acid,  $\text{C}_{20}\text{H}_{12}\text{O}_4\text{Cl}_2$ , m. p.  $212^\circ$  (decomp.) (diacetyl derivative, m. p.  $182^\circ$  [decomp.]), which is oxidised by nitric acid to the

quinone,  $\text{CO} \begin{array}{c} \text{CPh}_2 \cdot \text{C} \cdot \text{CCl} : \text{CCl}_2 \\ \text{O} \text{---} \text{C} \cdot \text{CO} \text{---} \text{CO} \end{array}$ , which crystallises from benzene in garnet-red needles, m. p.  $194^\circ$  (decomp.), containing 1 mol.  $\text{C}_6\text{H}_6$ .  
C. S.

**Action of Cyanuric Chloride on Magnesium Organic Compounds.** ADRIANO OSTROGOVICH (*Chem. Zeit.*, 1912, 36, 738—739).—The interaction of cyanuric chloride and magnesium phenyl bromide in ethereal solution yields successively dichlorophenyltriazine,  $\text{C}_5\text{N}_3\text{Cl}_2\text{Ph}$ , which crystallises in prismatic needles, m. p.  $119\text{--}120^\circ$  (compare Elzanowski, *Diss.*, Freiburg, Switz.), and chlorodiphenyltriazine,  $\text{C}_3\text{N}_3\text{ClPh}_2$ , which forms small, concentrically-arranged, thin needles, m. p.  $135\text{--}136^\circ$  (compare Ephraim, *Abstr.*, 1893, i, 735).  
F. B.

**The Degradation of Monosodium Urate Under the Influence of Radium Emanation-D.** JOHANNES KERB and PAUL LAZARUS (*Biochem. Zeitsch.*, 1912, 42, 82—90).—It has been claimed by Gudzent that radium-D converts the urate into a more soluble substance. The authors could, however, find no difference in the behaviour of a suspension of the urate whether exposed or not exposed to radium, provided that other conditions of experiment were absolutely identical. The increase in the solubility of the suspension depends on other conditions, more especially on the sterility of the mixtures and the alkalinity of the glass of the vessels. When the solution is quite sterile and the material of the vessel is chemically inactive, the urate does not decompose, even in presence of large quantities of emanation-D. There is, however, a rapid degradation of the substance in the presence of moulds.  
S. B. S.

**The Colour and Absorption of the Dirosanilidines of  $\beta$ -Hydroxyacetaldehyde and Formic Acid.** FRITZ REITZENSTEIN and GOTTLIEB BÖNITSCH (*J. pr. Chem.*, 1912, [ii], 86, 1—58. Compare *Abstr.*, 1907, i, 648, and following abstract).—In order to determine the influence of the group  $\cdot\text{CH}:\text{CH}:\text{CH}\cdot$  on the colour of the triphenylmethane dyes, the authors have prepared a number of dirosanilidines of  $\beta$ -hydroxyacetaldehyde having the formulæ:



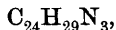
by condensing the isomeric amino-derivatives of tetramethyl-*p*-diaminotriphenylmethane and tetramethyl-*p*-diaminodiphenyltolylmethane with the acetal of propargaldehyde, and spectrographically examined the dyes obtained from them by oxidation [ $\text{R} = 4:4'$ -tetramethyldiaminodiphenylmethyl,  $\cdot\text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ ].

It is found that the introduction of this group produces dyes of a green shade. The position of the absorption bands of the dyes in aqueous or alcoholic solution is tabulated.

The acetal of  $\alpha$ -bromo- $\beta$ -ethoxypropaldehyde, prepared by heating  $\alpha\beta$ -dibromopropaldehyde with 1% alcoholic hydrogen chloride, is a

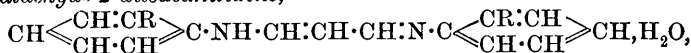
colourless liquid, b. p. 106—112°/15 mm. (compare Fischer and Giebe Abstr., 1898, i, 167).

3'-Amino-4 : 4'-tetramethyldiamino-4''-methyltriphenylmethane,



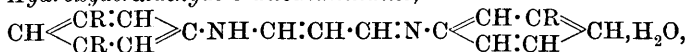
obtained by condensing tetramethyl-*p*-diaminobenzhydrol with *o*-toluidine by means of strong sulphuric acid, forms crystalline, stellar aggregates, and melts at 141° to a pale blue liquid.

When dissolved in dilute hydrochloric acid and the solution heated for one day with the acetal of propargaldehyde on the water-bath, 2''-amino-4 : 4'-tetramethyldiaminotriphenylmethane yields *β*-hydroxyacraldehyde-2-dileucanilidine,



which forms a light yellow powder.

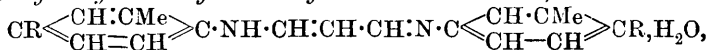
*β*-Hydroxyacraldehyde-3-dileucanilidine,



prepared in a similar manner from 3'-amino-4 : 4'-tetramethyldiaminotriphenylmethane is a yellow powder, sintering at 105°, m. p. 135°; the *hydrochloride* and *platinichloride* are mentioned.

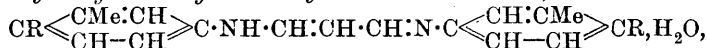
*β*-Hydroxyacraldehyde-4-dileucanilidine is obtained in an impure condition from 4'-amino-4 : 4'-tetramethyldiaminotriphenylmethane; the *picrate*,  $\text{C}_{49}\text{H}_{54}\text{N}_6, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , forms light yellow crystals (decomp. 125°).

*β*-Hydroxyacraldehyde-5-methyl-4-dileucotoluididine,



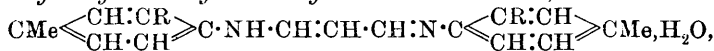
prepared from 4''-amino-4 : 4'-tetramethyldiamino-3''-methyltriphenylmethane, is a yellow, crystalline powder (decomp. 115—120°); the *hydrochloride* is greyish-green.

*β*-Hydroxyacraldehyde-6-methyl-4-dileucotoluididine,



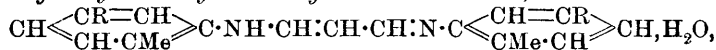
from 4''-amino-4 : 4'-tetramethyldiamino-2''-methyltriphenylmethane, decomposes at 90°, m. p. 130°; the *picrate*,  $\text{C}_{51}\text{H}_{58}\text{N}_6, \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ , has m. p. about 170°, with previous sintering at 92°.

*β*-Hydroxyacraldehyde-5-methyl-2-dileucotoluididine,



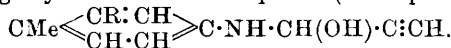
prepared from 6''-amino-4 : 4'-tetramethyldiamino-3''-methyltriphenylmethane, forms a light yellow powder, sintering at 85°, m. p. 120°.

*β*-Hydroxyacraldehyde-4-methyl-3-leucotoluididine,

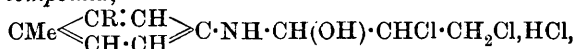


forms a light yellowish-green powder, decomposing at 75°, m. p. 120°.

5''-Amino-4 : 4'-tetramethyldiamino-2''-methyltriphenylmethane combines with propargaldehyde in aqueous solution at a low temperature, yielding the light yellow *additive* compound (decomp. 177°),

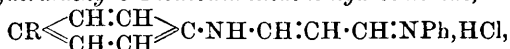


If the combination is effected in the presence of dilute hydrochloric acid, the compound,



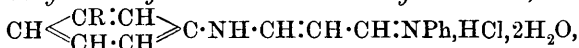
is produced, which crystallises in slender, citron-yellow needles containing  $2\text{H}_2\text{O}$  (decomp.  $253^\circ$ ).

*β-Hydroxyacraldehyde-4-leucodianioline hydrochloride,*



prepared by the addition of 4:4'-tetramethyldiamino-4''-aminotriphenylmethane dissolved in alcoholic hydrogen chloride to an alcoholic solution of the additive compound of aniline and propargaldehyde,  $\text{NHPh} \cdot \text{CH}(\text{OH}) \cdot \text{C} \equiv \text{CH}$  (Claisen, Abstr., 1904, i, 14), forms bluish-green crystals, sintering at  $155^\circ$ , m. p.  $178^\circ$ .

*β-Hydroxyacraldehyde-3-leucodianioline hydrochloride,*



obtained in similar manner from 3''-amino-4:4'-tetramethyldiamino-triphenylmethane, has m. p.  $192^\circ$ , with previous sintering at  $160^\circ$ .

*β-Hydroxyacraldehyde-6-methyl-3-leucodi-p-toluididine hydrochloride,*



prepared from 5''-amino-4:4'-tetramethyldiamino-2''-methyltriphenylmethane and the additive compound of *p*-toluidine and propargaldehyde,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{NH} \cdot \text{CH}(\text{OH}) \cdot \text{C} \equiv \text{CH}$ , is a yellow, crystalline substance, which darkens at  $156^\circ$  and has m. p.  $180^\circ$ .

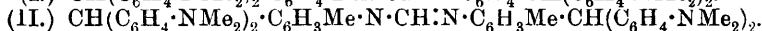
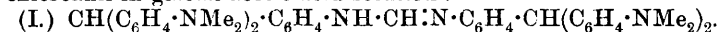
When heated with aniline on the water-bath and the resulting product treated with dilute hydrochloric acid, the acetal of *β*-ethoxyacraldehyde yields the hydrochloride of *β*-hydroxyacraldehydedi-anilidine,  $\text{NHPh} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{NPh}, \text{HCl}$  (Claisen, *loc. cit.*).

*β-Hydroxyacraldehyde-6-methyl-3-dileucotoluididine,*



prepared from 5''-amino-4:4'-tetramethyldiamino-2''-methyltriphenylmethane, is light yellow in colour, and has m. p.  $194^\circ$ . F. B.

**Colour and Absorption of the Dirosanilidines of Formic Acid.** FRITZ REITZENSTEIN and GOTTLIEB BÖNITSCH (*J. pr. Chem.*, 1912, [ii], 86, 58—72).—A description of the preparation of compounds of the following formulæ, together with an account of the spectrographic examination of the dyes obtained from them by oxidation with chloroanil in glacial acetic acid solution:



Di-*m*-tolylformamidine, prepared by heating *m*-toluidine with ethyl orthoformate, forms long, lustrous needles, m. p.  $125^\circ$  (compare Niemietowski, Abstr., 1887, 935).

The condensation of ethyl orthoformate and 4''-amino-4:4'-tetramethyldiaminotriphenylmethane in boiling amyl ether solution gives rise to 4-dileucoformanilidine (formula I), m. p.  $199$ — $200^\circ$ , whilst in 30% acetic acid solution a hydrate,  $\text{C}_{47}\text{H}_{52}\text{N}_6 \cdot 2\text{H}_2\text{O}$ , m. p.  $70^\circ$ , is

produced. When dissolved in a mixture of alcohol and acetic acid, the formanilidine is oxidised by chloroanil to *p*-aminomalachite-green; in glacial acetic acid a blue dye is formed.

Diphenylformamidine condenses with tetramethyldi-*p*-aminobenzhydrol in the presence of concentrated sulphuric acid, yielding the sulphate of 4-dileucoformanilidine,  $C_{44}H_{52}N_6 \cdot H_2SO_4$ , which forms a very light, white powder, decomposing at  $160^\circ$ , m. p.  $200^\circ$ .

*o*-, *m*-, and *p*-Ditolylformamidines condense with tetramethyldi-*p*-aminobenzhydrol in dilute hydrochloric acid solution, yielding compounds of the formula  $C_{24}H_{29}N_3$ ; of these, the ortho-compound is a white powder, m. p.  $140^\circ$ .

The condensation of *o*- and *p*-ditolylformamidines with tetramethyldi-*p*-aminobenzhydrol in the presence of strong sulphuric acid gives rise to compounds,  $C_{49}H_{56}N_6$  (formula II above), of which the ortho-derivative, on oxidation with chloroanil in glacial acetic acid solution, yields a blue dye and the para-derivative a bluish-green. F. B.

**Tetraformaltrisazine from Formaldehyde and Hydrazine Hydrate, a New Reducing Agent for Analytical Chemistry.** KARL A. HOFMANN and DOUGLAS STORM (*Ber.*, 1912, 45, 1725—1730).—

*Tetraformaltrisazine*,  $\begin{array}{c} \text{NH} \cdot \text{CH}_2 \cdot \text{N} \cdot \text{CH}_2 \cdot \text{NH} \\ | \qquad \qquad | \\ \text{NH} \cdot \text{CH}_2 \cdot \text{N} \cdot \text{CH}_2 \cdot \text{NH} \end{array}$ , which is readily prepared from formaldehyde and hydrazine hydrate, is a reducing agent free from alkali and acid, and milder in its action than hydrazine. It crystallises in lustrous, silky, flat needles, sometimes radially grouped, or long, doubly refractive plates pointed at the end; decomp.  $225^\circ$ . It tastes sweet.

The precipitate with mercuric chloride dries to a colourless powder,  $C_4H_{12}N_6 \cdot 3HgCl_2$ . The precipitate with silver nitrate soon changes to a very fine mirror; palladium chloride behaves similarly; gold chloride is reduced to a blue colloid, which is subsequently precipitated as a dark powder. In alkaline solution copper salts are reduced to cuprous oxide, mercury, gold and silver salts to the metal, whilst platinum and palladium chlorides yield stable, deep reddish-brown solutions.

In presence of excess of sodium hydroxide, chromate, molybdate, vanadate, selenite, and tellurite remain unchanged even at  $100^\circ$ , but on addition of ammonium chloride, indigo-blue molybdenum oxide, red selenium, or black tellurium are precipitated.

The compound is very stable towards alkali, but readily decomposed by acids. Carbon dioxide eliminates hydrazine, leaving colourless, polymeric formalazine,  $(CH_2N_2CH_2)_n$ .

Tetraformaltrisazine contains only hydrazine nitrogen. Two of the hydrazine groups are more readily oxidised in alkaline solution than the third.

With benzaldehyde, benzylideneazine and polymeric formalazine are formed.

When formalazine is heated in an atmosphere of nitrogen at  $300$ — $400^\circ$ , a yellow oil distils of objectionable odour. This spontaneously returns to formalazine even in alcoholic solution.

E. F. A.

**Thiophenols. II. *p*:*p*'-Azophenyl Methyl Sulphide and Its Derivatives.** KURT BRAND and A. WIRSING (*Ber.*, 1912, 45, 1757—1771).—*p*:*p*'-Azoxyphenyl methyl sulphide,  $\text{ON}_2(\text{C}_6\text{H}_4\cdot\text{SMe})_2$ , is obtained by the action of *p*-nitrophenyl methyl sulphide (Abstr., 1909, i, 855) on a boiling solution of sodium methoxide in methyl alcohol. It forms light yellow needles, m. p. 135—136°. By digestion on the water-bath for several hours with excess of methyl sulphate, removal of the excess by repeated evaporation with methyl alcohol and water, and precipitation of the aqueous solution with potassium iodide, it gives long, yellow needles, m. p. 130—132° (decomp.), of *p*:*p*'-azoxyphenyldimethylsulphinium iodide,  $\text{ON}_2(\text{C}_6\text{H}_4\cdot\text{SMe}_2\text{I})_2$ .

*p*:*p*'-Hydrazophenyl methyl sulphide,  $\text{N}_2\text{H}_2(\text{C}_6\text{H}_4\cdot\text{SMe})_2$ , is obtained by reducing *p*-nitrophenyl methyl sulphide with zinc dust and sodium hydroxide in alcoholic solution. When pure, it forms colourless crystals, m. p. 104°; it is oxidised to the azo-compound when air is passed through the alcoholic solution. Treatment with concentrated hydrochloric acid does not give rise to a semidine transformation, but produces *p*-aminophenyl methyl sulphide hydrochloride (Abstr., 1911, i, 39, 285), the oxygen thereby becoming available forming *p*:*p*'-azophenyl methyl sulphide and other oxidation products.

*p*:*p*'-Azophenyl methyl sulphide,  $\text{N}_2(\text{C}_6\text{H}_4\cdot\text{SMe})_2$ , is prepared by reducing *p*-nitrophenyl methyl sulphide with zinc dust and sodium hydroxide, and oxidising the filtered solution by passing air through it. It forms yellowish-red leaflets, and has m. p. 177—178°. With concentrated mineral acids and strong organic acids, it gives deep blue solutions; the formation of this colour is a very delicate test for traces of the compound. When dry hydrogen chloride is led into a chloroform solution, blue needles, with a metallic glance, of *p*:*p*'-azophenyl methyl sulphide hydrochloride are precipitated, but they lose hydrogen chloride even on filtering.

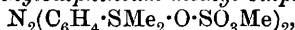
*p*:*p*'-Azophenyl methyl sulphide sulphate,  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}_2\cdot 2\text{H}_2\text{SO}_4$ , is obtained as shining, green needles, when a solution of the sulphide in glacial acetic acid is precipitated with concentrated sulphuric acid. The trichloroacetate,  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}_2\cdot 2\text{CCl}_3\cdot\text{CO}_2\text{H}$ , is produced by mixing chloroform solutions of the sulphide and trichloroacetic acid; it forms green, shining needles, possessing a strong metallic glance. Cryoscopic measurements in trichloroacetic acid as solvent indicate that the salt is unimolecular.

The following double salts have also been obtained:

$\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}_2\cdot\text{HCl}\cdot\text{HgCl}_2$ ,  
indigo-blue crystals;  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}_2\cdot\text{HCl}\cdot\text{FeCl}_3$ , green leaflets;  
 $(\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}_2\cdot\text{HCl})_2\cdot\text{FeCl}_3$ ,

bluish-violet needles having a green shimmer;  $\text{C}_{14}\text{H}_{14}\text{N}_2\text{S}_2\cdot\text{HCl}\cdot\text{SnCl}_4$ , green leaflets. They were prepared by the action of *p*:*p*'-azophenyl methyl sulphide with the metallic chloride in glacial acetic acid solution, the addition of hydrochloric acid being necessary in the case of the first and third salt.

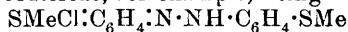
*p*:*p*'-Azophenyldimethylsulphinium methyl sulphate,



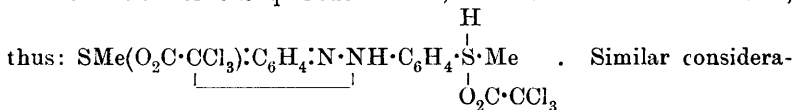
is obtained by digesting azophenyl methyl sulphide with excess of methyl sulphate on the water-bath until the blue colour changes to

red and the product is completely soluble in water. It forms thick, red crystals, which commence to decompose at  $170^{\circ}$ , and blacken at  $185$ — $190^{\circ}$ . When the aqueous solution is treated with potassium iodide, slender, yellowish-red needles of *p*:*p'*-azophenyldimethylsulphinium iodide,  $N_2(C_6H_4 \cdot SMe_2I)_2$ , are obtained, m. p.  $174$ — $175^{\circ}$ . The corresponding *sulphinium bromide*,  $N_2(C_6H_4 \cdot SMe_2Br)_2$ , forms yellowish-brown needles, and has m. p.  $174^{\circ}$ . The chloride could only be obtained in solution.

The blue colour produced when *p*:*p'*-azophenyl methyl sulphide is treated with acids is ascribed to the formation of a quinonoid isomeride, the hydrochloride, for example, being



(compare Hantzsch, Abstr., 1908, i, 469, 484). In the case of the trichloroacetate and sulphate, the one molecule of acid is concerned in the formation of the quinonoid form, the other in salt formation,



T. S. P.

**New Azo-colouring Matters from Aminodiphenylene Oxide.** ALPHONSE MAILHE (*Compt. rend.*, 1912, 154, 1815—1817).—Nitrodiphenylene oxide is readily reduced by iron and hydrochloric acid to the corresponding amine, which is easily diazotised. The diazonium salts can very readily be coupled with amines and phenols, giving azo-dyes (compare Borsche and Bothe, Abstr., 1908, i, 528).

With aniline, the diazonium chloride yields *anilineazodiphenylene oxide*,  $O < \underset{C_6H_3N : N \cdot C_6H_4 \cdot NH_2}{C_6H_4}$ , yellow crystals, m. p.  $93^{\circ}$ , giving a red solution in acids, which dyes silk orange-yellow. Other such azo-compounds have been prepared by coupling with *m*-toluidine, dimethylaniline, diphenylamine, and  $\alpha$ - and  $\beta$ -naphthylamine. They are mostly yellow in colour, and in the case of the last three, the azo-compounds when in solution are turned deep blue by mineral acids.

Diphenylene oxide diazonium chloride has also been coupled up with a number of phenols, the following azo-compounds having been obtained:  $O < \underset{C_6H_3N : N \cdot C_{10}H_6 \cdot OH(\beta)}{C_6H_4}$ , a brown powder, m. p.  $95^{\circ}$ .

$O < \underset{C_6H_3N : N \cdot C_{10}H_4}{C_6H_4} < \underset{[2]}{(SO_3H)_2[6 : 8] \cdot OH}$ , which gives a red solution in alcohol and presents a different absorption spectrum to the corresponding benzene azo-compound.

$O < \underset{C_6H_3N : N \cdot C_{10}H_5}{C_6H_4} < \underset{[2]}{SO_3H[8] \cdot OH}$ , orange-red crystals, which in an acid medium dye silk orange-yellow.

$O < \underset{C_6H_3N : N \cdot C_{10}H_4}{C_6H_4} < \underset{[2]}{(SO_3H)_2[3 : 6] \cdot OH}$ , a scarlet dye, which on silk

dyes a bright red. Its solution is turned carmine by sulphuric acid. It shows a remarkable absorption spectrum. All the rays above  $0.580\mu$  being absorbed.

By coupling with salicylic acid, an *azo-compound* is obtained, furnishing yellow crystals, which, when mordanted with chromium, dye an orange-yellow.

The above *azo-compounds* differ from the corresponding benzeneazo-compounds in their absorption spectra, and in that they possess brighter colours.

W. G.

**The Production of Carbamide by Hydrolysis of Proteins.** ROBERT FOSSE (*Compt. rend.*, 1912, 154, 1819—1821).—Proteins are hydrolysed by aqueous solutions of potassium, sodium or barium hydroxide, or potassium or sodium carbonate, and even by a suspension of pure slaked lime in water, carbamide being one of the products. Water, alone or acidified with acetic acid, does not produce this result. The quantity of carbamide produced from gelatin and a boiling solution of potassium hydroxide increases at first very rapidly, attains a maximum, and then slowly decreases.

W. G.

**Changes in the Physical Conditions of Colloids. XIII. The Relationship of Albumin to Inorganic Colloids and to the Salts of the Heavy Metals.** WOLFGANG PAULI and LEO FLECKER (*Biochem. Zeitsch.*, 1912, 41, 461—512. Compare Abstr., 1909, i, 618; 1910, i, 344).—For the purpose of the experiments, ox-serum albumin which had been submitted to a dialysis against distilled water lasting eight weeks, and the following inorganic colloids were employed: Ferric hydroxide, chromic hydroxide (positive colloids), and the sulphides of arsenic, antimony, copper, cadmium, and gold, and tungstic and molybdic acids (negative colloids). It was found that the suspensoids (colloids precipitated by small quantities of salts), as contrasted with the lyocolloids (colloids requiring larger concentrations of salts for precipitation), show no inhibition of precipitation of proteins when present in excess, and electrolytes invariably inhibit the precipitation of the protein-colloid complex. The protein precipitates by lyocolloids, on the other hand, are soluble in excess of the colloid, and in presence of excess of a lyocolloid, the presence of neutral salts favours the precipitation, and alkalis favour the precipitation when positive lyocolloids are present, acids favouring precipitation in the presence of the negative lyocolloids. Only when the protein is in excess do electrolytes inhibit the precipitation in the presence of lyocolloids, whereas under all conditions in the mixtures of suspensoids and proteins, they exert an inhibitory action on the precipitation. The precipitate of a suspensoid in the presence of protein contains only a fraction of the protein, whereas the precipitate in the presence of a lyocolloid contains the greater part, if not the whole, of the protein. The difference between the lyophobic suspensoids and the lyocolloids depends on the fact that the former are not stable unless minute quantities of electrolyte are present, for on prolonged dialysis they are precipitated. When brought into contact with protein free from electrolytes, the protein takes up the electrolytes, and produces an irreversible precipitate of the suspensoid. If

salts are present in the system, these will form adsorption compounds with the protein, and the latter will, therefore, not so readily adsorb the electrolytes from the suspensoid, which render the latter stable; hence, the inhibitory action of the salts on the precipitation of suspensoids by protein. The protective action of salts is, however, greater than that which can be accounted for by the above explanation. The authors explain this phenomenon on the assumption that the protein enters into combination with the salt in the method already postulated in Pauli's former papers, and yields a stable complex of colloid-protein-salt. The relationships between lyocolloids and proteins are the same as those between any two colloids of opposite charges, the complex formed taking the charge of that substance which is in excess. In this connexion it must be remembered that the protein can function both as an acid and a base.

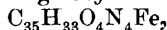
The precipitation of proteins by salts of heavy metals was also investigated. This phenomenon belongs to the group of irregular series ("unregelmässige Reihen"). If the protein be mixed with the salt in low concentrations, a precipitate is formed. In higher concentrations, the mixture remains clear over a certain zone, with the re-formation of a precipitate when the concentration reaches still higher limits. The precipitation in the lower limits of salt concentration is explained on the assumption that the salt undergoes hydrolytic dissociation, and that the metallic oxide enters into combination with the protein, owing to the fact that the acidic functions of the latter are stronger than the basic functions. In this case, the anion of the salt can be detected in the dialysate of the complex. The metallic salts thus formed are assumed to be internal anhydrides. If, however, excess of the metal is present, another complex is formed, with the production of an electrically charged protein complex, the formation of which may be represented as follows (in the case of the iron compounds):  $(x\text{Fe}(\text{OH})_3 \cdot \text{Protein}) + y\text{FeCl}_3 = x(\text{Fe}(\text{OH})_3 \cdot \text{Protein}) y\text{Fe} \cdot + 3y\text{Cl}$ . New coloured ions with positive charge are thus formed, the number of which is diminished by presence of excess of the metallic salt. According to Pauli's theory, the protein ions are heavily hydrated, and when these ions are present in the largest quantity, the viscosity of the mixture will attain a maximum. The measurement of viscosities over the zone of no-precipitation of ferric chloride-protein mixture reveals the presence of a mixture of maximum viscosity, which viscosity diminishes in mixtures containing larger quantities of metallic salt. The mixture with this maximum viscosity also shows the greatest amount of translation when placed in an electric field and investigated by the method of electrocataphoresis. It also shows the maximum diminution of electrolytic conductivity, and the absence of free  $\text{Fe}'$  ions in the mixture. The commencing point of reprecipitation in the highest zone is a function of the anion, the action of which is discussed by the authors.

S. B. S.

The Nature of So-called Artificial Globulin. ROBERT BANKS GIBSON (*J. Biol. Chem.*, 1912, 12, 61—64).—Moll's artificial serum-globulin is an intermediate step in the formation of alkali metaprotein.

W. D. H.

**Constitution of Hæmin.** WILLIAM KÜSTER (*Ber.*, 1912, 45, 1935—1946).—[With A. GREINER.]—The crude product obtained in the preparation of "hæmin" by Mörner's method is extracted with boiling benzene and then with chloroform at the ordinary temperature. The extracts are evaporated, leaving a residue consisting of *methylhæmin*,  $C_{35}H_{34}O_4N_4ClFe$ , large, brown rhombs, and a little dimethylhæmin. Methylhæmin is soluble in 0.2% sodium hydroxide and in hot aqueous sodium carbonate; during solution, the chlorine is displaced, although not quantitatively. The halogen is also removed by treatment with aniline, yielding *dehydrochloromethylhæmin*,



an almost black powder, the solution of which in methyl alcohol and a few drops of dilute sulphuric acid yields the hæmin again by precipitation with hydrochloric acid. Dimethylhæmin is soluble in benzene, but is finally converted into an almost insoluble modification.

The methylation of acethæmin by Nencki's method yields methylhæmin, dimethylhæmin, and a *substance*,  $C_{37}H_{39}O_4N_4Cl_2Fe$ , m. p. 154—160°, which is apparently an additive compound of methyl chloride and dimethylhæmin.

[With P. DEIHLE].—Hæmatoporphyrin, prepared by the Nencki-Zaleski method, yields a *dimethyl* ester,  $C_{36}H_{42}O_6N_4$ , by treatment with alkali and methyl sulphate, but by repeated solution in acetone and precipitation by water, it is gradually converted into an *anhydro*-compound,  $C_{34}H_{36}O_5N_4$ , which is scarcely attacked by alkali and methyl sulphate, but is converted into a *dimethyl* ester,  $C_{36}H_{40}O_5N_4$ , by methyl alcohol and hydrogen chloride.

The product obtained by the action of hydrogen bromide in acetic acid on hæmin is converted by treatment with methyl alcoholic potassium hydroxide into a blackish-red, crystalline *substance* containing four methoxy-groups. Mesoporphyrin, obtained from acethæmin by Zaleski's hydrogen iodide process, is oxidised by chromic and sulphuric acids, yielding methylethylmaleimide and hæmatic acid.

The preceding experiments lead the author to the view that two of the nitrogen atoms in hæmin are basic, and are so related to the two carboxyl groups that one nitrogen is united with one carboxyl group as a betaine complex, the other nitrogen is united with the ferri-chloride group, leaving one carboxyl group, which alone can be easily esterified. These views are developed to explain what occurs in the molecule when hæmin is converted into hæmatoporphyrin and into mesoporphyrin.

C. S.

**The Formation of Guanylic Acid from Yeast Nucleic Acid.** WALTER JONES (*J. Biol. Chem.*, 1912, 12, 31—35).—The methods at present in vogue for obtaining guanosine are difficult. In the present research an abundant yield was obtained by the action of pig's pancreas on yeast-nucleic acid. The digest was boiled, filtered, and treated at the boiling point with lead acetate. On cooling, the filtrate deposited a granular lead compound, which was filtered off, suspended in hot water, and decomposed with hydrogen sulphide. The filtrate from the lead sulphide was treated with potassium acetate

and poured into excess of alcohol. The precipitate so obtained was washed with alcohol and dried. It was purified by a repetition of the process, and was then found to possess the properties of the potassium salt of guanylic acid. The yield was 50% of the theoretical, and so large amounts are readily prepared. The active agent concerned in the reaction is destroyed by heat, and is more active at 40° than at 20°, but it is doubtful if it is a true catalyst, since a given amount of the pancreatic extract will decompose a given amount of yeast-nucleic acid and no more. It is suggested that the term *tetranuclease* should be given to it. It is probable that there are several tetranucleases, for this one has no action on thymus-nucleic acid. These two tetranucleotides also differ in their carbohydrate radicle: that in yeast-nucleic acid being *d*-ribose, that in thymus-nucleic acid being a hexose.

W. D. H.

**Digestion of Casein by Pepsin from the Calf, Pig, and Ox.** W. VAN DAM (*Zeitsch. physiol. Chem.*, 1912, 79, 247—273. Compare Abstr., 1910, i, 290).—Recent literature concerning the identity of pepsin and chymosin is discussed critically. The digestion of casein by the stomach enzymes of pig, calf, and ox is studied in solutions of hydrochloric acid, sodium dihydrogen phosphate, mixtures of hydrochloric acid and also of acetic acid with sodium acetate; in short, in solutions of such hydrogen ion concentration that casein is not soluble in them. It is in all respects parallel to the rate of clotting. Thus in 0.3*N*-hydrogen chloride solution there is the same difference in the rate of digestion and clotting as in experiments by Mett's method. The products of digestion in strongly and weakly acid solutions are identical. There are no grounds for assuming the two enzymes are not the same.

E. F. A.

**Action of Trypsin. II. (a) The Influence of the Products of Hydrolysis on the Rate of Hydrolysis of Caseinogen by Trypsin. (b) The Autohydrolysis of the Caseinates.** E. H. WALTERS (*J. Biol. Chem.*, 1912, 12, 42—54).—The products of the tryptic digestion of caseinogen have a slight impeding action on the velocity of the reaction, and this increases as the quantity of products increases. When a filtered solution of Grubler's trypsin is heated to 40°, a white, flocculent precipitate separates, and the filtrate from this contains the active hydrolysing agent. Neutral caseinogenates of lithium, sodium, and potassium in sterile solutions undergo autohydrolysis, 5% being hydrolysed in ninety-six hours at 57°. The basic caseinogenates undergo autohydrolysis rather more rapidly. The velocity constant for this change in the basic compounds of calcium and barium is about three times as great as that for the lithium and sodium compounds, indicating that some factor other than hydrogen or hydroxyl ions plays a part. Strong, but not weak, solutions of these salts have a slight tendency to coagulate after a long time. The velocity constant calculated from the unimolecular formula diminishes as the reaction proceeds, and this rapid falling off cannot be accounted for by the influence of the products of hydrolysis. The temperature-coefficient for the autohydrolysis of basic sodium caseinogenate between

37° and 73° is 7. The incomplete nature of autohydrolysis indicates that in the hydrolysis of caseinogen by trypsin (a unimolecular reaction) the position of equilibrium is shifted in the direction protein  $\rightarrow$  products by the enzyme. W. D. H.

**The Action of Proteolytic Enzymes on Clupein.** F. Rogoziński (*Zeitsch. physiol. Chem.*, 1912, 79, 398—414).—Trypsin, pancreatin, pancreatic fistula juice, and erepsin produce a rapid and extensive proteolysis of the clupein molecule, which is similar to that caused by boiling with mineral acids. Papain,  $\beta$ -lieno-protease (from spleen), and yeast juice act more feebly. The splenic enzyme is the strongest and yeast juice the weakest of the three. Pepsin-hydrochloric acid produces no recognisable effect on this protamine.

W. D. H.

**Cleavage of Carbohydrates by Diastase.** H. Bierry (*Bied. Zentr.*, 1912, 41, 504; from *Bot. Centr.*, 1911, 117, 568).—Certain diastases of mammals, such as amylase, maltase, and sucrase, require the presence of electrolytes, the electronegative ion having an especially important rôle. The original paper contains results of an investigation of ferments which cause the cleavage of hydrolysed sugars, with methods for collecting animal digestive liquids and for estimating the sugar in the digestive solutions. N. H. J. M.

**The Condition of Malt Diastase after it has Acted.** HENRI VAN LAER (*Bull. Soc. chim. Belg.*, 1912, 26, 223—226).—The peculiarities exhibited in a starch conversion by diastase are due to the adsorption compounds formed by the enzyme with the substrate and with the products of the reaction.

It is shown that diastase is recovered unaltered at the close of the reaction, and that it is just as active towards a second quantity of starch as an equal portion of fresh diastase, provided the temperature selected is one at which the enzyme is not destroyed. Diastase thus conforms strictly to Ostwald's definition of a catalyst. E. F. A.

**The Synthesising and Hydrolysing Actions of Emulsin in Alcoholic Solution.** ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1912, 154, 1737—1739, and *J. Pharm. Chim.*, 1912, [vii], 6, 13—18. Compare Abstr., 1911, i, 1053; this vol., i, 522).—Emulsin acting on a solution of dextrose in 85% alcohol forms  $\beta$ -ethyl glucoside, which, on the other hand, it hydrolyses in aqueous solution.  $\beta$ -Ethyl glucoside, so prepared, is converted into its *d*-isomeride by the action of alcoholic hydrogen chloride. A similar synthesising action takes place with dextrose in other alcohols, giving the corresponding glucosides. This has been effected with methyl, propyl, and *isobutyl* alcohols.

When emulsin acts on a glucoside in alcoholic solution, the first effect is to hydrolyse the glucoside, and then the dextrose so formed unites with the alcohol to give an alkyl glucoside. W. G.

## Organic Chemistry.

Action of Ozone on Organic Compounds. III. CARL D. HARRIES (*Annalen*, 1912, 390, 235—268).—The object of the present investigation is to explain the formation of ozonides containing an amount of oxygen greater than that corresponding with the degree of unsaturation of the organic compound. The author is of opinion that the ozonised oxygen produced by the silent discharge in a 10-tube ozoniser is a mixture of different modifications of oxygen, and contains oxozone,  $O_4$ , in addition to ozone. By treating the crude mixture with sodium hydroxide and with concentrated sulphuric acid, the oxozone is destroyed and the purified gas produces normal ozonides only.

[With FRITZ EVERS.]— $\Delta^{\beta}$ -Butylene is prepared from purified *sec.*-butyl alcohol by distillation with phosphoric oxide. It is shown to be free from isomerides, and consists probably almost entirely of the *cis*-modification; the presence of a little of the *trans*-form probably will not be of importance in the following experiments, because the ozonides of ethylenic stereoisomerides (for example, those of oleic and elaidic acids) scarcely differ in behaviour.

The butylene is ozonised by the Harries-Koetschau method; the methyl chloride used as solvent is specially treated to free it from unsaturated impurities. The ozonised oxygen contains 11—14% of "crude ozone." After being washed with 5% sodium hydroxide and with concentrated sulphuric acid, the gas contains 5.8—9.3% of "pure ozone." This mixture still contains moisture, which is removed by passing the gas through coils cooled by ether-carbon dioxide. By treatment with "pure" ozone,  $\Delta^{\beta}$ -butylene gives, after the evaporation of the solvent, a 75% yield of a viscous oil, which is separated by distillation under reduced pressure into *butylene ozonide*,  $O \begin{smallmatrix} \diagup O \cdot CHMe \\ \diagdown O \cdot CHMe \end{smallmatrix}$ ,

b. p. 15—16°/20 mm.,  $D_{20}^{25}$  1.0217,  $n_D^{25}$  1.38546, a colourless liquid having a stupefying odour and dissolving readily in water, and *bisbutylene ozonide*,  $(C_4H_8O_3)_2$ , an extremely viscous, almost odourless, non-volatile liquid, which explodes at about 125°.

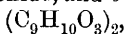
By treatment with "crude" ozone in a similar manner,  $\Delta^{\beta}$ -butylene gives an 86% yield of a viscous liquid which is separated by distillation under reduced pressure into impure *butylene oxozonide*,  $C_4H_8O_4$ , b. p. 20—22°/22 mm.,  $D_{20}^{20}$  1.0336,  $n_D^{20}$  1.38404, and *bisbutylene oxozonide*,  $(C_4H_8O_4)_2$ , a viscous liquid having an odour of paraldehyde, exploding at 125°, and having  $D_{19}^{19}$  1.1604 and  $n_D$  1.43167.

By further treatment with "crude" ozone, butylene ozonide remains unchanged, whilst the bimolecular form is converted into bisbutylene oxozonide. By treatment with water, butylene oxozonide undergoes extensive decomposition at once, but the bimolecular form appears to change, at least in part, to the bimolecular form of the normal ozonide.

All four substances are decomposed by boiling water, yielding acetaldehyde, acetic acid, hydrogen peroxide, and oxygen. The rate

of the decomposition has been determined by estimating after definite intervals of time the amount of acetic acid and also the active oxygen by aqueous potassium iodide.

[With ERIK RIEDL VON RIEDENSTEIN.]—The ozonisation of allylbenzene is effected in carbon tetrachloride. With "pure" ozone, the product is a viscous, malodorous liquid, which is separated by fractional distillation into *phenylallyl ozonide*,  $\text{O} \begin{smallmatrix} \text{O} \cdot \text{CH}_2 \\ \text{O} \cdot \text{CH} \cdot \text{CH}_2 \text{Ph} \end{smallmatrix}$ , b. p. 67–71°/0.4–0.8 mm.,  $D_{21}^{21}$  1.1362,  $n_D^{21}$  1.51371,  $n_D^{21}$  1.51761,  $n_D^{21}$  1.53722, a colourless, mobile liquid which explodes feebly when heated, and is much less odorous than the crude ozonide, and *bisphenylallyl ozonide*,



a viscous, colourless, non-volatile liquid which explodes at 104–106°, and has  $D_{21}^{21}$  1.1766 and  $n_D^{21}$  1.54216. Both ozonides are only slightly attacked by boiling water, but are easily decomposed by hot glacial acetic acid, yielding thereby formaldehyde, phenylacetaldehyde and its peroxide, and phenylacetic acid.

When ozonised in hexane by "crude" ozone, allylbenzene yields an explosive white substance, which has absorbed considerably more oxygen than the compounds described previously; probably ozone has also entered the benzene nucleus, since the product of decomposition is a viscous, brown oil having powerful reducing properties.

Propenylbenzene in carbon tetrachloride yields with "pure" ozone a yellow oil, which rapidly decomposes with the formation of benzoic acid, and with "crude" ozone a viscous oil which also rapidly decomposes, but appears to contain an amount of oxygen greater than that corresponding with a mono-ozonide. The difference of behaviour of allylbenzene and propenylbenzene towards "pure" ozone is utilised to show that allylbenzene is converted into propenylbenzene by boiling alcoholic potassium hydroxide.

$\alpha$ -Methylstyrene, which is prepared best by heating phenyl-dimethylcarbinyl chloride and pyridine at 120°, is converted by "pure" ozone into an unstable *ozonide* (probably a mixture of the mono- and the bi-molecular normal ozonides), which decomposes in hot glacial acetic acid, yielding oxygen, formaldehyde, acetophenone, and a crystalline *substance*, m. p. 182–183°, which is assumed to be bimolecular acetophenone peroxide. C. S.

**The Decomposition of Bromoform.** GEORGE J. SARGENT (*J. Physical Chem.*, 1912, 16, 407–420).—The experiments made by Gladstone and Tribe (1875) on the reduction of bromoform in alcoholic solution by the zinc-copper couple have been repeated.

The gaseous products are mainly methane and acetylene. The yield of acetylene rises from 13.5% to 22.3% as the concentration of the bromoform is increased from 1:4 to 4:5 of alcohol. When one part of water was added to the 1:4 solution, the yield of acetylene was 30.6% instead of 13.5%. It is suggested that the bromoform molecule is less protected by the solvent in presence of water in which it is less soluble. The addition of benzene instead of water does not materially increase the yield of acetylene.

The results are discussed in relation to the question of the con-

stitution of iron carbide in cast iron, etc. It is supposed that in the reduction of bromoform the radicle  $\text{CH:}$  is liberated and is either polymerised or reduced according to circumstances. Similarly, in the decomposition of iron carbide the radicle  $\text{CH}_2:$  is liberated, and polymerises to ethylene, butylene, etc., or is reduced to ethane, etc.

It is therefore unnecessary to postulate the existence of a series of isomorphous iron carbides of general formula  $(\text{CFe}_3)_n$  to account for the various hydrocarbons obtained (compare Campbell, Abstr., 1897, ii, 214). The same argument applies to uranium carbide and other carbides which yield a variety of gaseous products. R. J. C.

**The Yield in the Grignard Reaction.** PIERRE JOLIBOIS (*Compt. rend.*, 1912, 155, 213—215).—In preparing magnesium ethyl iodide by the interaction of magnesium and ethyl iodide in dry ether, if the whole of the ethyl iodide is present at the start, a yield of about 41% is obtained, there being an evolution of ethane and ethylene (compare Cahours, *Annalen*, 1860, 114, 240, and Löhr, Abstr., 1891, 682). If, on the other hand, the ethyl iodide is added drop by drop as the magnesium dissolves, the yield is 91%. The amount of Grignard reagent formed can be measured by titration with an ethereal solution of iodine:  $\text{MgEtI} + 2\text{I} = \text{MgI}_2 + \text{EtI}$ .

If to the Grignard reagent, carefully prepared and freed from ether, an excess of ethyl iodide is added, decomposition takes place according to the equation:  $\text{MgEtI} + \text{EtI} = \text{MgI}_2 + \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$ .

In the preparation of a magnesium alkyl iodide, it must not be left in contact with an excess of the alkyl iodide, and if it is required to use a known quantity, it is possible by means of the ethereal iodine solution to estimate the active magnesium. W. G.

**Action of Hydrogen Peroxide on Glycerol.** JEAN EFFRONT (*Bull. Soc. chim.*, 1912, [iv], 11, 744—747).—When a mixture of hydrogen peroxide (10 volumes) with glycerol is distilled, with occasional fresh additions of hydrogen peroxide, the glycerol is quantitatively oxidised to two molecules of formic acid and one of carbon dioxide.

Examination of the liquid when the above oxidation has not been completed, demonstrates the presence of glyceric and glycollic acids as intermediate products.

Attention is drawn to the rather striking analogy between the action of hydrogen peroxide and of enzymes on proteins, amino-acids, etc. (compare Effront, this vol., i, 534). D. F. T.

**Constitution of the Complex Metallic Salts of the Fatty Acids.** J. V. DUBSKY (*Chem. Weekblad*, 1912, 9, 562—564).—A review of earlier work on the complex metallic salts of the fatty acids, and a suggested graphic representation of the configuration of compounds of the type  $[\text{Me}_3\text{Ac}_6]\text{X}_3$ , in which Ac represents a fatty acid residue. A. J. W.

**Ghedda or East Indian Wax.** ANDREAS LIPP and EUGEN KUHN (*J. pr. Chem.*, 1912, [ii], 86, 184—199).—The wax differs from ordinary beeswax in containing only one alcohol, namely, ceryl alcohol, which is present mainly in the form of esters.

It has m. p. 62—63°, acid value 5—7·5, ester value 86—92, and solidifies at 59—58°.

The alcohols and hydrocarbons present in the wax were isolated by hydrolysing it with alcoholic potassium hydroxide, neutralising the excess of alkali with hydrochloric acid, and fractionally extracting the solid, obtained by evaporation of the resulting solution, with light petroleum. The first three fractions yielded a mixture of ceryl alcohol and two hydrocarbons,  $C_{26}H_{54}$  and  $C_{30}H_{62}$ , which crystallise in lustrous, silvery leaflets, m. p. 58° and 70° respectively, and are probably identical with the hydrocarbons (m. p. 59·5° and 68°) isolated from ordinary beeswax by Schwalb (Abstr., 1885, 962; 1887, 124). The remaining fractions yielded ceryl alcohol, which has m. p. 76°, and yields a *benzoyl* derivative crystallising in small, white needles, m. p. 53·5°.

The identity of the alcohol was established by its conversion into cerotic acid by heating it with soda-lime.

Cerotic acid has m. p. 77·5—78°; the methyl ester, m. p. 60°; the amide, m. p. 106°, and *anilide*, m. p. 97°, crystallise in slender, white needles (compare Marie, Abstr., 1896, 346). F. B.

**The Properties of Phytin.** M. A. JEGOROFF (*Biochem. Zeitsch.*, 1912, 42, 432—439).—The author calls attention to the differences in the properties of various phytin preparations as regards their precipitability by molybdate solution. He confirms Starkenstein's results, which show that more substance is precipitated from a solution by molybdate after drying than before, and there is little difference in this respect whether the preparation is dried at the ordinary temperature in a vacuum or at 100°. The substance is more readily dried and loses more weight in an indifferent gas than in air. More precipitate is also obtained after treatment with hydrogen peroxide. The author has succeeded by means of dialysis in separating commercial phytin into three fractions, of which one is found in the dialysate, the second as an insoluble precipitate in the dialysor, and the third in solution in the dialysor. He criticises certain recent papers in which the existence of a phytase is claimed, and draws the conclusion that the existence of such an enzyme has not been proved. S. B. S.

**Phytin and Phosphoric Acid Esters of Inositol.** II. R. J. ANDERSON (*J. Biol. Chem.*, 1912, 12, 97—113. Compare this vol., i, 607).—The following salts of phytic acid have been prepared:

*Calcium magnesium potassium phytate*,  $C_6H_{12}O_{27}P_6Ca_5Mg_2K_2$ , a colourless, amorphous powder.

*Penta-calcium phytate*,  $C_6H_{14}O_{27}P_6Ca_5$ , obtained by precipitating phytic acid with calcium acetate.

*Tetra-calcium phytate*,  $C_6H_{16}O_{27}P_6Ca_4 \cdot 12H_2O$ , is a semicrystalline or granular powder.

*Penta-magnesium phytate*,  $C_6H_{14}O_{27}P_6Mg_5 \cdot 24H_2O$ , is a crystalline powder.

*Hexa-cupric phytate*,  $C_6H_{12}O_{27}P_6Cu_6$ , formed on precipitating phytic acid with copper acetate.

*Octa-silver phytate* is an amorphous powder.

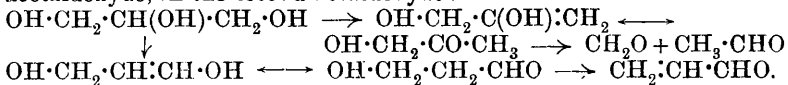
*Hepta-silver phytate*,  $C_6H_{17}O_{27}P_6Ag_7$ , is formed on precipitating the dilute nitric acid solution of the octa-silver phytate with alcohol.

On heating inositol with dry pyrophosphoric acid (3 mols.) at  $200-220^\circ$ , a *dipyrophosphoric ester* of inositol is obtained. To purify it, the mixture is boiled with dilute hydrochloric acid to transform pyrophosphoric acid into orthophosphoric acid, and the inositol derivative is then precipitated by the addition of barium chloride and a like volume of alcohol.

When inositol is heated with 6 mols. of pyrophosphoric acid, a *di-inositoltripyrophosphoric acid* is obtained. E. F. A.

**Preparation of Acraldehyde.** ALFRED WOHL and BRUNO MYLO (*Ber.*, 1912, 45, 2046—2054).—The preparation of acraldehyde from glycerol by the use of potassium hydrogen sulphate or of other catalysts, namely, phosphoric or boric acid, or aluminium sulphate, gives very variable yields, and the product often contains besides acraldehyde, sulphurous acid and acetaldehyde.

The dehydration of glycerol can occur at the primary or the secondary alcoholic group, the final product in the first case being acetaldehyde, in the second acraldehyde:



In accordance with this explanation the preparation of acraldehyde should be favoured by a low temperature, since secondary hydroxyl groups dehydrate more readily than primary ones; it is actually shown that overheating favours the formation of acetaldehyde.

By starting with potassium hydrogen sulphate mixed with a comparatively small quantity of glycerol, and adding more glycerol gradually, a 60% yield of acraldehyde can be obtained, but the product contains 10% of sulphurous acid. Sulphates of aluminium (compare Senderens, *Abstr.*, 1910, i, 649) and of other metals which can yield sulphuric acid at comparatively low temperatures behave similarly with glycerol. Sodium and potassium sulphates yield no acrolein.

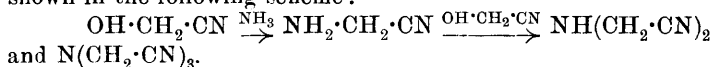
On the other hand, the sulphates of the alkaline earths and the heavy metals cause a similar decomposition of glycerol, but the acraldehyde produced is free from sulphurous acid; magnesium sulphate is most effective, and easily yields 44% of a very pure product on a small scale; the catalytic effect of the other sulphates seems to fall in the order of the basicity of their oxides.

A special apparatus is described suitable for the production of large quantities of acraldehyde by the passage of glycerol vapour through an electrically heated vertical copper tube containing anhydrous magnesium sulphate as the catalytic agent, with subsequent fractional condensation of the issuing vapours. The apparatus, which yields a kilogram of pure acraldehyde in a day (yield 60% of the theoretical), is fully described in the original. D. F. T.

**Action of Formaldehyde on Potassium Cyanide.** HARTWIG FRANZEN (*J. pr. Chem.*, 1912, [ii], 86, 133—149).—In order to obtain

experimental evidence in support of the view that the naturally-occurring amino-acids are formed in plants by the cyanohydrin reaction, the author has investigated the action of potassium cyanide on formaldehyde in aqueous solution. It was anticipated that the reaction of these substances would lead to the formation of glycollic, aminoacetic, glyceric, malic, and aspartic acids, but only the two first-named acids, together with iminodiacetic and nitrilotriacetic acids, could be isolated from the product.

With respect to the mechanism of the reaction, the author imagines that the potassium cyanide and formaldehyde react to form the compound  $\text{OK} \cdot \text{CH}_2 \cdot \text{CN}$ , which is hydrolysed to  $\text{OH} \cdot \text{CH}_2 \cdot \text{CN}$ , and finally to ammonia and glycollic acid; the nitriles of aminoacetic, iminodiacetic, and nitrilotriacetic acids are formed from these products as shown in the following scheme:



For details of the separation of the acids the original should be consulted.

The *monosilver* salt of nitrilotriacetic acid,  $\text{C}_6\text{H}_8\text{O}_6\text{NAg}$ , crystallises in long, lustrous, colourless needles.

The *mercuric* salt of iminodiacetic acid,  $\text{C}_4\text{H}_5\text{O}_2\text{NHg}$ , forms a crystalline powder, consisting of very small leaflets. F. B.

**New Transformations of Anhydrodextrose.** EMIL FISCHER and KARL ZACH (*Ber.*, 1912, 45, 2068—2074. Compare this vol., i, 239).—The similarity of anhydrodextrose and dextrose in chemical behaviour extends to the effect of oxidation and reduction; the acid and alcohol obtained are named anhydrogluconic acid and anhydrosorbitol respectively, but it is not certain that the configuration of these two substances is identical with that of gluconic acid and sorbitol.

*Anhydrosorbitol*,  $\text{C}_6\text{H}_{12}\text{O}_5$ , is obtained by the reduction of anhydrodextrose in feebly alkaline aqueous solution by sodium amalgam; it forms colourless plates from alcohol, and needles from ethyl acetate, m. p.  $113^\circ$  (corr.), and tastes sweet at first, but afterwards slightly bitter;  $[\alpha]_D^{20} - 7.47^\circ$  (in water). Except in m. p. and optical activity, anhydrosorbitol is very similar to the isomeric natural styracitol (*Asahina*, *Abstr.*, 1909, i, 288).

*Anhydrogluconic acid*,  $\text{C}_6\text{H}_{10}\text{O}_6$ , is obtained by the oxidation of anhydrodextrose in aqueous solution by bromine; it is isolated as the *calcium* salt, which crystallises with  $4\text{H}_2\text{O}$ . The free acid crystallises in leaflets, m. p.  $123\text{--}125^\circ$  (corr.), which when exposed in a desiccator lose the elements of water, forming the *lactone*,  $\text{C}_6\text{H}_8\text{O}_5$ , which crystallises in cubes, m. p.  $115^\circ$  (corr.). The fresh solution of the latter in water is practically tasteless, but shortly becomes sour, probably giving an equilibrium mixture of lactone and free acid; the optical rotation shows a corresponding change from  $[\alpha]_D^{20} + 82.3^\circ$  to  $[\alpha]_D^{20} + 66.4^\circ$ ; by neutralisation of the aqueous solution, the *calcium*, *copper*, and *barium* salts of the acid were obtained.

An alcoholic solution of the lactone when saturated with ammonia deposits *anhydrogluconamide*,  $C_6H_{11}O_5N$ , needles, m. p. about  $149^\circ$  (decomp.); the amide gives a tasteless aqueous solution, which slowly undergoes hydrolysis, the change being accompanied by a fall in  $[\alpha]_D^{20}$  from  $+77.7^\circ$  to  $+52.8^\circ$  in seven days.

From the easy formation of a lactone, the conclusion is drawn that anhydrogluconic acid contains a hydroxyl group in the  $\gamma$ -position to the carboxyl. Lack of material prevented any further investigation of the structure.

D. F. T.

**Dispersoid Chemistry of Cellulose.** I. P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 41—43).—It has been found that colloidal solutions of cellulose can be obtained by the action of a large number of aqueous salt solutions on filter-paper or cotton-wool if the concentration, temperature, and pressure are suitably chosen. In general, the activity of a salt increases with its solubility and its capacity for combining with water, and for this reason, rise of temperature and pressure are favourable factors in many cases. In the case of saturated solutions of very soluble salts, the action takes place very rapidly at the ordinary boiling temperature.

Colloidal solutions containing about 1% of cellulose form solid jellies when cooled, and in many cases these exhibit a high degree of elasticity.

H. M. D.

**Acetolytic Degradation of Cellulose.** FRIEDRICH KLEIN (*Zeitsch. angew. Chem.*, 1912, 25, 1409—1415. Compare Skraup, Abstr., 1899, i, 852; Franchimont, 1900, i, 141; Skraup and König, Abstr., 1901, i, 370; Maquenne and Goodwin, Abstr., 1904, i, 799; Schliemann, Abstr., 1911, i, 179).—An exhaustive investigation of the action of acetic anhydride and sulphuric acid on cellulose. In the main, the results obtained are in accord with those of the earlier investigators, particularly those recorded by Schliemann (*loc. cit.*), except in that the formation of acetates of bioses other than cellobiose by the acetolysis of cellulose, regarded as probable by this investigator, was not observed.

It is established beyond dispute that at least one-third part of the monoses of cellulose are united as in cellobiose, for it is possible to obtain 30% of the theoretical yield of cellobiose octa-acetate from cellulose. The formation of cellobiose acetate is accompanied by that of cellulose-dextrin acetates soluble in alcohol, the specific rotatory powers of which increase from  $+11^\circ$  to about  $+34^\circ$  with a corresponding increase in the proportion of the acetyl radicle.

It is very probable that these substances are intermediate products in the degradation of cellulose to cellobiose, further hydrolysis of which does not, for an unknown reason, take place.

Other products of the acetolysis of cellulose are certain indefinite substances, soluble in water, which appear to be acetosulphates of cellobiose, dextrose, or some other degradation product of cellulose.

It is interesting to note that complete acetylation renders further

hydrolysis extremely difficult; for example, cellulose triacetate when acted on by a mixture of acetic anhydride (4 parts) and sulphuric acid (1 part) for seven days is converted mainly into esters soluble in water and only to the extent of 5% of the theoretical yield of cellobiose acetate. Cellulose-dextrin acetate, when treated similarly, yields products soluble in water, but no cellobiose acetate. It seems probable, therefore, that in the formation of cellobiose acetate, complete acetylation is preceded by hydrolysis or some other reaction, such as the ester-like union of sulphuric acid in the immediate neighbourhood of the oxygen-bridge linking, which is in this way kept open for subsequent hydrolytic attack.

W. H. G.

**Comparative Acetylation of Cellulose, Hydrocellulose, and Alkalised Cellulose.** HERMANN OST and TOMIO KATAYAMA (*Zeitsch. angew. Chem.*, 1912, 25, 1467—1470. Compare Ost, Abstr., 1911, i, 712; Klein, preceding abstract).—In order to obtain further knowledge of the differences between cellulose, hydrocellulose, and cellulose which has been treated with a 25% solution of sodium hydroxide at 110—120° for several hours ("alkalised" cellulose), the authors have studied the products obtained by treating these substances with a mixture of acetic anhydride, glacial acetic acid, and either sulphuric acid or zinc chloride. In all cases, the products obtained were found to have the composition corresponding with that of cellulose triacetate. Hydrocellulose, and more particularly alkalised cellulose, yield a greater proportion of acetates soluble in acetone than cellulose (cotton-wool) when similarly treated, the proportion of acetates soluble in acetone increasing in each case as the length of treatment with the acetylating mixture becomes greater.

It is remarkable that the highly polymerised cellulose triacetate soluble in chloroform, which forms an elastic, pliable film, has the same specific rotatory power ( $-20.5^{\circ}$  to  $-21^{\circ}$ ) as the triacetate, which does not yield a coherent film. The acetates soluble in acetone derived from cotton wool and hydrocellulose have a specific rotatory power of  $-17^{\circ}$  to  $-18^{\circ}$ , whilst the acetate soluble in acetone derived from alkalised cellulose is slightly more optically active, having  $[\alpha]_D -21.9^{\circ}$  (in chloroform).

Prolonged treatment of cellulose and hydrocellulose with the acetylating mixture leads to the formation of cellobiose octa-acetate, which, under suitable conditions, is converted into dextrose- $\alpha$ -penta-acetate.

W. H. G.

**A New Method of Isolating Betaine Hydrochloride from Molasses Residue. Separation of Glycine, Betaine, and Glutamic Acid. Absence of Betaine from the Fission Products of Certain Proteins.** H. STOLTZENBERG (*Ber.*, 1912, 45, 2248—2252).—Molasses residue contains alkali salts, carbohydrates, readily soluble non-saccharine matter, glutamic acid, and betaine. For the separation of betaine, the author proposes to take advantage of the fact that, whilst potassium chloride, glutamic acid hydrochloride, and betaine hydrochloride have closely similar solubilities in water, the

solubility of the two former in concentrated hydrochloric acid is very much less, whilst that of betaine hydrochloride is slightly greater than in pure water. The residues are therefore saturated with gaseous hydrogen chloride, the precipitate filtered, and the betaine hydrochloride isolated from the concentrated filtrate by means of alcohol.

The utility of the above solubility determinations in the investigation of the presence of betaine among the products of hydrolysis of proteins by hydrochloric acid was also investigated. From a mixture of glycine, betaine hydrochloride, and glutamic acid hydrochloride, the latter was deposited in 76% yield after saturation of the aqueous solution with hydrogen chloride. The filtrate, on concentration and treatment with alcohol, deposited 62% of betaine hydrochloride, whilst, from the residue, 76% of the glycocoll was obtained in the form of glycine ester hydrochloride.

Betaine was not found by this method among the fission-products of silk, goose feathers, blood, and other proteins. H. W.

**Composition and Properties of Glycine Picrate and the Separation of Glycine from Alanine.** PHÆBUS A. LEVENE and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1912, 12, 285—294).—Glycine picrate is composed of 2 mol.-weights of glycine and 1 of picric acid. It softens at 199—200°, and decomposes at 202°. It is very soluble in hot water, but at 0°, 100 c.c. dissolves only 1·7 grams.

To separate glycine from alanine, the mixture is dissolved in hot water containing more picric acid than is required to combine with the glycine. The solution is cooled to 0°, and glycine picrate crystallises out. The filtrate is then treated with sulphuric acid and freed from picric acid with ether. The sulphuric acid is precipitated by an equivalent of titrated barium hydroxide solution. The alanine is left as a residue when the filtrate from the barium sulphate is concentrated to dryness. This still contains a little glycine, but that in the form of picrate is 90% pure. W. D. H.

**Picrolonates of the Monoamino-acids.** PHÆBUS A. LEVENE and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1912, 12, 127—139. Compare Abderhalden and Weil, this vol., i, 422).—The procedure adopted is as follows: The amino-acid and picrolonic acid in molecular proportions, or with amino-acid in excess, are dissolved in a minimum amount of boiling water. On cooling, the picrolonate crystallises. Only in the case of *d*-alanine, *dl*-serine, and *d*-glutamic acid was there a tendency to carry down an excess of picrolonic acid which is readily removed by means of ether. The salts show characteristic crystalline form, but they decompose when they meet. The picrolonates appear to give good results in separating phenylalanine from glutamic and aspartic acids.

*dl*-Alanine picrolonate forms long, slender crystals, m. p. 216° (decomp.).

*dl*-Aspartic acid picrolonate crystallises in long, slender prisms with square ends; it blackens at 130°.

*dl*-Glutamic acid picrolonate separates in very fine, short spindles, decomp. 184°.

*d*-Glutamic acid picrolonate, which is similar to the inactive salt, has  $[\alpha]_D^{20} + 8.5^\circ$ .

Glycine picrolonate crystallises in very characteristic rhomboid prisms, m. p.  $214-215^\circ$  (decomp.).

*d*-isoLeucine picrolonate forms long, slender, six-sided crystals grouped in stars, m. p. about  $170^\circ$ ,  $[\alpha]_D^{20} + 32.8^\circ$ .

*l*-Leucine picrolonate softens at  $145^\circ$ , m. p.  $150^\circ$ ,  $[\alpha]_D^{20} + 19.6^\circ$ . The picrolonate of natural leucine is seen under the microscope to consist of a mixture of long, slender, and rhomboid crystals.

*dl*-Leucine picrolonate forms rosettes of six-sided crystals.

*l*-Phenylalanine picrolonate forms two types of crystals: long, slender rods clustered in stars, and short, rectangular prisms, m. p.  $208^\circ$  (decomp.). A 25% racemised sample had  $[\alpha]_D^{20} + 22.8^\circ$ .

*dl*-Phenylalanine picrolonate consists entirely of short, rectangular prisms, m. p.  $211-212^\circ$ .

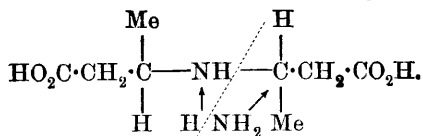
*dl*-Serine picrolonate crystallises in long, slender rods; it darkens above  $200^\circ$ .

Tyrosine picrolonate crystallises in rods grouped in rosettes, which blacken and sinter at  $260^\circ$ .

*d*-Valine picrolonate has m. p.  $170-180^\circ$ ,  $[\alpha]_D^{20} + 23.4^\circ$ . E. F. A.

The Mutual Relationship of the Optically Active Forms of  $\beta\beta'$ -Iminodibutyric Acid and  $\beta$ -Aminobutyric Acid. HELMUTH SCHEIBLER (*Ber.*, 1912, 45, 2272-2297).—Under the action of ammonia, crotonic acid is converted into  $\beta$ -aminobutyric acid and  $\beta\beta'$ -iminodibutyric acid. Prolonged heating has previously been shown to favour the production of the former at the expense of the latter acid. The author shows that an almost complete transformation of crotonic into  $\beta$ -aminobutyric acid can be achieved by prolonged heating of the former with ammonia, separation of the amino-acid formed, and subjection of the residue to a second treatment. Confirmation of the view put forward by Stadnikoff, that the formation of  $\beta\beta'$ -iminodibutyric acid is due to the interaction of  $\beta$ -aminobutyric acid and crotonic acid is found in the production of this substance by the action of  $\beta$ -aminobutyric acid on barium crotonate. In order to decide in what manner the fission of  $\beta\beta'$ -iminodibutyric acid occurs under the action of ammonia, the author has prepared the active  $\beta\beta'$ -iminodibutyric acids. Synthetic  $\beta\beta'$ -iminodibutyric acid consists of a mixture of the *meso*- and racemic forms, which can be separated by fractional crystallisation of the platinichlorides of their dimethyl esters from methyl alcohol. The racemic acid was resolved by fractional crystallisation of the brucine salt. *l*- $\beta\beta'$ -Iminodibutyric acid was transformed by ammonia into *l*- $\beta$ -aminobutyric acid. Partial racemisation occurred at the same time, but not to a greater extent than when pure active  $\beta$ -aminobutyric acid was similarly treated. Hence it appears that the ammonia attaches itself to the imino-group in some manner, and that the C-N bond between the imino-group and one carbon skeleton becomes broken. The imino-group becomes converted into the amino-group. Substitution of an amino-group takes place in the other half of the molecule, probably without a Walden

inversion occurring, since the loss in activity can be explained on the ground of racemisation. The reaction may be represented thus :



The transformation of *l*- $\beta\beta'$ -iminodibutyric acid into *l*-aminobutyric acid shows that the two halves of the imino-acid molecule possess the same configuration as the similarly active amino-acids. This follows also from the synthesis of the active imino- from active amino-acid, which was most readily performed by the union of methyl  $\beta$ -aminobutyrate with methyl crotonate. *d*-Methyl  $\beta$ -aminobutyrate and methyl crotonate yielded a mixture of *meso*-imino-ester and *d*- $\beta\beta'$ -iminodibutyric ester. When inactive material was employed, the two inactive esters were not obtained in equal quantities, an excess of at least 6% of racemic ester pointing to an asymmetric synthesis.

The best conditions for the preparation of  $\beta\beta'$ -iminodibutyric acid and of  $\beta$ -aminobutyric acid respectively from crotonic acid and ammonia are fully described, as is the preparation of the former from  $\beta$ -aminobutyric acid and barium crotonate.

Methyl  $\beta\beta'$ -iminodibutyrate was used as starting point for the preparation of the active acid. After saponification by barium hydroxide and removal of barium, the acid was resolved by crystallisation of the *brucine* salt from alcohol, whereby *l*- $\beta\beta'$ -iminodibutyric acid was obtained. The acids obtained from the mother liquor from the first crystallisation of the *brucine* salt contained the *meso*-acid, which was characterised by esterification of the acids by methyl alcohol and hydrogen chloride, and subsequent isolation of the *hydrochloride* of the *methyl* ester of *meso*- $\beta\beta'$ -iminodibutyrate, m. p. 114—115° (corr.), and its *platinichloride*, m. p. 134—135°. The separation of *d*-iminodibutyric acid from the *meso*-acid can be effected by crystallisation of the *platinichlorides* of the *methyl* esters from methyl alcohol, in which that derived from the *d*-acid is the less soluble. The isolation of the *d*-acid from the mixture of acids obtained from the second mother liquor (see above) was effected by esterification and conversion into the *platinichloride* and crystallisation from methyl alcohol, whereby the *meso*-acid was removed. Removal of the racemic form was brought about by crystallisation of the *methyl* ester *hydrochlorides* from methyl acetate. The pure *d*-methyl ester *hydrochloride*, when hydrolysed with hydrochloric acid, yielded pure *d*-iminodibutyric acid. The latter could also be crystallised from its mixture with excess of the racemic acid after seeding with a crystal of the pure *d*-acid. At the same time a certain amount of resolution of the racemic acid by simple crystallisation occurred, since the yield of *d*-acid exceeded in amount that calculated from the activity of the mixture, and the mother liquors were *l*ævorotatory. An attempt to resolve the syrupy racemic acid directly by this method was unsuccessful.

The racemic and *meso*-forms of  $\beta\beta'$ -iminodibutyric acid were similarly separated by crystallisation of the *platinichlorides* of their

methyl esters from methyl alcohol, the *r*-compound, m. p. 195—196°, being less soluble than the *meso*-compound, m. p. 134—135°.

*r*-Methyl  $\beta\beta'$ -iminodibutyrate hydrochloride has m. p. 142—143° (corr.). *r*- $\beta\beta'$ -Iminodibutyric acid has m. p. about 158—160° (corr., decomp.), and could not be obtained in well-defined crystals.

*meso*-Methyl  $\beta\beta'$ -iminodibutyrate hydrochloride has m. p. 114—115° (corr.). The free imino-acid could not be obtained in the crystalline form. Its hydrochloride and platinichloride are crystalline.

*l*- $\beta\beta'$ -Iminodibutyric acid, m. p. 179—180° (decomp.), has  $[\alpha]_D^{20} - 65.3^\circ$  in aqueous solution,  $[\alpha]_D^{20} - 56.1^\circ$  in *N*-hydrochloric acid solution. The methyl ester hydrochloride, m. p. 163—164° (corr.), has  $[\alpha]_D^{20} - 42.2^\circ$  ( $\pm 0.4^\circ$ ) in methyl-alcoholic solution. Its methyl ester platinichloride, has m. p. 200—201° (corr., decomp.).

*d*- $\beta\beta'$ -Iminodibutyric acid, m. p. 179—180° (corr., decomp.), has  $[\alpha]_D^{20} + 65.5^\circ$  in aqueous solution. Its methyl ester hydrochloride, m. p. 163—164° (corr.), has  $[\alpha]_D^{20} + 42.1^\circ$  in methyl-alcoholic solution, and its methyl ester platinichloride has m. p. 200—201° (corr., decomp.).

*l*- $\beta\beta'$ -Iminodibutyric acid was heated with aqueous ammonia at 110° during twenty hours, whereby it was converted into impure *l*-aminobutyric acid,  $[\alpha]_D^{20} - 16.2^\circ$ , which increased to  $-20.3^\circ$  after recrystallisation from a mixture of methyl and ethyl alcohols. *d*- $\beta$ -Aminobutyric acid, when similarly treated, decreased in activity from  $+35.3^\circ$  to  $+16.5^\circ$ . *d*- $\beta\beta'$ -Iminodibutyric acid, under similar treatment, yielded impure *d*-aminobutyric acid ( $[\alpha]_D + 10.6^\circ$ ).

Active aminobutyric acids of the same sign as the imino-acid used were obtained when aqueous solutions of the active ammonium  $\beta\beta'$ -iminodibutyrate were heated under pressure. A solution of barium  $\beta\beta'$ -iminodibutyrate under similar conditions was decomposed into barium crotonate and ammonium crotonate.

Methyl crotonate and methyl  $\beta$ -aminobutyrate were maintained at 37° during several weeks. On distillation, methyl  $\beta\beta'$ -iminodibutyrate was obtained. The latter was converted into its platinichloride, which, by crystallisation from methyl alcohol, was separated into the platinichlorides of the *r*- and *meso*-esters. A similar experiment with methyl crotonate and methyl *d*-aminobutyrate showed that methyl *d*- $\beta\beta'$ -iminodibutyrate and methyl *meso*- $\beta\beta'$ -iminodibutyrate were formed. H. W.

**Action of Bromine and Sodium Hydroxide on Carbamide and Guanidine Derivatives.** I. VIKTOR VON CORDIER (*Monatsh.*, 1912, 33, 759—796).—Arising out of the observation that monoacetyl-carbamide when treated with sodium hypobromite in the Hüfner apparatus yields only one atom of nitrogen as gas (Abstr., 1908, ii, 983), the behaviour of a number of carbamide and guanidine derivatives towards sodium hypobromite has been studied.

The salts of carbamide and of guanidine with a variety of acids, like the free bases, all part with their nitrogen quantitatively.

Thiocarbamide and its derivatives either do not react at all or give very little nitrogen, but this influence is restricted to the thiocarbamide residue, and does not extend to a second carbamide or guanidine residue introduced as a substituent.

Bromine prevents the quantitative elimination of the nitrogen of the amino-group in which it has entered: this is exemplified by the behaviour of monobromoguanidine, which gives up only one nitrogen.

This applies equally to the acid groups  $-\text{CO}\cdot\text{CH}_3$ ,  $-\text{CO}\cdot\text{C}_6\text{H}_5$ ,  $-\text{CO}\cdot\text{NH}_2$ , all of which prevent the quantitative measurement of the nitrogen of the amino-group in question.

Phenyl and tolyl groups as in phenyl carbamide, phenylguanylthiocarbamide, phenylbiguanide, and ditolylcarbamide entirely prevent the elimination of nitrogen from the molecule.

An increase in the distance of the phenyl group from the amino-nitrogen as in benzylcarbamide overcomes the influence of the phenyl, as here both nitrogens are eliminated.

In the case of cyclic monoureides with bivalent acid esters, partial hydrolysis must be assumed, regenerating one amino-group. Parabanic acid and alloxan yield one atom; alloxantin yields two atoms of nitrogen. Veronal, which gives no nitrogen, affords an exception.

Mono- and especially cyclic diureides, for example, hydantoin and uric acid, give irregular results, which do not indicate any connexion between their constitution and the elimination of nitrogen.

The only faintly acid cyanogen group does not appear to hinder the elimination of nitrogen. The nitro-group behaves similarly in nitrocarbamide, nitrourethane, and nitroguanidine.

The methyl group sometimes hinders the elimination of nitrogen, as in methylguanidine nitrate, mono- and *s*-di-methylcarbamide; in other instances, it is without effect, for example, *as*-dimethylcarbamide and methylbiguanide.

The basic amino-group in semicarbazide does not hinder the nitrogen elimination, two atoms being liberated.

The method of elimination of nitrogen with sodium hypobromite can be used in such cases as glycine guanidine carbonate to determine whether or no an additive compound is present: five nitrogen atoms are here liberated.

E. F. A.

**Methylated Guanidines. II.** MARTIN SCHENCK (*Arch. Pharm.*, 1912, 250, 306—329. Compare *Abstr.*, 1911, i, 842).—Of the eleven theoretically possible methylated guanidines obtained by replacing successively the five hydrogen atoms of guanidine by methyl groups, only the three containing the group  $\text{NMe}\cdot\text{C}(\text{NH}_2)_2\cdot\text{N}\cdot$  have not been prepared; reactions which might be expected to produce these three actually result in the formation of substances containing  $\text{NH}\cdot\text{C}(\text{NHMe})_2\cdot\text{N}\cdot$ . The following new compounds are described:  $\beta\beta$ -Dimethylguanidine forms an *aurichloride*, m. p.  $248^\circ$  (decomp.), *platinichloride*, decomp.  $225^\circ$ , and picrate, m. p.  $230^\circ$ , not  $224^\circ$ .  $\beta\beta\beta'$ -Trimethylguanidine *platinichloride* has m. p.  $172$ — $173^\circ$ .  $\beta\beta\beta'\beta'$ -Tetramethylguanidine,  $\text{NH}\cdot\text{C}(\text{NMe}_2)_3$ , obtained, ultimately in the form of the *aurichloride*, m. p.  $142$ — $144^\circ$ , by the action of alcoholic ammonia on tetramethylthiocarbamide methiodide at  $100^\circ$  for nine hours, forms a *platini-chloride*, which is extremely soluble in water, and a *picrate*, m. p.  $130^\circ$ .  $\alpha\beta\beta'\beta'$ -Tetramethylguanidine,  $\text{NMe}\cdot\text{C}(\text{NHMe})_2\cdot\text{NMe}_2$ , obtained from  $\alpha\beta\beta'$ -trimethyl- $\psi$ -thiocarbamide and 33% alcoholic dimethylamine at the ordinary temperature or by heating  $\alpha\beta\beta'$ -trimethyl-

$\psi$ -thiocarbamide hydriodide or  $\alpha\beta'$ -dimethyl- $\beta$ -ethyl- $\psi$ -thiocarbamide hydriodide with alcoholic dimethylamine, forms an *aurichloride*, m. p. 115—117°, and a *picrate*, m. p. 158—160°. The action of methylamine on tetramethyl- $\psi$ -thiocarbamide hydriodide results in the formation of, not a tetramethylated guanidine, but  $\alpha\beta\beta'$ -trimethylguanidine and dimethylamine.

*Pentamethylguanidine*,  $\text{NMe}\cdot\text{C}(\text{NMe}_2)_2$ , obtained by treating tetramethyl- $\psi$ -thiocarbamide with 33% alcoholic dimethylamine at the ordinary temperature for fourteen days, forms an *aurichloride*, m. p. 130—132°, and *picrate*, m. p. 160—162°. C. S.

**Pentamethylenedicarbimide.** JULIUS VON BRAUN and H. DEUTSCH (*Ber.*, 1912, 45, 2199—2200).—An ethereal solution of  $\alpha$ -di-iodopentane was added to a mixture of silver cyanate and sand. On gently warming, the ether was expelled and an energetic action then ensued, whereby *pentamethylenedicarbimide* was obtained in small quantity. It could not be obtained pure, since on keeping, more rapidly on warming, it became transformed into an amorphous insoluble mass, possibly the polymeric cyanurate. With fatty and fatty-aromatic alcohols and amines, it yielded compounds of low m. p. and small ability to crystallise. With purely aromatic phenols and amines, on the other hand, it yielded well-crystallised products of high m. p.; thus, *diphenylpentamethylenedicarbimide*,  $\text{CH}_2(\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh})_2$ , has m. p. 202°, and the corresponding *derivative* from ethylaniline, m. p. 134°. Phenol and pentamethylenedicarbimide yield a *diphenyl urethane*,  $\text{CH}_2(\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Ph})_2$ , m. p. 113—114°. H. W.

**The Products of Explosion of Hydrogen Cyanide.** G. SALOMONE (*Gazzetta*, 1912, 42, i, 617—622).—An accidental explosion of 100 grams of anhydrous hydrogen cyanide led to the formation of white fumes with an odour of hydrocyanic acid, and of an amorphous, brown mass with an odour of bitter almonds. Heating this mass led to the evolution of hydrogen cyanide, and of ammonia and carbon monoxide at a higher temperature. The solid was a polymeride of hydrogen cyanide, and yielded small quantities of ammonium formate and formamide with water. Extraction with dry ether yielded a crystalline polymeride of cyanic acid, not identical with either cyamelide or cyanuric acid, having a molecular weight corresponding with the formula  $\text{C}_5\text{H}_5\text{O}_5\text{N}_5$ , and yielding a *potassium* salt,  $\text{C}_5\text{H}_2\text{O}_5\text{N}_5\text{K}_3\cdot 6\text{H}_2\text{O}$ , and a *silver* salt,  $\text{C}_5\text{H}_2\text{O}_5\text{N}_5\text{Ag}_3\cdot \text{H}_2\text{O}$ . The pentacyanic acid had m. p. 148.5°. C. H. D.

**Armstrong's Benzene Formula.** HANS VON LIEBIG (*J. pr. Chem.*, 1912, [ii], 86, 175—183).—A criticism of Armstrong's centric formula, together with an explanation of the difference in properties of benzene and *cyclooctatetraene* (Willstätter, this vol., i, 17), based on the author's hypothesis of the oscillatory nature of the double linking (*Abstr.*, 1908, i, 445) and on the assumption that the carbon atoms of *cyclooctatetraene* are arranged in such a manner that the molecule contains four parallel double linkings. F. B.

**Hydrogenation of Benzene.** FRIEDRICH W. HINRICHSSEN and RICHARD KEMPF (*Ber.*, 1912, 45, 2106—2113).—Caoutchouc in

benzene is not attacked by hydrogen in the presence of platinum-black, but a large volume of hydrogen is absorbed, and *cyclohexane* is formed. The platinum is not poisoned unless vulcanised caoutchouc has been employed. The same result is observed when benzene alone is used, and the rate of absorption of the hydrogen indicates that the hydrogenation of benzene to *cyclohexane* is a reversible process.

When petroleum, b. p. 65—95°, is employed in the place of benzene, a considerable absorption of hydrogen is still observed, indicating the presence of unsaturated and of aromatic hydrocarbons. If the petroleum has been shaken with fuming sulphuric acid prior to use, a very much smaller absorption of hydrogen is observed. No further absorption of hydrogen occurs when caoutchouc is dissolved in petroleum which has been previously saturated with hydrogen in the presence of platinum-black.

*cycloHexane* is very conveniently separated from benzene by nitrating the latter and then fractionally distilling.

The presence of a trace of benzene in *cyclohexane* is ingeniously detected as follows. The *cyclohexane* (about 20 grams) is treated with a mixture of 41 c.c. of concentrated sulphuric acid and 36 c.c. of concentrated nitric acid. The temperature remains unchanged if the *cyclohexane* is pure, but is raised 1° by the addition of even only 0.1 c.c. of benzene. C. S.

**Syntheses in the Fatty Aromatic Series. V.  $\omega$ '-Diarylparaffins.** JULIUS VON BRAUN and H. DEUTSCH (*Ber.*, 1912, 45, 2171—2188).—The action of sodium on fatty aromatic halogen compounds has been investigated. The reactivity of the latter appears to be largely independent of the molecular weight, and also of the nature of the halogen present. In all cases diarylparaffins are formed, the yield being apparently dependent on the number of methylene groups present in the original material: when this number is odd, diarylparaffins constitute the main product of the reaction (70—80%); when, however, the number is even, the yield of diarylparaffins is much lower (15—20% if ether is used as solvent). The secondary products consist of phenyl alkyl compounds without admixture of olefines.

Fully aromatic halogen compounds may be obtained in good yield by means of Grignard's reaction if the reagent is prepared at a low temperature and then treated with chloromethyl ether. From the ether thus obtained, the corresponding haloid can be made by treatment with halogen acid. Thus magnesium phenylpropyl bromide and chloromethyl ether yielded a mixture of propylbenzene, *phenylbutyl methyl ether*, b. p. 108°/11 mm. (above 45%), and  $\alpha$ -diphenylhexane (12%). From the second compound, phenylbutyl bromide was obtained by treatment with fuming hydrobromic acid during five hours at 130—140°. Similarly, magnesium phenylamyl bromide and chloromethyl ether yielded *phenylhexyl methyl ether*, b. p. 140°/13 mm.

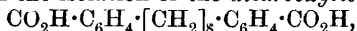
Phenylpropyl chloride, when treated with sodium, yielded propylbenzene and  $\alpha$ -diphenylhexane, b. p. 206—208°/200 mm. The latter is a colourless, viscous liquid, which does not solidify at 0°. Phenylamyl chloride, under similar treatment, gave *n*-amylbenzene, b. p. 200—201°/745 mm.,  $D_4^{20}$  0.8662,  $n_D^{20}$  1.4943, in 25% yield, and

$\alpha\kappa$ -diphenyldecane (compare Borsche and Wollemann, this vol., i, 24) in 75% yield. Similarly, from phenylheptyl chloride, *n*-heptylbenzene, b. p. 235°,  $D_4^{20}$  0.8570,  $n_D^{20}$  1.4865 (30%), and  $\alpha\chi$ -diphenyltetradecane, b. p. 262—265°/8 mm. (70%), were prepared.

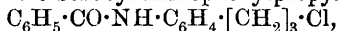
The products of the action of sodium on an ethereal solution of phenylhexyl chloride were hexylbenzene, b. p. 219—220°,  $D_4^{20}$  0.8613,  $n_D^{20}$  1.490 (yield above 85%), and  $\alpha\mu$ -diphenyldodecane, b. p. 240°/20 mm. When ether was replaced by benzene, the yield of the latter compound was increased (up to 50%). Phenylbutyl chloride and sodium in ethereal solution yielded butylbenzene, b. p. 180—181°,  $D_4^{20}$  0.8612,  $n_D^{20}$  1.4936 (80%), and  $\alpha\theta$ -diphenyloctane, b. p. 208—210°/8 mm. In benzene solution, better yields (up to 60%) of the latter compound were obtained. When sodium acted on phenylethyl chloride, ethylbenzene, b. p. 137°, and  $\alpha\delta$ -diphenylbutane, m. p. 52°, were formed, together with a *product* of higher b. p., from which no definite substance could be isolated.

$\alpha$ -Phenyl- $\gamma$ -xylolpropane, b. p. 202—206°/20 mm., was readily obtained by the condensation of phenylpropyl chloride and *o*-xylene in the presence of aluminium chloride. Similarly, phenylhexoyl chloride and toluene gave an 80% yield of *tolyl phenylamyl ketone*, b. p. 248—252°/14 mm., which yields oily condensation products with phenylhydrazine, hydroxylamine, and semicarbazide. In the toluene-half of the molecule, the carbonyl and methyl groups are in the para-position to one another, since the ketone is oxidised by dilute nitric acid with the formation of terephthalic acid. Reduction of the ketone by hydriodic acid, led to the formation of  $\alpha$ -phenyl- $\zeta$ -*p*-tolylhexane.

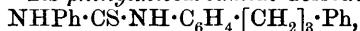
Definite nitro- and sulphonic acid derivatives of the diarylparaffin could not be obtained. The action of oxalyl chloride on a solution of  $\alpha\theta$ -diphenyloctane in carbon disulphide in the presence of aluminium chloride resulted in the isolation of the *dicarboxylic acid*,



m. p. 245—250°, the *sodium* salt of which is sparingly soluble in water, whereas the *potassium* and *ammonium* salts dissolve readily. Oxidation of the acid by alkaline permanganate yielded terephthalic acid, which was quite free from phthalic acid. The acid was converted into its *ethyl* ester, m. p. 53—55°, by successive treatment with phosphorus pentachloride and ethyl alcohol, and into the corresponding *diamide*, m. p. 242°. Evidence was obtained to show that a certain quantity of the monocarboxylic acid was also formed during the action of oxalyl chloride on  $\alpha\theta$ -diphenyloctane, but its isolation was not accomplished. In the diphenylpropane series, however, a derivative substituted in only one nucleus was readily obtained in the following manner: *o*-benzoylaminophenylpropyl chloride,



was condensed with benzene in the presence of aluminium chloride to *o*-benzoylaminodiphenylpropane, m. p. 207°, which was readily converted into the *hydrochloride* of *o*-aminodiphenylpropane, m. p. 205°. The *free base* has b. p. 208—212°/15 mm. It does not yield a crystalline picrate. Its *phenylthiocarbamide* derivative,



has m. p. 132°. Its *benzylidene* derivative is an oil, whereas its

*p*-nitrobenzylidene derivative,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot [\text{CH}_2]_3 \cdot \text{Ph}$ , has m. p.  $59^\circ$ . Diazotisation converted the amine into the corresponding phenol, b. p.  $198\text{--}202^\circ/15\text{ mm}$ . H. W.

**Halogeno-salts of Tellurium [Tellurihalides].** ALEXANDER GUTRIER and FERDINAND FLURY [with C. EWALD] (*J. pr. Chem.*, 1912, [ii], 86, 150—166).—By methods similar to those previously described (Abstr., 1911, i, 182), the authors have prepared the telluribromides and tellurichlorides of ethylenediamine and a large number of aromatic amines. The chloro- and bromo-salts have the general composition,  $(\text{NHR}_2)_2\text{TeX}_6$ , and are respectively yellow and red in colour. Of the salts of aromatic amines, those of aniline, pyridine, and quinoline have been described by Lenher (Abstr., 1900, i, 379).

*Ethylenediamine tellurichloride*,  $(\text{C}_2\text{H}_{10}\text{N}_2)\text{TeCl}_6$ , crystallises in compact needles, the aniline salt in slender, felted needles, the *methyl-aniline* salt,  $(\text{NH}_2\text{MePh})_2\text{TeCl}_6$ , in tabular, often scaly crystals, and the *dimethylaniline* salt in stout, fibrous crystals. The chloro-salt of *ethylaniline* forms soft leaflets, of *diethylaniline*, compact, parallel aggregates of very small platelets, often having an irregular hexagonal outline; the *o*- and *p*-toluidine salts form lath-like crystals, the *m*-isomeride, strongly refractive, stout crystals. Of the isomeric *xylylidene tellurichlorides*, the *o*-4-compound crystallises in lustrous, elongated, pointed prisms, the *m*-4-compound in brownish-yellow platelets or needles, and the *p*-compound in lustrous platelets or laths. The pyridine salt,  $(\text{C}_5\text{H}_5\text{NH})_2\text{TeCl}_6$ , crystallises in thin, hexagonal plates or laths, the 2-methylpyridine and quinoline salts in prisms; the *benzylamine* compound forms bright yellow aggregates of lamellar or prismatic crystals, the *benzylethylamine* salt, lustrous, stellar aggregates of prisms, and the  *$\alpha$ -naphthylamine* salt, greenish-yellow needles.

Of the telluribromides, the *ethylenediamine* salt crystallises in glistening red needles, the *propylenediamine* salt,  $(\text{C}_3\text{H}_{12}\text{N}_2)\text{TeBr}_6$ , in lustrous, bright red platelets, the aniline salt in soft, microscopic, felted prisms, the *methylaniline* salt in lustrous, scaly platelets, the *dimethylaniline* salt in small, light red plates, the *ethylaniline* salt in glistening, brownish-red platelets, and the *diethylaniline* salt in glistening, rectangular crystals. The bromo-salt of *o*-toluidine forms flat, brownish-red laths; the *m*-isomeride, glistening, red crystals, the *p*-isomeride, very small, lustrous, felted laths.

Of the isomeric *xylylidene telluribromides*, the *o*-4-compound crystallises in lustrous, brownish-red platelets, the *m*-4-compound in small glistening plates, and the *p*-compound in small, brownish-red laths.

Pyridine telluribromide forms bright red laths or platelets, the 2-methylpyridine compound, small, lustrous needles, the quinoline salt, crystalline, red or orange-red granules, the *benzylamine* salt, large, lustrous, brownish-red leaflets, the *benzylethylamine* salt, small, bright red crystals, the  *$\alpha$ -naphthylamine* salt, brownish-red platelets, and the  *$\beta$ -naphthylamine* salt, small, lustrous, orange-red leaflets.

The salts have been crystallographically examined by Lenk, who finds that the chloro-salts of aniline, methylaniline, diethyl-

aniline, *o*-toluidine, *o*-4-xylydine, pyridine, benzylethylamine, and the bromo-salts of propylenediamine, aniline, ethylaniline, diethylaniline, *p*-toluidine, benzylethylamine, and  $\alpha$ -naphthylamine are rhombic, whilst the tellurichlorides of *m*- and *p*-toluidine, *p*-xylydine, quinoline, and  $\alpha$ -naphthylamine, together with the bromo-salts of methylaniline, *o*- and *m*-toluidines, and the three xylydines crystallise in the monoclinic system. The telluribromides of *m*-4-xylydine and pyridine, and the chloro-salt of benzylamine are either rhombic or monoclinic.

F. B.

***o*-Nitrodialkylanilines.** GEORG WEISSENBERGER (*Monatsh.*, 1912, 33, 821—841).—*o*-Chloronitrobenzene and dimethylamine in absolute alcoholic solution readily interact in presence of copper powder, giving nearly the theoretical quantity of *o*-nitrodimethylaniline. This and its homologues are yellow, oily liquids of strong odour, volatile in steam.

The influence of the nitro-group on the amino-group is evident in their behaviour towards nitrous acid, when no nitroso-compound is formed. They do not react with aldehydes or diazo-compounds. The ferrocyanides are soluble and not characteristic; the ferricyanides are insoluble. They are decomposed on heating, but can be distilled in a vacuum.

The hydrochlorides of the nitrodialkylanilines undergo a true thermal dissociation when heated into acid and base, the change taking place suddenly and at a definite temperature. It is shown not to be a case of primary melting and secondary dissociation.

Ammonia behaves somewhat differently towards copper powder than do its alkyl derivatives. When heated with *o*-chloronitrobenzene, the yield of *o*-nitroaniline is only about 1.5%.

The following salts of *o*-nitrodimethylaniline are described: the *sulphate* forms colourless platelets, which become yellow on exposure to the air, *m. p.* 126—127°; the *hydrobromide* forms short, colourless needles or rhombic prisms, *decomp.* 172°; the *hydriodide* dissociates at 126°; the *aurichloride* forms long, yellow prisms, which explode when heated in the air, but decompose and blacken at 152° in sealed tubes; the *ferrocyanide* forms short, brown prisms; the *ferricyanide* gives well-formed yellow crystals.

*o*-Nitrodiethylaniline is an orange-yellow oil of characteristic odour. The *picate* forms lustrous, golden platelets, *m. p.* 119—120°; the *platinichloride* forms yellow, microscopic needles; the *aurichloride* gives pale yellow needles; the *sulphate* crystallises in broad tablets, *m. p.* 143°; the *hydrochloride* gives lustrous needles or short columns, *decomp.* 156°; the *hydrobromide* forms glass-like platelets, which are hygroscopic, *decomp.* 160°; the *hydriodide* forms colourless needles, which dissociate at 112°. The *ferrocyanide* crystallises in brown prisms; the *ferricyanide* forms long, yellow, monoclinic pyramids, which have sharp angles.

*o*-Aminodiethylaniline [*Diethyl-o-phenylenediamine*], prepared by reduction of the nitro-derivative with tin and hydrochloric acid, is a viscid, colourless oil of refreshing odour, *b. p.* 312.5°/744 mm. The *stannichloride* crystallises in bunches of silky needles, *m. p.* 145°; the

*picrate* gives golden-yellow prisms, m. p.  $236^{\circ}$ ; the *hydrochloride* consists of long, colourless needles; the *aurichloride* forms pale yellow, short columns; the *platinichloride* separates in egg-yellow, microscopic needles; the sulphate forms long, colourless needles.

*o*-Nitrodipropylaniline yields a *picrate* crystallising in lustrous, golden needles, a yellow, crystalline *platinichloride*, an *aurichloride* consisting of microscopic, yellow prisms, and a *sulphate* forming colourless, feathery crystals. The *hydrochloride* is a crystalline powder; the *hydrobromide* forms lustrous platelets, and the *hydriodide* separates in short, colourless needles. The *ferricyanide* forms characteristic yellow crystals.

The following salts of *o*-nitroaniline are described: the *picrate* forms red, coral-like crystals, m. p.  $73^{\circ}$ ; the *sulphate* gives colourless needles m. p.  $144^{\circ}$ ; the *hydriodide* is characterised by lustrous platelets, which dissociate at  $141^{\circ}$ .

E. F. A.

**Action of Dilute Sulphuric Acid on Phenyl- and *p*-Tolylhydroxylamine, in the Presence and the Absence of Phenol.** EUGEN BAMBERGER (*Annalen*, 1912, 390, 131—190).—Many of the results recorded in the paper have appeared in brief notices during the last twelve years. In short, the author's explanation of the transformation of arylhydroxylamines into *p*-aminophenols is represented by the scheme:  $\text{NHPh}\cdot\text{OH} \rightarrow \text{C}_6\text{H}_5\cdot\text{N} < + \text{H}_2\text{O} \rightarrow \text{H} > \text{C}_6\text{H}_4\cdot\text{NH} \rightarrow \text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , the formation of by-products being explained by the addition of molecules other than those of water to the complex  $\text{C}_6\text{H}_5\cdot\text{N} <$ . When  $\beta$ -phenylhydroxylamine and dilute sulphuric acid (1:10 by vol.) are heated on a boiling-water bath, the main products are about equal quantities of *p*-aminophenol and azoxybenzene; in addition, about 10% of aniline, and small quantities of *p*-hydroxydiphenylamine, *p*-aminophenolsulphonic acid, benzidine, and *p*-aminodiphenylamine are produced.

When  $\beta$ -phenylhydroxylamine mixed with about ten times its weight of sand is slowly stirred into concentrated sulphuric acid at  $-18^{\circ}$ , and the mixture is kept at  $0^{\circ}$  for seventy hours, the chief product is *p*-aminophenolsulphonic acid (in two forms, quadratic plates and slender needles); *p*-aminophenol is also produced, together with very small quantities of quinol and *pp'*-diaminodiphenyl oxide (7).

The interaction of  $\beta$ -phenylhydroxylamine, phenol (5 mols.), and sulphuric acid (1:3 by vol.) for five minutes at the b. p. yields aniline, *p*-aminophenol, a small quantity of a substance, m. p.  $179^{\circ}$  (probably 4-amino-2'-hydroxydiphenyl), and, as the most characteristic product, 4-amino-4'-hydroxydiphenyl,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , m. p.  $271\cdot5^{\circ}$ , glistening needles. This substance forms a *hydrochloride* and a *sulphate*, both of which are sparingly soluble, and yields by diazotisation a *diazonium chloride*,  $\text{C}_{12}\text{H}_9\text{ON}_2\text{Cl}\cdot 2\text{H}_2\text{O}$ , which crystallises in red needles with a blue shimmer, the colour changing to yellow when the salt is dehydrated over sulphuric acid in a vacuum. The same colour change is produced by absolute alcohol, and from the yellow alcoholic solution, dry ether precipitates the anhydrous diazonium chloride in yellow needles, which rapidly absorb moisture in the air and become

red. The diazonium chloride can be recrystallised from boiling water without appreciable decomposition by rapid manipulation; its orange-red aqueous solution turns citron-yellow in the presence of hydrochloric acid, and intensely red in the presence of hydroxyl ions, the substance being an extraordinarily sensitive reagent for the detection of the latter. The diazonium chloride is converted into 4:4'-dihydroxydiphenyl by prolonged boiling of its aqueous solution.

In an atmosphere of carbon dioxide,  $\beta$ -*p*-tolylhydroxylamine reacts with cold dilute sulphuric acid in fourteen hours to form toluquinol, 4-iminotoluquinol being an intermediate product.

[With L. BLANGEY.]—By treatment for fourteen days at the ordinary temperature and then for the same time at 0°, toluquinol and methyl alcohol containing a little concentrated sulphuric acid yield toluquinol methyl ether, cresorcinol dimethyl ether, and a substance, m. p. 125—125·5°, needles or prisms, which is probably a trihydroxyditolyl trimethyl ether,  $\text{OMe} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{C}_6\text{H}_2\text{Me}(\text{OMe})_2$ , since it is converted by boiling hydriodic acid, D 1·7, into a substance, m. p. 187·5—188·5°, which is soluble in alkalis and has the composition of a trihydroxyditolyl.

The action of ethyl alcohol and sulphuric acid on toluquinol is quite similar; cresorcinol diethyl ether, trihydroxyditolyl triethyl ether,  $\text{C}_{20}\text{H}_{26}\text{O}_8$ , m. p. 77—77·5°, and toluquinol ethyl ether (5-ethoxy-*o*-cresol),  $\text{OEt} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OH}$ , m. p. 55—55·5°, are formed.

When heated on the water-bath for forty minutes with dilute sulphuric acid (1:10 by vol.),  $\beta$ -*p*-tolylhydroxylamine yields toluquinol, *p*-toluidine, and small quantities of *p*-azoxytoluene and 5-amino-*o*-cresol.

[With JOSEF BRUN.]—By slowly stirring  $\beta$ -*p*-tolylhydroxylamine into concentrated sulphuric acid at -20°, and keeping the mixture at 0° for eighteen hours, there are produced an amorphous, reddish-yellow base,  $\text{C}_7\text{H}_7\text{N}$ , m. p. 155—160°, and an amorphous, dark grey base,  $4\text{C}_7\text{H}_7\text{N}, \text{H}_2\text{O}$ , sintering at about 220°; the compositions of the two bases are given with reserve.

In dilute sulphuric acid,  $\beta$ -*p*-tolylhydroxylamine and *p*-nitrotoluene do not interact, since the products, azoxytoluene, *p*-toluidine, and toluquinol, are the same as those obtained from  $\beta$ -*p*-tolylhydroxylamine and dilute sulphuric acid alone. When a mixture of the two tolyl compounds, however, is stirred slowly into concentrated sulphuric acid at -3° to 4°, and the mixture is kept for two days, the reaction yields the sulphate of 2-nitro-4'-amino-5-methyldiphenylmethane.

When heated with dilute sulphuric acid for twenty minutes,  $\beta$ -*p*-tolylhydroxylamine and phenol (4 mols.) yield *p*-azoxytoluene, *p*-hydroxyphenyl-*p*-tolylamine, and toluquinol. C. S.

**Beckmann Rearrangement of Hydroxamic Acids.** LAUDER WILLIAM JONES (*Amer. Chem. J.*, 1912, 48, 1—28).—An account of the transformation of certain hydroxamic acids has been given by Thiele and Pickard (*Abstr.*, 1900, i, 29), in the course of which phenylacetylhydroxamic acid, m. p. 121°, was described. A phenylacetylhydroxamic acid has now been obtained of m. p. 145—145·5°, which is probably isomeric with Thiele and Pickard's compound. The benzoyl derivative

of the new acid,  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{OBz}$ , m. p.  $120\cdot5$ — $121\cdot5^\circ$ , forms colourless needles, and yields a crystalline *potassium* salt which undergoes explosive decomposition accompanied by a Beckmann rearrangement at the ordinary temperature with formation of benzylcarbimide and potassium benzoate:



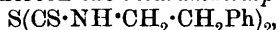
The corresponding *sodium* salt is more stable, but suffers a similar decomposition when heated. The *silver* salt explodes after being heated for a few minutes at  $70^\circ$ . The *acetyl* derivative of phenylacethydroxamic acid,  $\text{CH}_2\text{Ph}\cdot\text{CO}\cdot\text{NH}\cdot\text{OAc}$ , m. p.  $148$ — $149^\circ$ , forms long, flat crystals; its *potassium* salt does not decompose at  $25^\circ$ , but explodes if heated for four or five minutes at  $50^\circ$ . The *propionyl*, *n-butyryl*, and *isobutyryl* esters of phenylacethydroxamic acid have m. p.  $138$ — $139^\circ$ ,  $113$ — $114^\circ$ , and  $111$ — $112^\circ$  respectively.

A discussion is given of the mechanism of the Beckmann rearrangement, and evidence is presented in support of the views advanced by Stieglitz (Abstr., 1897, i, 43; 1903, i, 235). It is shown, however, that in the transformations of the hydroxamic acids there are certain factors, due to the influence of stereoisomerism, which cannot be fully explained by Stieglitz' hypothesis.

E. G.

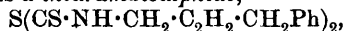
**Syntheses in the Fatty Aromatic Series. VI. Preparation of Fatty Aromatic Thiocarbimides by the Thiuramdisulphide Method.** JULIUS VON BRAUN and H. DEUTSCH (*Ber.*, 1912, 45, 2188—2198. Compare von Braun, Abstr., 1902, i, 271). Fatty aromatic thiocarbimides may be readily prepared by successive treatment of thiuramdisulphides with sodium and iodine. The yields are generally good, and all operations can be carried out in cold solutions.

An alcoholic solution of phenylethylamine was treated with carbon disulphide, and to the dithiocarbamate so formed, an alcoholic solution of iodine was added, whereon the *thiuramdisulphide*,



separated. It had m. p.  $83$ — $84^\circ$ , with simultaneous decomposition into the corresponding thiocarbimide, *s*-dialkylthiocarbamide, sulphur, and hydrogen sulphide. When acted on successively by sodium and iodine it yielded phenylethylthiocarbimide,  $\text{C}_2\text{H}_4\text{Ph}\cdot\text{NCS}$ , b. p.  $141$ — $144^\circ/11$  mm. The latter combines with ammonia to form phenylethylthiocarbamide, m. p.  $137^\circ$ , with aniline to form phenylphenylethylthiocarbamide, m. p.  $111^\circ$  (Michaelis, Schröber, and Linow, Abstr., 1893, i, 703, give  $106^\circ$ ), with phenylethylamine to form diphenylethylthiocarbamide, m. p.  $95^\circ$  (Neubert gives  $85^\circ$ ). It also combines with fatty amines, yielding, for example, *phenylethyl dimethylthiocarbamide*, m. p.  $112^\circ$ .

Phenylpropylamine was readily prepared by the reduction of phenylpropionitrile by means of sodium and alcohol. Like phenylethylamine, it yields a *thiuramdisulphide*,



m. p.  $62^\circ$ , which is more readily decomposed than the lower homologue, and similarly yields *phenylpropylthiocarbimide*, b. p.  $156$ — $160^\circ/12$  mm. (slight decomp.). The following thiocarbimides were prepared from

it; *phenylpropylthiocarbamide*, m. p. 111°; *phenylphenylpropylthiocarbamide*, m. p. 77°; *di-phenylpropylthiocarbamide*, m. p. 100°.

From phenylbutylamine an oily *thiuramdisulphide* was obtained, which was converted into *phenylbutylthiocarbimide*, b. p. 166—174°/12 mm. (slight decomp.). The latter united with the corresponding amines to form *phenylphenylbutylthiocarbamide*, m. p. 95°; *diphenylbutylthiocarbamide*, m. p. 49°; *phenylbutylpiperidylthiocarbamide*, m. p. 65°.

It is noteworthy that, whereas benzyl- and phenyl-ethylthiocarbimides possess powerful odours, phenylpropylthiocarbimide smells but faintly, and phenylbutylthiocarbimide is practically odourless when pure.

Benzhydramine yielded a yellow, oily, readily decomposable *thiuramdisulphide*, from which *benzhydrylthiocarbimide*,  $\text{CHPh}_2\cdot\text{N}^+\cdot\text{CS}$ , m. p. 58° was prepared in good yield, and which was perfectly stable at the ordinary temperatures. The following thiocarbimides were prepared: *phenylbenzhydrylthiocarbamide*,  $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{CHPh}_2$ , m. p. 181°; *dibenzhydrylthiocarbamide*, m. p. 211°; *benzhydrylisoamylthiocarbamide*, m. p. 110°. Benzhydrylthiocarbimide was further combined with hydrazine to yield *benzhydrylthiosemicarbazine*, m. p. 144°, the *benzylidene* derivative of which had m. p. 184°.

The *thiuramdisulphide* derived from anisamine was oily and readily decomposed, whilst the corresponding *thiocarbimide* could not be distilled without considerable decomposition. A fraction of b. p. 170—175°/16 mm., was isolated, which analysis showed to be pure. From it were obtained *phenylanisylthiocarbamide* and *dianisylthiocarbamide*, m. p. 142°.

The above method of preparing thiocarbimides appears to be general. Failure was met with *p*-nitrobenzylamine, the *thiuramdisulphide* of which, when treated with sodium ethoxide and subsequently with iodine, yielded no trace of thiocarbimide. H. W.

**The System Water-cycloHexanol.** ROBERT DE FORCRAND (*Compt. rend.*, 1912, 155, 118—121).—A determination of the solidification temperatures of mixtures of water and cyclohexanol up to a mixture containing 10% water. The curve is given and shows a eutectic at 4.73% water. The first portion of the curve is practically a straight line showing a constant molecular depression. The second half of the curve shows a notable inflexion in the neighbourhood of 3% water, corresponding with a compound,  $\text{C}_6\text{H}_{11}\cdot\text{OH} + \frac{1}{2}\text{H}_2\text{O}$ .

W. G.

**Catalytic Preparation, by the Wet Method, of Esters Resulting from Cyclanols and Organic Acids.** JEAN B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1912, 155, 168—170).—Esters of fatty alcohols and organic acids are readily obtained by the catalytic action of aluminium sulphate, potassium hydrogen sulphate, or sulphuric acid on a boiling mixture of the alcohol and acid, the best results being furnished by sulphuric acid (compare Abstr., 1911, i, 600, 637; ii, 1080). When applied to the cyclohexanols a difficulty arises in that they are converted on boiling with 4% sulphuric acid into cyclohexenes. This continues to take place to some extent even

in the presence of organic acids. By modifying the temperature, however, good yields of the esters can be obtained from these alcohols.

By mixing together *cyclohexanol* (1 mol.) and formic acid (2 mols.) at the ordinary temperature and adding 4% sulphuric acid, an immediate reaction occurs, *cyclohexyl formate* being produced without the formation of any *cyclohexene*. A similar result is obtained with the three methyl*cyclohexanols*. With the higher homologues of formic acid, the best results are obtained by keeping the mixture at 100—110° for one hour, when a yield of 90% is obtained.

W. G.

**Oxidation of *p*-Thymol.** Dehydrodi-*p*-thymol. HENRI COUSIN and HENRI HÉRISSEY (*Compt. rend.*, 1912, 155, 215—217 \*).—*p*-Thymol (compare Guillaumin, *Abstr.*, 1910, i, 375), like its isomerides thymol and carvacrol, is oxidised by ferric chloride or by the oxydase of mushrooms, giving dehydrodi-*p*-thymol (compare *Abstr.*, 1908, i, 84, 727, 783; 1910, i, 476). *p*-Thymol is dissolved in alcohol, diluted with a large quantity of water, mixed with a solution of ferric chloride, and left to remain for six days at 16—18°. A pale yellow, voluminous precipitate slowly forms, which on purification gives crystals of dehydrodi-*p*-thymol,  $\text{OH}\cdot\text{C}_6\text{H}_2\text{Pr}^{\beta}\text{Me}\cdot\text{C}_6\text{H}_2\text{Pr}^{\beta}\text{Me}\cdot\text{OH}$ , m. p. 96—97°. This can be similarly prepared by replacing the ferric chloride by a glycerol extract of *Russula delica*, and keeping a current of air passing through the liquid. It gives no coloration with ferric chloride, is soluble in alkalis, being reprecipitated by acids, and generally exhibits phenolic characteristics. Benzoyl chloride, in the presence of alkalis, converts it into its *dibenzoyl* derivative, m. p. 184—185°. W. G.

**Nitration of Guaiacol.** ALFONS KLEMENC (*Monatsh.*, 1912, 33, 701—707. Compare this vol., i, 459).—6-Nitroguaiacol was obtained previously (*loc. cit.*) by boiling 5-nitroveratric acid with aniline. It is more easily prepared in quantity by nitration of guaiacol dissolved in ether with red fuming nitric acid. A mixture of 45% of 6-nitroguaiacol, 25% of 4-nitroguaiacol, and a varying proportion of 4:6-dinitroguaiacol is obtained. The preponderance of 6-over 4-nitroguaiacol is unusual.

No nitro-derivative of acetylguaiacol could be obtained under similar conditions, but on nitrating in acetic acid in fairly concentrated solution, 5-nitroguaiacyl acetate was obtained as the sole product. Acetylation of a phenolic group decreases the velocity of nitration very much more than etherification. The nature of the solvent has very little influence.

Previously, 4-nitroguaiacol had only been prepared by way of *p*-nitrosoguaiacol (Rupe, *Abstr.*, 1898, i, 72).

Further nitration of either 4- or 6-nitroguaiacol yielded the same dinitroguaiacol, identical with that described by Herzig (*Abstr.*, 1884, 464).

*Acetyl-6-nitroguaiacol* crystallises in colourless platelets, m. p. 40°.

E. F. A.

**Fluorene Series. III.** JULIUS SCHMIDT, FRIEDRICH RETZLAFF, and AUGUST HAID (*Annalen*, 1912, 390, 210—234).—When heated

\* and *J. Pharm. Chim.*, 1912, [vii], 6, 147—153; *Bull. Soc. Chim.*, 1912, [iv], 11, 853—857.

with concentrated sulphuric acid on the water-bath, fluorene yields a mixture of three disulphonic acids, called the  $\alpha$ ,  $\beta$ , and  $\gamma$  respectively, which are isolated in the form of the barium salts. *Fluorene- $\alpha$ -disulphonic acid*, the barium salt of which is the least soluble, proves to be the 2:7-disulphonic acid. When heated with potassium hydroxide and a little water at 320—325° for about twenty minutes, potassium fluorene-2:7-disulphonate is converted into 2:7:9:9-tetra-

*hydroxyfluorene*,  $\begin{matrix} \text{C}_6\text{H}_3(\text{OH}) \\ \text{C}_6\text{H}_3(\text{OH}) \end{matrix} > \text{C}(\text{OH})_2$ , m. p. 278° (*tetrabenzoate*, m. p.

260°). The positions of the hydroxyl groups are deduced from the following properties. When heated with phosphorus pentachloride at 250°, the tetrahydroxyfluorene is converted into 9:9-dichloro-2:7-

*fluorenequinone*,  $\text{CCl}_2 < \begin{matrix} \text{C}_6\text{H}_3\text{O} \\ \text{C}_6\text{H}_3\text{O} \end{matrix}$ , m. p. 165°, yellow needles, which is

insoluble in alkalis. When heated with phosphorus pentachloride in a sealed tube for eight hours at about 220°, the tetrahydroxyfluorene is converted into 2:7:9:9-tetrachlorofluorene, m. p. 215°, colourless needles, identical with the compound obtained by Schmidt and Wagner from 2:7-dinitrofluorenone.

2:7-Dinitrofluorenone, which is best prepared by boiling fluorenone and red nitric acid, D 1.525, for two hours, is reduced by tin and hydrochloric acid to 2:7-diaminofluorenone hydrochloride,

$\text{C}_{13}\text{H}_{10}\text{ON}_2 \cdot 2\text{HCl}$ ,  
which does not melt at 360° and forms a *phenylhydrazone*,  
 $\text{C}_{19}\text{H}_{16}\text{N}_4 \cdot 2\text{HCl}$ ,

yellow leaflets, sintering above 250°. 2:7-Diaminofluorenone, m. p. about 290°, dark violet needles, forms a *picrate*, m. p. 230° (decomp.), *phenylhydrazone*, m. p. 230° (decomp.), red needles, *oxime*, m. p. 255°, *p*-nitrophenylhydrazone, m. p. 280°, crimson needles, and *tetra-acetyl* derivative, m. p. 222°, yellow needles. By diazotisation and subsequent heating with water, 2:7-diaminofluorenone is converted into 2:7-dihydroxyfluorenone, red needles.

When treated with concentrated sulphuric acid and red nitric acid, D 1.525, fluorenone is converted into 2:3:6:7-tetranitrofluorenone, m. p. 248° (decomp.), yellow, rhombic plates. This compound, which is also obtained by heating 2:6:7-trinitrofluorenone with concentrated nitric and sulphuric acids, crystallises from glacial acetic acid in large, amber crystals containing  $\text{C}_2\text{H}_4\text{O}_2$ , forms an *oxime*, decomp. 249°, yellow needles (*acetyl* derivative,  $\text{C}_{15}\text{H}_7\text{O}_{10}\text{N}_5$ , m. p. 223°), and *semicarbazone*, m. p. 271° (decomp.), and is reduced by tin and hydrochloric acid to the *hydrochloride* of tetra-aminofluorenyl alcohol,  $\text{C}_{13}\text{H}_{14}\text{ON}_4 \cdot 4\text{HCl}$ ; the free base is extremely unstable.

2:3:6:7-Tetranitrofluorenone does not react with phenylhydrazine or *p*-nitrophenylhydrazine; 2:6:7-trinitrofluorenone readily forms a *p*-nitrophenylhydrazone, decomp. 170—185°. C. S.

**Splitting of Aminoarylcarbinols by the Action of Bromine.**  
LATHAM CLARKE and RICHARD HARKNESS PATCH (*J. Amer. Chem. Soc.*, 1912, 34, 912—917).—Clarke and Esselen (*Abstr.*, 1911, i, 725) have shown that when a solution of 2:5-dibromo-4-aminobenzhydrol in

chloroform is treated with bromine, it is decomposed with formation of 2:4:6-tribromoaniline and benzaldehyde. It has since been found that this is a general reaction for aminobenzhydrols. The work has now been extended to aminoarylcarbinols containing an aliphatic residue, and also to tertiary carbinols.

By the action of bromine on 4-dimethylaminophenylethylcarbinol, *p*-bromodimethylaniline hydrobromide and propaldehyde are produced. 4-Dimethylaminophenylisobutylcarbinol similarly yields *p*-bromodimethylaniline hydrobromide and isovaleraldehyde.

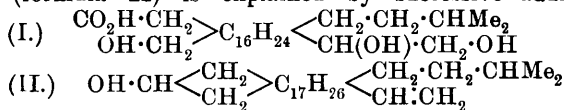
4-Dimethylaminodiphenylmethylcarbinol was obtained by Fecht (Abstr., 1907, i, 927) as an oil. If prepared from benzanilide, dimethylaniline, and phosphoryl chloride, it can be obtained in transparent prisms, m. p. 67°. When treated with bromine, it yields *p*-bromodimethylaniline hydrobromide and acetophenone.

Dimethylaminotriphenylcarbinol is decomposed by bromine with formation of a fair yield of *p*-bromodimethylaniline, but only a small quantity of benzophenone; it is probable that most of the carbinol is converted by the bromine into fuchsonedimethylimonium bromide. Tetramethyldiaminotriphenylcarbinol and hexamethyltriaminotriphenylcarbinol were also treated with a chloroform solution of bromine; in each case a small amount of *p*-bromodimethylaniline was obtained, but no ketone could be isolated, most of the carbinol having been converted into fuchsone derivatives.

E. G.

**The Action of Perhydrol on Cholesterol in the Presence of Sulphuric Acid.** STÉPHANE MINOVICI and EUGÈNE VLAHUTZA (*Bull. Soc. chim.*, 1912, [iv], 11, 747—754).—When an intimate mixture of 10 grams of cholesterol, 33 c.c. of perhydrol, and 67 c.c. of sulphuric acid (D 1·8) is warmed on a water-bath with constant agitation, a clotted mass is obtained, which can be purified by solution in alkali, reprecipitation by dilute hydrochloric acid, and subsequent evaporation of the ethereal solution in a vacuum.

The white, amorphous acidic substance, m. p. 112° (decomp.),  $[\alpha]_D + 17\cdot39^\circ$  (in ether), thus obtained has the composition  $C_{26}H_{46}O_5$  (probable structure given in formula I), and its formation from cholesterol (formula II) is explained by successive addition of



hydroxyl groups at the vinyl group, oxidation of the cyclic alcoholic radicle to a ketonic group with subsequent disruption of the ring, and finally elimination of a methyl group from the  $C_{17}H_{26}$  nucleus.

The *potassium*, *sodium*, *caesium*, and *rubidium* salts are deliquescent; the amorphous *ammonium* salt, m. p. 150° (decomp.), was obtained by the action of an alcoholic solution of ammonia on an ethereal solution of the acid. The *silver* salt, a red amorphous powder, on treatment with the calculated amount of methyl iodide yields the *methyl* ester, an amorphous powder, m. p. 70°. The other esters are generally of syrupy consistency.

D. F. T.

**The Formation of Basic Derivatives of Cholesterol and the Preparation of  $\alpha$ -Cholestylamine.** OTTO DIELS and ERICH STAMM (*Ber.*, 1912, 45, 2228—2232).—Cholesterol readily reacts with chloroacetyl chloride to form cholesteryl chloroacetate, from which cholesteryl piperidylacetate can be prepared. The corresponding amino-derivative could not be obtained by the action of ammonia.  $\alpha$ -Cholestylamine was obtained by the reduction of  $\alpha$ -cholestanoneoxime. The latter substance and the corresponding semicarbazone have unexpectedly low and indefinite m. p.'s, possibly owing to the formation of liquid crystals.

*Cholesteryl chloroacetate*, prepared by warming cholesterol with chloroacetyl chloride, has m. p.  $162^{\circ}$ . *Cholesteryl piperidylacetate* has m. p.  $114.5^{\circ}$ . The *hydrochloride* of the latter was analysed.

*$\alpha$ -Cholestanone-p-nitrophenylhydrazone* separates from alcohol in yellow needles, which soften at  $179^{\circ}$ , and are completely melted at  $184^{\circ}$ .

*$\alpha$ -Cholestanoneoxime* is a white, amorphous powder, which softens at  $75^{\circ}$ , and has m. p.  $95$ — $100^{\circ}$ . It forms a well-crystallised additive product with carboxyethylcarbimide, m. p.  $161^{\circ}$  (decomp.). When reduced by sodium in boiling amyl-alcoholic solution, it is transformed into  *$\alpha$ -cholestylamine*, m. p.  $110$ — $120^{\circ}$ , the *hydrochloride* of which was also analysed.

H. W.

**Chlorination of Benzoic Acid.** J. TH. BORNWATER and ARNOLD F. HOLLEMAN (*Rec. trav. chim.*, 1912, 31, 221—248).—An endeavour to clear up the question as to the result of chlorinating benzoic acid (compare Claus and Bücher, *Abstr.*, 1887, 828; Lossen, 1904, i, 159). In this paper the question is only dealt with from the qualitative side. In the first part of the paper directions are given for the preparation of the pure mono- and di-chlorobenzoic acids from various derivatives of toluene, after which some of the physical properties of the monochlorobenzoic acids are compared, from which a method for the qualitative separation of benzoic and the monochlorobenzoic acids is drawn up.

By the action of chlorine on a slight excess of benzoic acid in the presence of ferric chloride at about  $20^{\circ}$ , in the absence of light, the principal product is *m*-chlorobenzoic acid, together with some 2:5- and 3:4-dichlorobenzoic acids. When one atom of chlorine has been introduced, the rate of substitution is much greater, and the second entrant chlorine atom seems to be directed by the atom already present rather than by the carboxyl group.

On chlorinating benzoyl chloride by the passage of a current of chlorine with intermittent exposure to light, additive products are formed, the principal one being the hexachloride of benzoic acid, together with some benzene hexachloride.

The last part of the paper contains fusion-point curves and tables of results for mixtures of benzoic acid with each of the monochloroacids, and also mixtures of the three monochloroacids taken in pairs.

W. G.

**Derivatives of Ethyl  $\alpha$ -Cyanophenylacetate and Ethyl  $\alpha$ -Cyanobutyrate.** HARRY F. HADLEY (*J. Amer. Chem. Soc.*, 1912, 34, 923—928).— $\alpha$ -Cyanophenylacetic and  $\alpha$ -cyanobutyric acids each contain an asymmetric carbon atom. The present work was undertaken with the object of separating the acids into their two enantiomorphous modifications. The salts of  $\alpha$ -cyanophenylacetic acid proved too unstable for the purpose. Attempts were made to resolve  $\alpha$ -cyanobutyric acid by means of its metallic salts and also by the fractional crystallisation of its salts with optically active alkaloids, but in each case without success.

Lead and cadmium  $\alpha$ -cyanophenylacetates, and barium, strontium, strychnine, and brucine  $\alpha$ -cyanobutyrate were prepared and analysed. Aniline  $\alpha$ -cyanobutyrate, has m. p.  $57^{\circ}$ ; the anilide was also prepared.

$\alpha$ -Cyano- $\alpha$ -ethylbutyranilide, m. p.  $217$ — $218^{\circ}$ , crystallises in long needles; the corresponding *p*-toluidide was also prepared. E. G.

**Influence of Calcium Benzoate on the Solubility of Calcium Cinnamate.** ANNE W. K. DE JONG (*Rec. trav. chim.*, 1912, 31, 256—257).—A solution of calcium benzoate saturated at  $26^{\circ}$ , on warming dissolves calcium cinnamate, and from the solution, on cooling, there separate out crystals of a double salt having the composition  $\text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\cdot\text{Ca}\cdot\text{CO}_2\text{Ph}\cdot 3\text{H}_2\text{O}$ . W. G.

**Derivatives of Diphenylbromoacetic Acid.** HEINRICH KLINGER and G. NICKELL (*Annalen*, 1912, 390, 365—370).—Diphenylbromoacetyl bromide,  $\text{CPh}_2\text{Br}\cdot\text{COBr}$ , m. p.  $64$ — $65^{\circ}$ , obtained by heating benzilic acid and phosphorus pentabromide (2 mols.) on the water-bath, is converted by warm aniline into diphenylanilinoacetanilide, m. p.  $181$ — $182^{\circ}$ , and by ethereal aniline (2 mols.) into diphenylbromoacetanilide, m. p.  $85$ — $86^{\circ}$ .

When diphenylchloro- or bromo-acetanilide is heated at  $140$ — $230^{\circ}$  for one and a-half hours, each yields a substance which crystallises from benzene in prismatic needles containing  $\text{C}_6\text{H}_6$ , m. p.  $225$ — $226^{\circ}$ , and may possibly be 1 : 3 : 3 : 4 : 6 : 6-hexaphenyl-2 : 5-diketopiperazine.

Diphenylaminoacetamide,  $\text{NH}_2\cdot\text{CPh}_2\cdot\text{CO}\cdot\text{NH}_2$ , m. p.  $144$ — $145^{\circ}$ , is obtained by passing dry ammonia into a cold ethereal solution of diphenylbromoacetyl bromide. C. S.

**The Condensation of Phenylglycollonitrile with Aromatic Aldehydes in the Presence of Thionyl Chloride.** STÉPHANE MINOVICI and Mlle. THÉODOSIE ZENOVICI (*Bull. Soc. chim.*, 1912, [iv], 11, 757—762).—Aromatic aldehydes can condense in several ways with phenylglycollonitrile (E. Fischer, Abstr., 1896, i, 262; Minovici, Abstr., 1899, i, 890; *Bull. de Chim. Roum.*, 1910, No. 1). The final product of the action of thionyl chloride on a mixture of an aromatic aldehyde with phenylglycollonitrile is of the structure  $(\text{CHPhCl}\cdot\text{CO}\cdot\text{NH})_2\text{R}$ , where R represents the benzylidene or some analogous radicle; chlorophenylacetoneitrile,  $\text{CHPhCl}\cdot\text{CN}$ , and chlorophenylacetamide,  $\text{CHPhCl}\cdot\text{CONH}_2$ , are probably intermediate products.

Thionyl chloride is cautiously added to an equimolecular quantity

of phenylglycollonitrile, and after thirty-six hours, an equimolecular quantity of aromatic aldehyde is introduced. After a time the mass solidifies; after extracting with ether, the residue is recrystallised from alcohol.

*Benzylidenebisphenylchloroacetamide*,  $(\text{CHPhCl}\cdot\text{CO}\cdot\text{NH})_2\text{CHPh}$ , obtained in the above manner using benzaldehyde, forms plates or fine needles, m. p. 192—194°.

*p-Methoxybenzylidenebisphenylchloroacetamide*,  
 $(\text{CHPhCl}\cdot\text{CO}\cdot\text{NH})_2\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ ,  
 prepared with the use of anisaldehyde, forms silky needles, m. p. 196—198°.

*p-isopropylbenzylidenebisphenylchloroacetamide*,  
 $(\text{CHPhCl}\cdot\text{CO}\cdot\text{NH})_2\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}_2$ ,  
 obtained analogously from cuminaldehyde, forms needles, m. p. 197—199°.

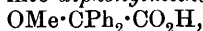
These three substances are hydrolysed by dilute hydrochloric acid in a sealed tube at 120°, giving the corresponding aldehyde together with phenylglycollic acid and ammonium chloride. They also react with aniline or phenylhydrazine on gentle warming; the action of aniline gives *benzylidenebisphenylanilinoacetamide*,

$(\text{NHPh}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH})_2\text{CHPh}$ ,  
 m. p. 202°; *p-methoxybenzylidenebisphenylanilinoacetamide*,  
 $(\text{NHPh}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH})_2\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ ,  
 m. p. 193°, and *p-isopropylbenzylidenebisphenylanilinoacetamide*,  
 $(\text{NHPh}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH})_2\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}_2$ ,  
 m. p. 220°, all crystallising in needles. The action of phenylhydrazine gives three analogous substances, likewise crystallising in needles; *benzylidenebisphenylphenylhydrazinoacetamide*,  
 $(\text{NHPh}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH})_2\text{CHPh}$ ,  
 m. p. 183° (decomp.); *p-methoxybenzylidenebisphenylphenylhydrazinoacetamide*,  $(\text{NHPh}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH})_2\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , m. p. 187° (decomp.), and *p-isopropylbenzylidenebisphenylphenylhydrazinoacetamide*,  $(\text{NHPh}\cdot\text{NH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{NH})_2\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{CHMe}_2$ , m. p. 196° (decomp.).  
 D. F. T.

**The Saponification of a Cyanohydrazone.** C. GASTALDI (*Gazzetta*, 1912, 42, i, 612—617).—The hydrolysis of  $\alpha$ -nitrophenyl-acetonitrile yields, instead of a carboxylic acid,  $\omega$ -nitrophenylmethane, carbon dioxide being lost (Wislicenus and Endres, *Abstr.*, 1902, i, 541). The hydrolysis of the similarly constituted phenylecyano-formaldehyde-*o*-nitrophenylhydrazone,  $\text{CN}\cdot\text{CPh}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , has therefore been studied, and it is found that saponification proceeds in the usual manner, but that carbon dioxide may be eliminated by heating the product to fusion.

*Phenylglyoxylic acid o-nitrophenylhydrazone*,  
 $\text{CO}_2\text{H}\cdot\text{CPh}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ ,  
 prepared by heating the cyano-compound with 10% alcoholic potash, separates from benzene in yellow crystals, m. p. 180—181°. The *potassium* salt forms rose-coloured crystals, with  $2\text{H}_2\text{O}$ ; the *silver* salt forms a pink, crystalline powder. The acid yields benzaldehyde-*o*-nitrophenylhydrazone on fusion.  
 C. H. D.

**Derivatives of Alkyloxydiphenylacetic Acid and Alkyloxydiphenyleneacetic Acid.** HEINRICH KLINGER (*Annalen*, 1912, 390, 371—376).—The halogen atoms in diphenylchloro- and bromo-acetic acids are much more easily displaced than those in diphenylene chloro- and bromo-acetic acids. Thus diphenylbromoacetyl bromide in methyl alcohol at 0° yields a substance, b. p. 191—192°/19 mm., which is converted by hydrolysis into *diphenylmethoxyacetic acid*,

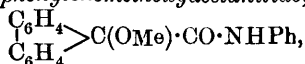


m. p. 99—100°.

*Diphenylethoxyacetic acid*, m. p. 113—114°, is obtained in a similar manner from diphenylbromoacetyl bromide and ethyl alcohol. Diphenylchloroacetyl chloride and alcohol yield 65% of ethyl diphenylchloroacetate.

*Methyl diphenylenemethoxyacetate*,  $\begin{matrix} \text{C}_6\text{H}_4 \\ \text{C}_6\text{H}_4 \end{matrix} > \text{C}(\text{OMe}) \cdot \text{CO}_2\text{Me}$ , m. p. 124°,

and the *ethyl* ester, m. p. 72°, are obtained by heating the corresponding esters of diphenylenechloroacetic acid with methyl-alcoholic silver nitrate. By hydrolysis they yield *diphenylenemethoxyacetic acid*, m. p. 181° (decomp.). Diphenylenebromoacetanilide and methyl-alcoholic silver nitrate yield *diphenylenemethoxyacetanilide*,



m. p. 195—196°.

*Diphenylene-ethoxyacetic acid*, m. p. 169°, is obtained by the hydrolysis of its *methyl* ester, m. p. 77°. *Diphenylene-ethoxyacetanilide*, m. p. 129—130°, is prepared from alcoholic silver nitrate and diphenylene-chloro- or -bromo-acetanilide.

C. S.

**Behaviour of Acid Dichlorides towards Ammonia.** JOHANNES SCHEIBER and MAX KNOTHE (*Ber.*, 1912, 45, 2252—2259).—The authors have examined the absorption spectra and the action towards ammonia of a number of acid dichlorides, and draw the conclusion that the formation of a nitrile acid by the interaction of an acid dichloride and ammonia cannot be regarded as evidence of the unsymmetrical structure of the former, but only shows a spatial proximity of the  $-\text{COCl}$  groups, or of the  $-\text{COCl}$  and  $-\text{SO}_2\text{Cl}$  groups.

*cis*- and *cis-trans*-Camphoryl chlorides in ethereal solution have absorption spectra which are similar and appreciably stronger than that of *cis*-camphoric acid (measured in aqueous solution in the form of its sodium salt).

*Quinolinyl dichloride*, b. p. 159°/19 mm., was prepared by the action of phosphorus pentachloride on quinolinic acid. Its symmetrical nature was shown by the formation of the same dimethyl ester from quinolinyl dichloride and sodium methoxide as from silver quinolinate and methyl iodide, whilst, also, the absorption spectra of quinolinic acid (in alcohol), methyl quinolinate (in ether), and quinolinyl dichloride (in ether) were similar. Aqueous ammonia transformed quinolinyl dichloride into 3-cyanopyridine-4-carboxylic acid, m. p. 175—176°, the constitution of which follows from its hydrolysis to nicotinic acid.

*iso*Phthalyl and terephthalyl dichlorides were quantitatively transformed by ammonia into the corresponding diamides.

Comparison of the absorption curves of *o*-toluenesulphonic acid and its chloride showed that the transformation of the group  $-\text{SO}_2\cdot\text{OH}$  into  $-\text{SO}_2\text{Cl}$  did not alter the nature of the absorption, which is increased. *o*-Sulphobenzoyl dichloride (m. p.  $40^\circ$ ) was found to show an absorption similar to that of *o*-sulphobenzoic acid, whilst the isomeric chloride (m. p.  $79^\circ$ ) showed much weaker absorption. Contrary to the usual practice, the authors consider the dichloride (m. p.  $40^\circ$ ) to be symmetrical; that of m. p.  $79^\circ$  to be unsymmetrical. H. W.

[Solutions of Hydrogen Cyanide and Benzaldehyde.] P. WIRTH (*Arch. Pharm.*, 1912, 250, 396—397).—The author replies to Rosenthaler's criticisms (*Abstr.*, 1911, i, 987) of his work (*Abstr.*, 1911, i, 875). C. S.

*o*- and *p*-Mercaptobenzaldehyde. PAUL FRIEDLÄNDER and EMIL LENK (*Ber.*, 1912, 45, 2083—2090).—Starting from *o*- and *p*-aminobenzaldehydes, *o*- and *p*-aldehydophenyl mercaptans, the first aldehydomercaptans to be prepared, have been obtained as volatile oils which easily polymerise.

*o*-Nitrobenzyl chloride when warmed with a solution of sulphanilic acid and excess of sodium carbonate, then treated with a solution of common salt and with a solution of sulphur in aqueous sodium hydroxide, and finally distilled with steam gives *o*-aminobenzaldehyde; this can be diazotised by dissolving in alcohol with the calculated quantity of nitrite and adding gradually to cold dilute sulphuric acid.

[*p*-Diazobenzaldehyde couples with  $\beta$ -naphthol giving *p*-aldehydobenzeneazo- $\beta$ -naphthol, needles, m. p.  $183^\circ$ , which reacts easily with hydrazine, phenylhydrazine, and hydroxylamine. *m*-Diazobenzaldehyde in a similar manner gives *m*-aldehydobenzeneazo- $\beta$ -naphthol, orange-red needles, m. p.  $156^\circ$ . *o*-Diazobenzaldehyde likewise couples with  $\beta$ -naphthol, giving a red dye, but this rapidly isomerises to 3-hydroxy-indazolyl-2- $\beta$ -naphthol,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{C}(\text{OH}) \end{smallmatrix} \text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$ , a colourless substance, m. p.  $235^\circ$  (compare Bamberger and Lublin, *Abstr.*, 1909, i, 509); the coupling product with  $\alpha$ -naphthol is similarly rearranged to 3-hydroxyindazolyl-2- $\alpha$ -naphthol, colourless needles, m. p.  $238^\circ$ .]

If a diazotised solution of *o*-aminobenzaldehyde sulphate is run into a suspension of cuprous thiocyanate in a solution of potassium thiocyanate, *o*-thiocyanobenzaldehyde,  $\text{CHO}\cdot\text{C}_6\text{H}_4\cdot\text{SCN}$ , colourless needles, m. p.  $76^\circ$ , is obtained; on mixing this with a warm aqueous solution of sodium sulphide and cooling, the sodium salt of *o*-mercaptobenzaldehyde separates in yellow crystals; free *o*-mercaptobenzaldehyde (*o*-aldehydophenyl mercaptan),  $\text{SH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$ , liberated by cautious treatment with acids, is a yellow oil of mercaptan-like odour, which on keeping quickly changes to a yellow resin. Oxidation of the mercaptan compound with potassium ferricyanide gives dibenzaldehyde *o*-disulphide,  $\text{S}_2(\text{C}_6\text{H}_4\cdot\text{CHO})_2$ , yellow needles, m. p.  $145^\circ$ . Other derivatives of the mercaptobenzaldehyde are *o*-methylthiolbenzaldehyde,  $\text{SMe}\cdot\text{C}_6\text{H}_4\cdot\text{CHO}$  (obtained by the action of methyl sulphate), which gives an *azine*,  $\text{SMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{SMe}$ , yellow leaflets,

m. p. 119°, *phenylhydrazone*, m. p. 127—129°, and *thionaphthen-2-carboxylic acid*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} \\ \text{S} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$  (obtained by the action of sodium chloroacetate), colourless needles, m. p. 114°. The last-named derivative on heating with quicklime gives thionaphthen.

*p*-Aminobenzaldehyde can be obtained by the action on *p*-nitrotoluene of a solution of sulphur in aqueous sodium hydroxide; it is then diazotised and run into a solution of cuprous and potassium thiocyanates, when *p*-thiocyanobenzaldehyde is obtained, almost colourless needles, m. p. 78°; this substance reacts with an aqueous solution of sodium sulphide, giving the sodium salt of *p*-mercaptobenzaldehyde. This sodium salt can also be obtained by running the diazotised solution of *p*-aminobenzaldehyde into a solution of excess of potassium xanthate and subsequently hydrolysing the resultant *ethyl p*-aldehydophenyl xanthate,  $\text{CHO} \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{CS} \cdot \text{OEt}$  (m. p. 135°), with sodium hydroxide. *p*-Mercaptobenzaldehyde is a colourless oil (sodium salt, yellow leaflets), which quickly polymerises to a white solid, m. p. about 130°; this on treatment with sodium hydroxide solution gives the salt of the simple substance. The unimolecular compound gives a *phenylhydrazone*, m. p. 137°, and can be oxidised by potassium ferricyanide to the *disulphide*, yellow needles, m. p. 108°; the last substance gives a *phenylhydrazone*, leaflets, m. p. 198°. *p*-Methylthiolbenzaldehyde, a colourless oil, b. p. 273° (obtained by the action of methyl sulphate on the mercaptan), gives an *oxime*, m. p. 110°, a *phenylhydrazone*, leaflets, m. p. 138°, and an *azine*, yellow needles, m. p. 119°.

D. F. T.

The Partial Catalytic Hydrogenation of Substances Containing more than One Double Bond. CARL PAAL (*Ber.*, 1912, 45, 2221—2228. Compare Paal and Hartmann, *Abstr.*, 1909, i, 926).—The author has studied the partial reduction of styryl methyl ketone, cinnamylidenemalonic acid, piperic acid, piperine, phorone, and distyryl ketone, and draws the conclusion that only those compounds possessing two double bonds in which the latter are separated by at least one carbon atom are capable of partial reduction. In all experiments, colloidal palladium was used as catalyst.

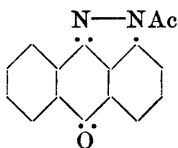
An alcoholic solution of styryl methyl ketone, when treated with the amount of hydrogen necessary for half-reduction, yielded unchanged styryl methyl ketone and  $\delta$ -phenylbutyl methyl ketone. Similarly, the half-reduction of an aqueous solution of sodium cinnamylidenemalonate led to the isolation of unchanged cinnamylidenemalonic acid and  $\omega$ -phenyl-*n*-propylmalonic acid. Piperic acid yielded *tetrahydropiperic acid*, m. p. 90—91°, together with unchanged piperic acid, whilst tetrahydropiperine and unchanged piperine were obtained when the latter was reduced.

Phorone, on the other hand, absorbed hydrogen very readily with the practically quantitative formation of *dihydrophorone* (*isobutyl isobutenyl ketone*), b. p. 176°. Its *semicarbazone* had m. p. 133—134°. Similarly, the main product of the half-reduction of distyryl ketone was phenylethyl styryl ketone. Dibenzylacetone was also formed in small quantity, together with substances of higher and less constant m. p.

When the solutions of phenylethyl styryl ketone were exposed to light, two substances, m. p. 125—126° and 180—188° respectively, were formed. H. W.

**Anthraquinonylmonohydrazines.** RICHARD MÖHLAU [with ARTUR VIERTEL and FR. REINER] (*Ber.*, 1912, 45, 2233—2244).—The preparation and properties of anthraquinonyl-1-hydrazine and anthraquinonyl-2-hydrazine are described.

*Anthraquinonyl-1-diazonium hydrogen sulphate* was prepared by the addition of sodium nitrite to a suspension of 1-aminoanthraquinone sulphate. When acted on by potassium hydroxide and potassium sulphite, it was transformed into *potassium anthraquinonyl-1-diazosulphonate*,  $C_{14}H_7O_5N_2SK$ , whilst, under the action of potassium sulphite and a little potassium hydroxide followed by heating the solution to 90°, *potassium anthraquinonyl-1-hydrazinedisulphonate*,  $C_{14}H_7O_2 \cdot N(SO_3K) \cdot NH \cdot SO_3K, 2H_2O$ , was formed. *Anthraquinonyl-1-hydrazine*, m. p. 210° (corr., decomp.), was prepared by reduction of the diazosulphonate by stannous chloride and hydrochloric acid. Its *hydrochloride* was analysed. By the action of equimolecular quantities of potassium anthraquinonyl-1-hydrazine disulphonate and the corresponding aldehyde in alcoholic solution in the presence of concentrated hydrochloric acid, the following hydrazones were prepared, the colours of which are appended: *benzylideneanthraquinonyl-1-hydrazone* (dark brownish-red), m. p. 214°, and its *acetyl* derivative (light yellow), m. p. 234°; *o-nitrobenzylideneanthraquinonyl-1-hydrazone* (reddish-brown), m. p. 268—270°; *m-nitrobenzylideneanthraquinonyl-1-hydrazone* (brownish-red), m. p. 285—287°; *p-nitrobenzylideneanthraquinonyl-1-hydrazone* (red), m. p. above 300°; *dimethyl-p-aminobenzylideneanthraquinonyl-1-hydrazone* (dark blue), m. p. 234—235°; *o-hydroxybenzylideneanthraquinonyl-1-hydrazone* (dark violet), m. p. 258—260°; *p-hydroxybenzylideneanthraquinonyl-1-hydrazone* (dark violet), m. p. 275—276°; *p-methoxybenzylideneanthraquinonyl-1-hydrazone* (deep violet with bronze glance), m. p. 232°; *piperonylanthraquinonyl-1-hydrazone* (deep violet), m. p. 253°; *cinnamylideneanthraquinonyl-1-hydrazone* (brownish-red), m. p. 201—202°; *ethyl anthraquinonyl-1-hydrazoneacetate* (reddish-brown), m. p. 169·5°. The latter substance, when treated with acetic anhydride and concentrated sulphuric acid, was transformed into *acetylpyrazole-anthrone* (annexed formula), m. p. 213° (corr.), which, under the action of alcoholic potassium hydroxide, followed by acidification, yielded *pyrazoleanthrone*, m. p. 277—278°. This substance was also obtained by heating anthraquinonyl-1-hydrazine with aniline and aniline hydrochloride at 150°.



*Anthraquinonyl-2-diazonium hydrogen sulphate* was prepared in the same manner as its isomeride (see above). It united with phenylmethylpyrazolone in aqueous solution in the presence of sodium acetate with the formation of *2-anthraquinonyl-4-diazo-1-phenyl-3-methyl-5-pyrazolone*, which was obtained in yellow needles and red leaflets. Each form has m. p. 247° and shows the same absorption

spectrum. At temperatures above  $110^{\circ}$ , the yellow modification is readily transformed into the red variety. *Potassium anthraquinonyl-2-hydrazinedisulphonate* was obtained by the same method as the 1-compound. When boiled with concentrated hydrochloric acid, it yielded the *hydrochloride* of *anthraquinonyl-2-hydrazine*, whilst, when boiled with 40% alcohol, it formed *potassium anthraquinonyl-2-hydrazinesulphonate*.

*Anthraquinonyl-2-hydrazine*, m. p.  $229^{\circ}$ , was prepared by boiling potassium anthraquinonyl-2-hydrazinedisulphonate with hydrochloric acid and subsequent treatment with sodium acetate. Its *hydrochloride* has m. p.  $238-239^{\circ}$  (decomp.). The following hydrazones were prepared by the action of the hydrazine with the requisite aldehyde or ketone in alcoholic or pyridine solution: *benzylideneanthraquinonyl-2-hydrazone* (dark red), m. p.  $286^{\circ}$ ; *p-nitrobenzylideneanthraquinonyl-2-hydrazone* (yellowish-red), m. p. above  $330^{\circ}$ ; *dimethyl-p-aminobenzylideneanthraquinonyl-2-hydrazones* (dark violet), m. p. about  $280^{\circ}$ ; *o-hydroxybenzylideneanthraquinonyl-2-hydrazone* (dark red), m. p.  $334^{\circ}$ ; *p-hydroxybenzylideneanthraquinonyl-2-hydrazone* (dark violet), m. p. above  $295^{\circ}$ ; *p-methoxybenzylideneanthraquinonyl-2-hydrazone* (reddish-violet), m. p.  $280-284^{\circ}$ ; *piperonylanthraquinonyl-2-hydrazone* (brownish-red), m. p. about  $290^{\circ}$ ; *2:3-dihydroxybenzylideneanthraquinonyl-2-hydrazone* (deep blue), m. p. about  $310^{\circ}$ ; *p-hydroxy-m-methoxybenzylideneanthraquinonyl-2-hydrazone* (yellowish-red), m. p.  $307-308^{\circ}$ ; *cinnamylideneanthraquinonyl-2-hydrazone* (reddish-brown), m. p.  $259^{\circ}$ ; *acetoneanthraquinonyl-2-hydrazone* (red), m. p.  $228^{\circ}$ ; *benzophenoneanthraquinonyl-2-hydrazone* (brownish-red), m. p.  $227^{\circ}$ ; *dibenzylideneanthraquinonyl-2-hydrazone* (reddish-orange), m. p.  $273^{\circ}$ ; the *anthraquinonyl-2-hydrazone* of *ethyl acetoacetate* (yellowish-orange), m. p.  $178^{\circ}$ . The latter compound, unlike the corresponding 1-isomeride, can be converted into a pyrazolone. Under the action of boiling acetic anhydride, it was transformed into 1- $\beta$ -anthraquinonyl-5-acetyl-3-methylpyrazolone, m. p.  $237^{\circ}$ , after darkening at  $225^{\circ}$ .  
H. W.

**A New Synthesis of Anthraquinonylhydrazines.** RICHARD MÖHLAU [with ARTUR VIERTTEL and ALFRED REDLICH] (*Ber.*, 1912, 45, 2244—2248).—Anthraquinonylhydrazines may be prepared by the interaction of hydrazine and  $\alpha$ -chloroanthraquinones.

Anthraquinonyl-1-hydrazine was prepared by boiling a solution of 1-chloroanthraquinone in pyridine with hydrazine hydrate during thirty minutes. In similar circumstances, 2-chloroanthraquinone and hydrazine hydrate do not react, but, when heated during eight hours at  $170^{\circ}$ , anthraquinonyl-2-hydrazine is formed. Similarly, 5-chloroanthraquinonyl-1-hydrazine, m. p.  $227^{\circ}$ , was formed when 1:5-dichloroanthraquinone and hydrazine hydrate were boiled in pyridine solution. When the above substance, or more simply 1:5-dichloroanthraquinone itself, was heated with hydrazine hydrate and pyridine at  $145^{\circ}$  during eight hours, *anthraquinonylene-1:5-dihydrazine*, m. p.  $258^{\circ}$ , was formed, which was converted by acetic anhydride into an *acetyl* compound. When a solution of the dihydrazine in concentrated sulphuric acid was warmed, a *dipyrazoleanthrone* was formed. 1:8-Dichloroanthraquinone, when boiled with hydrazine

hydrate in pyridine solution, formed transitorily 8-chloroanthraquinonyl-1-hydrazine, which passed into 8-chloropyrazoleanthrone, m. p. above  $360^{\circ}$ .

2:6-Dichloroanthraquinone was converted in small yield into anthraquinonylene-2:6-dihydrazine, m. p. above  $360^{\circ}$ , when heated with hydrazine hydrate and pyridine during eight hours at  $170^{\circ}$

H. W.

**Artificial Caoutchouc.** CARL D. HARRIES (*Zeitsch. angew. Chem.*, 1912, 25, 1457—1462). **Synthetic Caoutchouc** FRITZ HOFFMANN (*ibid.*, 1462—1467).—Lectures delivered before the Vereins Deutscher Chemiker at Freiburg in Breisgau dealing with the subject respectively from the scientific and the technical point of view.

**Chemistry of Caoutchouc. V. Theory of Vulcanisation.** III. DAVID SPENCE and J. YOUNG (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 28—34. Compare Abstr., 1911, i, 657).—Further experiments relating to the nature of the vulcanisation process have been made, in which the velocity of the change was determined. Pure white Ceylon-Para caoutchouc was intimately mixed with 10% of precipitated sulphur, and the vulcanisation carried out at a constant temperature ( $135^{\circ}$  or  $155^{\circ}$ ). After measured time intervals, the "fixed" sulphur was estimated, and the data thus obtained show that the reaction takes place at a constant speed. From the observed velocities at the two temperatures, the temperature-coefficient of the reaction is found to be 2.65. When the vulcanisation was carried out with 37% of sulphur, a similar constant velocity was observed, but instead of the whole of the sulphur being fixed, it was found that the process is completed when the proportion of fixed sulphur reaches 32%. This corresponds very closely with that required by the formula  $C_{10}H_{16}S_2$ , and this fact, together with the velocity observations, are considered to prove the untenability of the adsorption theory. The vulcanisation process, according to the authors, must therefore be considered essentially as a chemical process in which the above compound is formed.

Experiments on the vulcanisation of balata under the same conditions show that the course of the process is not only similar to that of the vulcanisation of caoutchouc, but that the velocity is very nearly the same in the two cases.

H. M. D.

[**Chemistry of Caoutchouc. Theory of Vulcanisation.**] WOLFGANG OSTWALD (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 34—36).—Polemical against Spence (compare previous abstract).

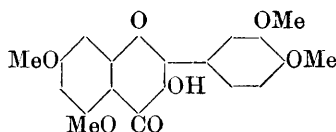
H. M. D.

**The Desulphurisation of Vulcanised Caoutchouc.** F. WILLY HINRICHSSEN and ERICH KINDSCHER (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 38—39).—The values obtained for the combined sulphur by treatment of vulcanised caoutchouc with metals in presence of alcoholic sodium hydroxide solution (compare *ibid.*, 1912, 10, 146) cannot be accepted as correct, in that this method fails to take into

account the sulphur which may be combined with inorganic constituents. It is now shown that a correction for this may be applied by estimation of the sulphur in the ash. When this correction is applied to the sulphur content of the extracted material, it is found that the observed percentage of combined sulphur diminishes considerably as the pressure in the autoclave, in which the disulphurisation is effected, is increased from four to ten atmospheres. The acetone soluble constituents are also found to vary to a very large extent according to the pressure.

H. M. D.

**Methylation of Glucosides.** JOSEF HERZIG and R. SCHÖNBACH (*Monatsh.*, 1912, 33, 673—681).—On methylation of quercitrin with diazomethane, the free hydroxyl groups in the quercetin residue are



readily methylated, whilst one methy group is slowly introduced into the rhamnose residue, a pentamethylquercitrin being obtained.

This when decomposed with dilute acids yields a colourless tetramethylquercetin, which probably has the annexed constitution (see following abstract).

The nature of the attachment of quercetin to rhamnose is thus established.

The monomethyl rhamnose has been obtained only as a syrup, yielding amorphous derivatives. Pentamethylquercitrin could not be hydrolysed by enzymes.

On methylation of strophantin a halt is reached at a compound,  $C_{43}H_{72}O_{19}$ , containing four methoxyl groups. On acid hydrolysis, strophantidin and a tetramethoxystrophantobiose are obtained; the latter has not been purified.

With other glucosides, products containing numerous methyl groups have been obtained.

Methylation with diazomethane is carried out in ethereal solution containing enough alcohol to dissolve the glucoside and at the ordinary temperature. Amorphous boron accelerates the change, but a much larger proportion of diazomethane is then required.

*Pentamethylquercitrin* is a pale yellow, amorphous powder.

*Tetramethylquercetin* crystallises in colourless needles, m. p. 195—198°.

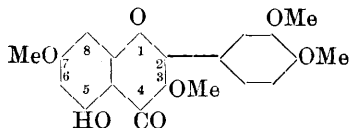
*Tetramethylnorstrophantin* forms a hygroscopic mass, m. p. below 100°.

E. F. A.

**Colourless Tetramethylquercetin.** JOSEF HERZIG [and PAULA BÖTTCHER] (*Monatsh.*, 1912, 33, 683—699. Compare preceding abstract).—Colourless tetramethylquercetin is converted quantitatively by means of methyl iodide and potassium hydroxide, or of methyl sulphate, or of diazomethane into pentamethylquercetin.

By the action of diazomethane on quercetin this tetramethylquercetin is obtained in addition to pentamethylquercetin. It is accordingly an intermediate product of methylation, whereas previously the yellow

tetramethylquercetin (annexed formula), which does not react with diazomethane, had been suggested as the intermediate product of methylation. The hindrance of the ortho-hydroxyl group towards methylation with diazomethane is only made manifest when the other hydroxyl groups are substituted.



Although resistant towards diazomethane, the yellow tetramethylquercetin can be methylated either with potassium hydroxide and methyl iodide or methyl sulphate.

On methylation of quercitrin with diazomethane, a red coloration is obtained in the early stages, giving way to yellow. This is attributed to the influence of the hydroxyl groups in positions 3 and 5.

Colourless tetramethylquercetin is shown to be identical with 5:7:3':4'-tetramethoxyflavonol (Kostanecki, Lampe, and Tambor, *Abstr.*, 1904, i, 517).

Pfeiffer (*Abstr.*, 1911, i, 595) has shown that hydroxyl groups in the ortho-position to the carbonyl group react with tin tetrachloride in benzene solution at the temperature of the water-bath, forming substitution compounds of the annexed type, whereas hydroxy-ketones with the hydroxyl groups in other positions only form additive compounds. It is now shown that such substitution compounds are given by 7-methyl-euxanthone and by yellow tetramethylquercetin, whereas colourless tetramethylquercetin forms an additive product.

Quercetin crystallises with  $2\text{H}_2\text{O}$ , and is then soluble in ester; anhydrous quercetin is insoluble.

*Monoacetyltetramethylquercetin*, from the colourless tetramethylquercetin, crystallises in colourless needles, m. p.  $160-163^\circ$ .

The colourless tetramethylquercetin has a great tendency to become coloured, particularly on crystallisation; from acetic acid it crystallises in pale yellow needles.

E. F. A.

**Constitution of the Aloins of the Natal Aloes.** EUGÈNE LÉGER (*Compt. rend.*, 1912, 155, 172—175. Compare *Abstr.*, 1898, i, 445; 1899, i, 157, i, 820; 1902, i, 549, 685).—A further proof of the presence of nataloin and homonataloin in Natal aloes, the latter of which Tschirch and Klaveness were unable to find (compare *Abstr.*, 1901, i, 399). Homonataloin on suitable hydrolysis yields a sugar, which can be isolated through its phenylbenzylhydrazone, and by its properties shown to be *d*-arabinose. Nataloin has not as yet been hydrolysed for its sugar, but as it, like homonataloin, yields furfuraldehyde on distillation with dilute sulphuric acid, it is probable that the two aloins have similar constitutions, and contain the same sugar.

W. G.

**Laserpitin.** OTTO MORGENSTERN (*Monatsh.*, 1912, 33, 709—749).—Laserpitin,  $\text{C}_{26}\text{H}_{40}\text{O}_7$ , obtained by extraction of colourless gentian root with light petroleum, forms rhombic crystals [ $a:b:c =$

0.47644:1:1.32865], m. p. 117—117.5° to a clear, colourless liquid,  $[\alpha]_D^{18.5} + 118.7^\circ$ . The hydrochloride crystallises in octahedra, m. p. 135—136°. With bromine a crystalline bromide,  $C_{26}H_{40}O_7Br_4$ , is obtained, m. p. 163—165°. Laserpitin could not be acetylated, but it forms a crystalline acetate,  $C_{26}H_{40}O_7 \cdot C_2H_3O_2$ , which loses the acetic acid on drying in a vacuum at 80°. Laserpitin does not react with phenylhydrazine.

On reduction in acetic anhydride solution with zinc dust, the acetate of the corresponding alcohol is produced as an amorphous, reddish-yellow compound. In presence of colloidal palladium and hydrogen it is reduced to *tetrahydrolaserpitin*,  $C_{26}H_{44}O_7$ , which forms crystals, m. p. 92—96°.

Quantitative hydrolysis proves that laserpitin contains two angelic acid residues, and by the action of alkali hydroxide, laserol is converted by the opening of the lactone ring into an acid. The acid character of laserol was further established by the quantitative elimination of carbon dioxide. The readiness with which the lactone ring closes again is in favour of its being a  $\gamma$ -lactone. The hydroxyl groups in laserol were identified by the preparation of *diacetyl-laserol*, an amorphous, reddish-yellow substance.

By the action of phenylhydrazine, a *phenylhydrazone* of laserol is formed, m. p. about 92°; this is a reddish-brown, amorphous powder. The keto-group was also identified by reduction and determination of the active hydrogen in dihydrolaserol by the method of Zerewitinoff.

The parent hydrocarbon could not be obtained by the action of hydrogen iodide and phosphorus.

On oxidation of laserol, formic acid and  $\gamma$ -hydroxy- $\delta$ -methylheptanoic acid were obtained, the latter acid yielding  $\alpha$ -methylbutyric, succinic, and malonic acids on oxidation.  $\gamma$ -Hydroxy- $\delta$ -methylheptanoic acid is an amorphous, yellow powder, m. p. 95—100°, decomp. 142—145°.

To sum up, laserpitin contains two hydroxyl groups esterified with angelic acid, a lactone ring, a keto-group, and the carbon atoms are present in open chains. The position of the keto-group and one hydroxyl is fixed by the discovery of the hydroxymethylheptanoic acid.  
E. F. A.

**The Composition of Picrotoxinin.** PAUL HORRMANN (*Ber.*, 1912, 45, 2090—2095).—The author finds that picrotoxinin has the composition  $C_{14}H_{16}O_6$ , instead of  $C_{15}H_{16}O_6$ , as previously stated (E. A. Schmidt, *Abstr.*, 1884, 845; Barth and Kretschy, *Abstr.*, 1884, 846).

Bromopicrotoxinin (Meyer and Bruger, *Abstr.*, 1899, i, 226), obtained by the action of bromine water on picrotoxinin, is a mixture of two isomerides,  $\alpha$ -bromopicrotoxinin, prisms, decomposing at 290°,  $[\alpha]_D^{17} - 69.9'$  (in chloroform), and  $\beta$ -picrotoxinin, needles, decomposing at 280°,  $[\alpha]_D^{17} - 129.14'$  (in chloroform); the two constituents of the mixture in which the  $\beta$ -isomeride preponderates can be separated by fractional crystallisation from acetic acid, and subsequently from alcohol. Both isomerides are reduced in alcoholic solution by zinc dust and ammonium chloride to pure picrotoxinin,  $C_{14}H_{16}O_6$  (not previously obtained pure), anhydrous needles, m. p. 20.5°, or some-

times prisms with water of crystallisation ( $\frac{1}{2}\text{H}_2\text{O}$ ),  $[\alpha]_D^{25} + 4^\circ 40'$  (in alcohol),  $+ 4^\circ 5'$  (in acetone) (compare Meyer and Bruger, *loc. cit.*). Bromination of pure picrotoxinin gives the same mono-substitution product as does the ordinary substance obtained directly from picrotoxin. D. F. T.

**Chlorophyll. XX. The Two Components of Chlorophyll.** RICHARD WILLSTÄTTER and MAX ISLER (*Annalen*, 1912, 390, 269—339).—Previous investigations have shown that two, and only two, fission products, namely, phytochlorin-*e* and phytorhodin-*g*, are obtained by the successive action of acids and alkalis on the chlorophyll of all plants examined, whether marine or land plants. These two products are obtained in approximately constant proportions, namely, 1 mol. of the phytorhodin to, at most, about 2.5 mols. of the phytochlorin. By the partition method with petroleum and aqueous methyl alcohol, the authors have separated chlorophyll into a bluish-green or greenish-blue chlorophyll-*a* and a yellowish-green chlorophyll-*b*; the former yields only phytochlorin-*e*, and the latter only phytorhodin-*g*, by fissive decomposition. These two components of chlorophyll are shown to be free from colourless or coloured concomitants and also from transformation products resulting by allomerisation.

Phæophytin is also shown to be a mixture of the two corresponding magnesium-free components. Usually, the proportion of these two components in phæophytin is the same as that in chlorophyll, namely, 1 mol. of component *b* to 2.5 mols. of component *a*. Some exceptions have been observed; phæophytin preparations from *Pinus* and from sage are richer in component *b*.

The proportion of the two components in chlorophyll, therefore, has been carefully examined, with results which show that the following precautions must be taken in order to obtain an accurate estimation. (1) During the extraction of the chlorophyll from the leaves, a fractional separation of the two components may occur. It is necessary, therefore, quantitatively to extract the colouring matter from the leaves. (2) According to the dilution of the extract and its content of water and of impurities, the phæophytin separates more or less incompletely; the portion remaining in the solution is richer in component *a*. It is necessary, therefore, that the chlorophyll in the extract shall be converted quantitatively into phæophytin before hydrolysis.

In estimating the proportion of the components *a* and *b* of the chlorophyll of any plant, therefore, the successive processes are complete extraction of the colouring matter, conversion without loss into crude phæophytin, isolation of the latter and its hydrolysis, as smoothly as possible, and finally the quantitative separation of the mixture of phytochlorin-*e* and phytorhodin-*g*. Since the chlorophyll of suitable plants can be converted into phytochlorin-*e* and phytorhodin-*g* without the formation of by-products, the amounts of the components, *a* and *b*, of chlorophyll can be estimated by determining colorimetrically the amounts of phytochlorin-*e* and phytorhodin-*g* produced therefrom, by comparison with standard solutions of the

pure substances. By the process indicated above, the authors have commenced an investigation of the proportions of the components *a* and *b* in the chlorophyll of many plants; the proportion is generally nearly constant, the mean of twenty-four experiments being 2.5 : 1 with an average variation from the mean of 10%. (Incidentally it has been shown that chlorophyll constitutes 0.7—1% of the dried leaves.)

It is necessary that the total chlorophyll extracted from the leaf, not just the portion which separates in the form of phæophytin, shall be converted into phytochlorin-*e* and phytorhodin-*g* by successive treatment with acid and alkali. The omission to fulfil this condition explains why other investigators have recorded such varying values of the proportions of the constituents of chlorophyll.

The necessity of quantitatively converting the chlorophyll in an extract into phæophytin and subsequently treating with concentrated alkali introduces disadvantages. In order to isolate the whole of the phæophytin, it is necessary to isolate as well a large amount of the accompanying substances. These substances, some of which are themselves hydrolysable, hinder the complete hydrolysis of the phæophytin, even under energetic treatment. The formation of phytochlorin-*e* and phytorhodin-*g* is not a simple process. After passing through the brown phase, the substance suffers hydrolysis, easily at the phytyl group, with difficulty at the  $\beta$ -CO<sub>2</sub>Me group. If the last hydrolysis is incomplete, the normal products of fission, phytochlorin-*e* and phytorhodin-*g*, are accompanied by more feebly basic derivatives. In addition to this, abnormal phytochlorins and phytorhodins may be produced through allomerism of the chlorophyll. Starting with pure phæophytin, the smooth course of the fission is easily controlled, because in a properly conducted experiment the sum of the phytochlorin-*e* and phytorhodin-*g* represents approximately two-thirds of the phæophytin. This control is impossible when an unknown amount of phæophytin is hydrolysed by alkali; in such circumstances, the only clue to a properly conducted hydrolysis is the production of the more feebly basic derivatives only in slight amount.

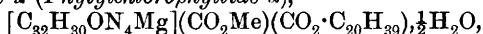
The complete extraction of the chlorophyll from the leaf is effected by alcohol, by percolation in the case of the powdered dry leaf, by digestion and decantation in the case of the fresh leaf. In order to prevent allomerisation of the chlorophyll, the alcoholic extract is added at once to aqueous-alcoholic oxalic acid. Water is added, and the phæophytin is extracted completely by ether. After the evaporation of the ether in a vacuum, the residual crude phæophytin, in quantities of about 0.3—0.6 gram, is dissolved in 1 c.c. of pyridine, heated on the water-bath, treated with 5—10 c.c. of boiling methyl-alcoholic potassium hydroxide, and then boiled for one minute over a naked flame. This treatment is necessary to hydrolyse completely the phæophytin, and at the same time to reduce to a minimum the decomposition of the phytorhodin-*g* by the alcoholic alkali. The solution is acidified and extracted with ether. The ethereal solution is extracted with 12% hydrochloric acid to separate the chlorins and rhodins from accompanying colourless or yellow impurities. The

12% hydrochloric acid extract is neutralised and shaken with ether. The ethereal solution is treated with 3% hydrochloric acid to remove the bulk of the phytochlorin, then with 5% hydrochloric acid, and finally with 9% hydrochloric acid to extract the phytorhodin. For details the paper must be consulted, but the final result is that the phytochlorin-*e* is obtained in 3% hydrochloric acid and the phytorhodin-*g* in 9% hydrochloric acid. These solutions are made up to volume with hydrochloric acid of the same strength (saturated with ether), and are compared in a Duboseq colorimeter with standard solutions of phytochlorin-*e* ( $C_{34}H_{36}O_6N_4$ ) and of phytorhodin-*g* ( $C_{34}H_{34}O_7N_4$ )

containing 1/20,000 mol. per litre. The results of numerous experiments show that, whether the fresh or the dried leaf is examined, the proportion of phytochlorin-*e* to phytorhodin-*g*, obtained from the chlorophyll of different plants, or from the chlorophyll of one and the same plant under different conditions of growth, is approximately constant, averaging 2.5 to 1.

The method whereby the components *a* and *b* of chlorophyll (from the leaf of the stinging-nettle) have been separated depends on the systematic fractional partition of the chlorophyll between aqueous methyl alcohol and petroleum; chlorophyll-*b* is obtained in the alcoholic layer, chlorophyll-*a* in the petroleum. The original paper must be consulted for details of the separation and purification.

*Chlorophyll-a (Phytylchlorophyllide-a),*



is a bluish-black, microcrystalline powder, which sinters and forms a viscous mass at 117—121°. It dissolves very easily in most solvents, but is very sparingly soluble in petroleum of b. p. 30—50°. The purity of the substance is guaranteed by the pure yellow colour obtained in the "phase" test, and by the fact that its fissive decomposition yields phytochlorin-*e*, but no other phytochlorins or phytorhodins. An ethereal solution of the substance is decomposed, gradually by 6%, instantly by 20%, hydrochloric acid. An excess of ethereal hydrogen chloride produces at once the blue colour of a phæophytin hydrochloride.

*Chlorophyll-b (Phytylchlorophyllide-b),*



is a dark green or greenish-black, glistening, microcrystalline powder, which sinters at 86—92°, and becomes viscous at 120—130°. It is, as a rule, somewhat less soluble than chlorophyll-*a*, but is quite insoluble in cold petroleum. It develops a transient, brilliant red coloration in the "phase" test, and yields by treatment with boiling alcoholic potassium hydroxide phytorhodin-*g* accompanied by a trace of phytochlorin-*e*. In ethereal solution it is converted into the phæophytin, slowly by 15%, rapidly by 20%, hydrochloric acid; ethereal hydrogen chloride produces instantly a green solution of the phæophytin hydrochloride.

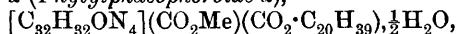
Phæophytins *a* and *b* can be obtained by the addition of alcoholic oxalic acid to suitable solutions obtained during the separation of chlorophylls *a* and *b* as above.

A separation can also be effected by Willstätter and Stoll's method

of fractional extraction with hydrochloric acid. The chlorophyll is extracted from the leaf and converted into phæophytin. A 0.25% ethereal solution of the latter is shaken with 27% hydrochloric acid, and finally with 29% hydrochloric acid, to remove the last trace of phæophytin-*a*. The ethereal solution is concentrated until phæophytin-*b* begins to separate. The hydrochloric acid extracts contain phæophytin-*a*, but since a partial hydrolysis of the phytol group occurs, it is best to keep the extracts until the hydrolysis is complete and to isolate the *a*-component in the form of phæophorbide-*a*.

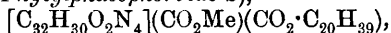
The separation of phæophytin-*a* and -*b* by Marchlewski's process with zinc hydroxide is incomplete, and yields products which are not free from ash.

*Phæophytin-a (Phytolphæophorbide-a),*



forms bluish-black, waxy lumps, which sinter at 110—114° and become viscous at 120°. It is deposited from hot alcoholic solution in microcrystalline aggregates. Concentrated solutions are olive-brown; dilute solutions are olive-green, similar to those of phytochlorin-*e*, but differing in exhibiting a faint red fluorescence. In glacial acetic acid, phæophytin-*a* (and, so also, the *b*-component) forms intensely blue or green complex metallic compounds with the acetates of copper, zinc, and other metals. Phæophytin-*a* gives a yellow phase with concentrated methyl-alcoholic potassium hydroxide, changing to green owing to the formation of a complex in which potassium exercises the function of the magnesium in chlorophyll. Phæophytin-*a* resembles methylphæophorbide in most respects, but has weaker basic properties; it is extracted from ethereal solution partly by 29%, almost completely by 32%, hydrochloric acid.

*Phæophytin-b (Phytolphæophorbide-b),*



is obtained as a greenish-black mass, more brittle than the *a* component. It sinters at 148—152°, becomes viscous, and decomposes at 160—170°. It gives a fine red, transient phase with concentrated alcoholic potassium hydroxide, and yields only phytorhodin-*g* by fissive hydrolysis. The basic properties of phæophytin-*b* are much weaker than those of component *a*; it is extracted only incompletely from ethereal solution by 35% hydrochloric acid.

[With E. HUG.]—Chlorophyllan has been prepared from grass according to the instructions of Hoppe-Seyler. By partial solution in petroleum it is shown to be a mixture containing fats, lecithin, and other substances. According to the authors, chlorophyllan is simply chlorophyll which has been decomposed by plant acid, and more or less extensively allomerised by the action of solvents. C. S.

**Tannic Acid, Ethyl Gallate, and the Supposed Ester of Tannic Acid.** HENRY C. BIDDLE and W. P. KELLEY (*J. Amer. Chem. Soc.*, 1912, 34, 918—923).—It is considered that the optical activity of tannic acid may be due to the presence of dextrose, either as an impurity or as an essential part of the substance in some combination of the nature of a glucoside. It has been found that on decomposing the dextrose by fermentation with yeast, the optical activity is com-

pletely destroyed without the whole of the tannic acid being hydrolysed to gallic acid.

The supposed ethyl tannate (m. p. 157°) described by Manning (Abstr., 1910, i, 851) has been prepared in accordance with his directions, and has proved to be identical with ethyl gallate.

Ethyl gallate begins to sinter at about 145°, and melts to a turbid liquid at 149—150°, which becomes clear at 157—158°. A study of this ester has shown that it probably exists in two crystalline forms, one consisting of hair-like needles, stable at the ordinary temperature, and the other, flat plates, stable at higher temperatures, and that the turbid condition of the fused ester is due to the presence of some of the needles.

E. G.

**Spirans. II. Detection of the Special Asymmetry Caused by the Spiran Carbon Atom.** HERMANN LEUCHS and ERICH GIESELER (*Ber.*, 1912, 45, 2114—2129. Compare this vol., i, 179).—It has been shown that bicyclic spirans can be regarded as derived from disubstituted malonic acids by double ring closure between the carboxyl groups and the two substituents. Such spirans are molecular asymmetric in consequence of the perpendicularity of the two planes in which lie the two rings which have the spiran carbon atom in common.

If one or both of the C:C groups in an allene of the type  $Cab=C:Ccd$  be replaced by a cyclic group, the configurations of the resulting substances are represented, for example, by

$$\begin{array}{c} a > \\ b < \end{array} C < \begin{array}{c} [CH_2]_x \\ [CH_2]_x \end{array} > C = C < \begin{array}{c} c \\ d \end{array} \quad \text{and} \quad \begin{array}{c} a > \\ b < \end{array} C < \begin{array}{c} [CH_2]_x \\ [CH_2]_x \end{array} > C < \begin{array}{c} [CH_2]_x \\ [CH_2]_x \end{array} > C < \begin{array}{c} c \\ d \end{array}.$$
 (Dotted lines represent bonds in a plane perpendicular to the plane of the paper.)

The molecular asymmetry of the former type of substance has been proved by the resolution of 1-methylcyclohexylidene-4-acetic acid by Perkin, Pope, and Wallach. Substances of the second type are bicyclic spirans, such as those mentioned above. Experiments on the resolution of such substances (or, rather, on substances in which  $c$  and  $d$  are the same as  $a$  and  $b$ , in order that there may be no question as to the true molecular asymmetry of the substances) are in progress.

The present communication, however, deals with another method whereby the asymmetry conditioned by the spiran carbon atom may be at least indicated, if not proved. If a substance contains  $n$  "asymmetric" atoms, the number of stereoisomerides,  $x$ , is in general given by the equation  $x=2^n$ ; therefore, if  $x$  is known,  $n$  can be calculated. The authors' experiments deal with the bis- $\gamma$ -lactone- $\alpha\alpha$ -spirans. The simplest member of this class is bis- $\gamma$ -butyrolactone-

$\alpha\alpha$ -spiran, 
$$\begin{array}{c} \text{*} \\ \text{CH}_2 \cdot \text{CH}_2 \\ \text{O} \text{---} \text{CO} \end{array} > C < \begin{array}{c} \text{CH}_2 \cdot \text{*CH}_2 \\ \text{CO} \text{---} \text{O} \end{array}, \text{ m. p. } 109\text{---}110^\circ, \text{ hexagonal plates,}$$

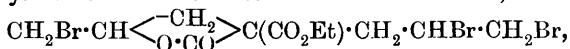
which is obtained in 11% yield by the interaction of sodium ethoxide, ethyl malonate, and  $\beta$ -bromoethyl acetate. This compound is unsuited for the purpose in question, since it does not contain "asymmetric" carbon atoms. (It is obtained in too small quantity

for its resolution [or that of an acid derived therefrom] to be effected by the usual methods). If, however, two similarly situated carbon atoms (those marked by an asterisk) are made equally asymmetric, and if these two atoms are the only sources of asymmetry in the molecule, the substance should exist in two inactive modifications, internally and externally compensated respectively. If, in addition, asymmetry is conditioned by the spiran carbon atom, then the substance should exist in three racemic forms. (Only three racemic modifications are possible in consequence of the symmetrical constitution of the substance. Diagrams are given of models whereby this point is made clear.) Substances of the required type are bis- $\gamma$ -valero-

lactone- $\alpha\alpha$ -spiran,  $\begin{array}{c} \text{CHMe}\cdot\text{CH}_2 \\ | \\ \text{O} \end{array} \text{---} \text{CO} \text{---} \text{C} \begin{array}{c} \text{CH}_2\cdot\text{CHMe} \\ | \\ \text{CO} \end{array} \text{---} \text{O}$ , and bis- $\delta$ -bromo-

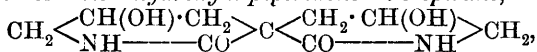
$$\gamma\text{-valerolactone-}\alpha\alpha\text{-spiran, } \text{CH}_2\text{Br}\cdot\text{CH}\begin{matrix} \text{CH}_2^- \\ \diagup \quad \diagdown \\ \text{O}\cdot\text{CO} \end{matrix} \text{C}\begin{matrix} \text{CH}_2^- \\ \diagup \quad \diagdown \\ \text{CO}\cdot\text{O} \end{matrix} \text{CH}\cdot\text{CH}_2\text{Br,}$$

obtained by Fittig and Hjelt (Abstr., 1883, 456) by the action of hydrogen bromide or of bromine on diallylmalonic acid or its ester. Fittig and Hjelt describe only one product, m. p. 130°, in the case of the brominated spiran. The authors show that this is a mixture; by working under somewhat different conditions, they have isolated the three isomerides required to substantiate their theory. The action of bromine on ethyl diallylmalonate in chloroform at 0–15° yields, in addition to a considerable quantity of an oil, 61.5% of crystalline product, which is separated, by fractional solution in and crystallisation from various solvents, into three isomeric *bis-δ-bromo-γ-valerolactone-α-spirans*, having m. p. 156–158°, 108–110°, and 153–154.5° respectively. The oil is shown to consist of the *lactone*,



by analysis and by the fact that at 160—170° it decomposes into ethyl bromide and a mixture of the preceding lactonespirans. These lactonespirans are also produced by the bromination of diallylmalonic acid in ether or glacial acetic acid.

The preceding three lactonespirans are represented as  $\gamma$ -lactones, because by prolonged treatment with concentrated aqueous ammonia they are converted into piperidine derivatives, not into pyrrolidine derivatives as would be the case if the substances were  $\delta$ -lactones. Thus, bis- $\delta$ -bromo- $\gamma$ -valerolactone-*aa*-spiran, m. p. 158°, is converted into two isomeric bis-5-hydroxy-2-piperidone-3 : 3-spirans,



one of which has m. p. 260° (decomp.), and is sparingly soluble in water, whilst the other is easily soluble and has m. p. 245° (decomp.). The lactonspiran, m. p. 153—154.5°, yields the former of these piperidine derivatives by treatment with ammonia; probably also the latter is produced, but the amount of material available is too small for its isolation. The lactonespiran, m. p. 108—110°, yields only one *bis-5-hydroxy-2-piperidone-3:3-spiran*, m. p. 235° (decomp.).

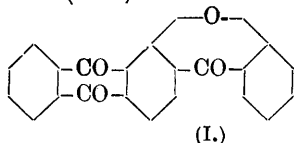
The behaviour of the three racemic lactonespirans with ammonia can be utilised to throw some light on their configurations. The

configurations may be represented thus:  $\left(\begin{smallmatrix} dd & ll \\ \swarrow & \searrow \end{smallmatrix}\right)$ ,  $\left(\begin{smallmatrix} dd & ll \\ \swarrow & \searrow \end{smallmatrix}\right)$  and  $\left(\begin{smallmatrix} ld & dl \\ \swarrow & \searrow \end{smallmatrix}\right)$ . During the conversion of the lactonespirans into hydroxypiperidonespirans, the lactone rings are ruptured, and consequently the asymmetry conditioned by the spiran carbon atom disappears. The lactonespirans having the first two configurations, therefore, yield the same intermediate product,  $(\text{CO}_2\text{H})_2\text{C}[\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Br}]_2$ , from which, by replacement of the bromine atoms by  $\text{NH}_2$ -groups and subsequent elimination of water, two isomeric bishydroxypiperidonespirans are produced, the configurations of which are represented by  $\left(\begin{smallmatrix} dd & ll \\ \swarrow & \searrow \end{smallmatrix}\right)$  and  $\left(\begin{smallmatrix} dd & ll \\ \swarrow & \searrow \end{smallmatrix}\right)$ . The lactonespiran having the third configuration given above can form only one bishydroxypiperidonespiran, the configuration of which is represented by  $\left(\begin{smallmatrix} ld & dl \\ \swarrow & \searrow \end{smallmatrix}\right)$ . This lactonespiran, therefore, is the one which has m. p. 108–110°. The other two lactonespirans have, each, one or other of the two remaining configurations.

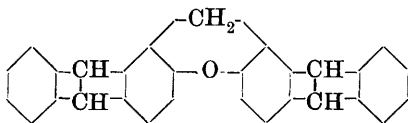
C. S.

**Anthraquinonexanthones.** FRITZ ULLMANN and DEZSÖ ÜRMÉNYI (*Ber.*, 1912, 45, 2259–2272).—The authors have prepared anthraquinone-2:1-xanthone, and find that it only yields very faint yellow shades in the dye-bath. The accumulation of anthraquinone groups in the molecule does not greatly improve the dyeing power. Di-1:2:1':2'-anthraquinonexanthone gives yellow tones.

*o*-1-Anthraquinonyloxybenzaldehyde, m. p. 238° (corr.), was best prepared by heating solutions of  $\alpha$ -chloroanthraquinone and salicylaldehyde in nitrobenzene with potassium carbonate, copper acetate, and copper powder. Its *oxime* was obtained in yellow needles, m. p. 202–206° (decomp.); its *phenylhydrazone* in reddish-brown needles, m. p. 229°. Towards oxidising agents, the aldehyde was remarkably stable, but chromic acid in boiling glacial acetic acid solution in the presence of a little concentrated sulphuric acid converted it into *o*-1-anthraquinonyloxybenzoic acid, m. p. 250°. The latter substance when treated with phosphorus pentachloride in nitrobenzene solution was transformed into anthraquinone-2:1-xanthone (formula I.), m. p. 365° (corr.).



(I.)



(II.)

2:2'-Dihydroxy-1:1'-dianthracylmethane, m. p. 240–242° (corr., decomp.), was obtained by the action of aqueous formaldehyde on 2-hydroxyanthracene in acetic acid or in alkaline solution. Its *diacetyl* derivative has m. p. 232° (corr.). *ms*-Methyl-1:2:1':2'-dianthracenexanthen, m. p. 274° (corr.), was similarly prepared by the

condensation of 2-hydroxyanthracene and acetaldehyde in glacial acetic acid solution in the presence of a few drops of concentrated hydrochloric acid. *ms*-Phenyl-1:2:1':2'-dianthracenexanthen, obtained similarly, had m. p. 278° (corr.), and separated from benzene with  $1C_6H_6$ .

1:2:1':2'-Dianthracenexanthen (formula II.) was readily prepared by the action of phosphoryl chloride on dihydroxydianthracylmethane in boiling xylene solution. It forms yellow needles, m. p. 322—323° (corr.).

1:2:1':2'-Dianthraceneacridine, m. p. 348—349° (corr.), was obtained by heating dihydroxydianthracylmethane with ammonia during eight to ten hours at 215—225°. Oxidation with chromic acid in boiling glacial acetic acid solution converted it into 1:2:1':2'-dianthraquinone-acridine, which did not melt below 440°.

2:2':1:1'-dianthraquinonylmethane, m. p. 246° (corr.), was obtained by the oxidation of diacetoxydianthracylmethane by means of chromic acid. It was converted into 2:2'-dihydroxy-1:1'-dianthraquinonylmethane by alcoholic potassium hydroxide. The crystals evolved gas and blackened between 290° and 315°, and, after melting, immediately resolidified. The diacetyl derivative when heated with acetamide was transformed into dianthraquinonexanthen, which did not melt at 425°. Oxidation with chromic acid transformed it into 1:2:1':2'-dianthraquinonexanthen (formula III.), m. p. 425°, which was, however, more readily obtained by oxidation of *ms*-methyl-dianthracenexanthen.

2:2'-Diacetoxy-1:1'-dianthraquinonylmethane, m. p. 246° (corr.), was obtained by the oxidation of diacetoxydianthracylmethane by means of chromic acid. It was converted into 2:2'-dihydroxy-1:1'-dianthraquinonylmethane by alcoholic potassium hydroxide. The crystals evolved gas and blackened between 290° and 315°, and, after melting, immediately resolidified. The diacetyl derivative when heated with acetamide was transformed into dianthraquinonexanthen, which did not melt at 425°. Oxidation with chromic acid transformed it into 1:2:1':2'-dianthraquinonexanthen (formula III.), m. p. 425°, which was, however, more readily obtained by oxidation of *ms*-methyl-dianthracenexanthen.

*ms*-Phenyl-1:2:1':2'-dianthraquinonexanthen (formula IV.), m. p. 378°, was obtained by the oxidation of *ms*-phenyl-1:2:1':2'-dianthracenexanthen by excess of chromic acid in glacial acetic acid solution.

H. W.

**Action of Hydrogen Peroxide on Acetothienone and  $\alpha$ -Thiophenic Acid.** MAURICE LANFRY (*Compt. rend.*, 1912, 155, 170—172).—Acetothienone and thiophenic acid are both decomposed by hydrogen peroxide, very slowly in the cold, but much more rapidly on heating, the only products obtainable being sulphuric acid and an orange-yellow, resinous liquid. The proportion of acetothienone decomposed increases with the time of the reaction, the quantity of active oxygen, and the concentration of the hydrogen peroxide. No trace of either thienylglyoxylic or thiophenic acids could be detected in the residue (compare Holleman, *Abstr.*, 1904, i, 474). Thiophenic acid behaves in a similar manner towards hydrogen peroxide, except that it is more resistant to the diluted reagent.

W. G.

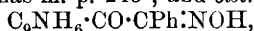
**Rearrangement of Quinine by Sulphuric Acid.** II. BRUNO BÖTTCHER and STEPHANIE HOROVITZ (*Monatsh.*, 1912, 33, 567—582. Compare *Abstr.*, 1911 i, 1011).—The optimum yield of  $\alpha$ - and  $\beta$ -iso-

quinine, formerly described as bases *A* and *B*, is obtained by heating quinine with sulphuric acid (*D* 1.61) at 100° for three hours. When carefully purified, *α*-isoquinine has m. p. 196.5° (corr.),  $[\alpha]_D - 245^\circ$ ; *β*-isoquinine has m. p. 189° (corr.),  $[\alpha]_D - 192^\circ$ . The salts of *α*-isoquinine have a blue fluorescence in aqueous solution; the *platinichloride* crystallises in red, well formed, rhombic prisms; the *oxalate* crystallises in octahedra; the *hydrochloride*,  $+\frac{1}{3}\text{H}_2\text{O}$ , forms colourless needles. The following salts of *β*-isoquinine are described: the *oxalate*,  $3\text{H}_2\text{O}$ , crystallises in bunches of needles; the *sulphate*,  $6\text{H}_2\text{O}$ , forms colourless needles; the *hydrochloride*,  $\frac{1}{3}\text{H}_2\text{O}$ , also forms needles; the *platinichloride*, yields reddish-yellow, rhombic prisms.

Both *α*- and *β*-isoquinine as well as nichine are formed on the rearrangement of quinine by hydrogen iodide; Skraup described the mixture of the two bases as *ψ*-quinine; Lippmann obtained *β*-isoquinine only.

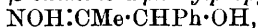
E. F. A.

**Cinchona Alkaloids. XVI. Preliminary Synthetic Experiments.** PAUL RABE (*Ber.*, 1912, 45, 2163—2171).—[With RICHARD PASTERNAK.]—The reaction between magnesium benzyl chloride and ethyl cinchonate in ether leads to the formation of *γ*-quinolyl benzyl ketone,  $\text{C}_9\text{NH}_6\cdot\text{CO}\cdot\text{CH}_2\text{Ph}$ , m. p. 91°, and *γ*-quinolyl-dibenzylcarbinol,  $\text{C}_9\text{NH}_6\cdot\text{C}(\text{CH}_2\text{Ph})_2\cdot\text{OH}$ , m. p. 163—164°. The former yields a *picrate*, m. p. 192° *methiodide*, m. p. 162—164°, *oxime*, the *hydrochloride* of which has m. p. 245°, and *oximino*-compound,



m. p. 216° (decomp.).

[With THEODOR HUNNIUS.]—Certain *αβ*-oximino-ketones can be reduced directly to the hydramines by the Paal-Skita method; thus in the presence of colloidal palladium, a solution of oximinodeoxybenzoin in alcohol and hydrochloric acid is reduced by hydrogen, under a pressure of 2 atmospheres, to *β*-amino-*αβ*-diphenylethyl alcohol. In a similar manner, oximinophenyl ethyl ketone is reduced to *β*-amino-*α*-phenylpropyl alcohol, *β*-oximino-*α*-phenylpropyl alcohol,



m. p. 112°, being obtained as a by-product.

[With PETER RIEPER.]—The partial synthesis of cinchonine from cinchotoxine depends on the fact that *N*-bromocinchotoxine, under the influence of sodium ethoxide, loses hydrogen bromide with the formation of the bicyclic quinuclidine ring. The following reactions are of the same type. Deoxybenzoin and sodium ethoxide in alcoholic solution react with *N*-chlorodimethylamine to form *phenyl α*-dimethylaminobenzyl ketone,  $\text{NMe}_2\cdot\text{CHPh}\cdot\text{COPh}$ , b. p. 193°/15 mm., a greenish-yellow, viscous liquid, having a characteristic odour (*methiodide*, m. p. 153°, *hydrochloride*, m. p. 206—210° [decomp.], *platinichloride*, decomp. 199°, *picrate*, decomp. 148°, *picrolonate*, m. p. 174°, decomp. 180°), and with *N*-chloropiperidine to form *phenyl α*-piperidylbenzyl ketone,  $\text{C}_5\text{NH}_{10}\cdot\text{CHPh}\cdot\text{COPh}$ , m. p. 82°, prisms (*methiodide*, m. p. 182°).

[With ERNST MILARCH.]—Sodioformylacetone and ethyl acetoacetate were brought into reaction with alcoholic ammonia, and the solution was subsequently treated with glacial acetic acid, in the hope

of preparing a derivative of 4-acetyldihydropyridine. However, the chief product of the reaction is *ethyl 2:6-dimethylpyridine-3-carboxylate*,  $C_{10}H_{13}O_2N$ , b. p. 244—245° or 129—130°/18 mm.,  $D_4^{20}$  1.060,  $n_D^{20}$  1.5070, which forms a *picrate*, m. p. 137°, and *picrolonate*, m. p. 142° (decomp.). C. S.

**Creatinine and its Oximes.** ERNST SCHMIDT (*Arch. Pharm.*, 1912, 250, 330—381).—The action of nitrous acid on creatinine yields, not nitrosocreatinines as might be expected, but the oxime of methylhydantoin, together with creatinineoxime as by-product. The mixture is separated by warm alcohol, in which the latter is almost insoluble.

The composition of the methylhydantoinoxime is proved by the analysis of the substance and of its silver derivative, by its hydrolysis by warm hydrochloric acid to hydroxylamine and methylparabanic acid, and by the formation of the substance from methylhydantoin and alkaline sodium nitroprusside.

[With EUGEN THUMANN.]—Creatinine dissolved in nitric acid, D 1.140, reacts with solid sodium nitrite at 0° to form the *oxime* of methylhydantoin,  $NOH:C \begin{smallmatrix} \text{CO}-\text{NH} \\ \text{NMe}\cdot\text{CO} \end{smallmatrix}$ , m. p. 193—194° (decomp.),

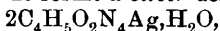
colourless needles. The oxime has feebly acidic, but no basic, properties, does not respond to the Liebermann test, and yields hydroxylamine by treatment with boiling hydrochloric acid. It reacts with silver nitrate in aqueous solution to form a *silver* derivative,  $C_4H_6O_4N_3Ag$ , the oxime having combined with the elements of water and changed to the oxime of methylhydantoic acid during the reaction. Methylhydantoinoxime reacts with hot aqueous phenylhydrazine hydrochloride and sodium acetate to form *methylhydantoin-phenylhydrazone*,  $NHPh:N:C \begin{smallmatrix} \text{NMe}\cdot\text{CO} \\ \text{CO}-\text{NH} \end{smallmatrix}$ , m. p. 238—240°, green needles, and reacts with boiling acetic anhydride to form the *diacetyl* derivative,  $NOAc:C \begin{smallmatrix} \text{CO}-\text{NAc} \\ \text{NMe}\cdot\text{CO} \end{smallmatrix}$ , m. p. 186°, colourless leaflets.

By evaporation with hydrochloric acid, methylhydantoinoxime is decomposed into hydroxylamine and methylparabanic acid. This acid and ammonia are produced by the reduction of the oxime by sodium amalgam and dilute acetic acid.

Methylhydantoinoxime is decomposed by boiling barium hydroxide, yielding ammonia, methylamine, and carbonic and oxalic acids. By treatment with alkaline potassium permanganate at 60°, the oxime is converted into a substance,  $C_4H_5O_3N_3$ , which appears to be isomeric with the oxime, but does not exhibit similar properties; it does not melt at 270°, does not react with hydrochloric acid or with phenylhydrazine, but does form an amorphous *silver* derivative. Its constitution is as yet undetermined.

[With W. HENNIG.]—*Creatinineoxime*,  $NH:C \begin{smallmatrix} \text{NMe}\cdot\text{C:NOH} \\ \text{NH}-\text{CO} \end{smallmatrix}$ , white needles, darkening at 250°, agrees in its properties and behaviour with Kramm's nitrosocreatinine obtained by the action of alkaline sodium

nitroprusside on creatinine (Abstr., 1899, i, 85). The following experiments, however, prove that the substance is really an oxime not a nitroso-compound. It forms a *silver* derivative,



*platinichloride*,  $2C_4H_5O_2N_4, H_2PtCl_6$ , and aurichlorides of different composition and m. p., reacts with hydrochloric acid under different conditions to form a *hydrochloride*,  $C_4H_5O_2N_4, HCl, H_2O$ , decomp. 200—205°, or methylparabanic acid, hydroxylamine, and ammonia, or ammonium tetra-oxalate, hydroxylamine, ammonia, and methylamine. Creatinineoxime yields a *diacetyl* derivative, m. p. 210°, by acetylation, is reduced to methylguanidine by tin and hydrochloric acid, and is converted into methylhydantoinoxime by sodium nitrite and nitric acid, D 1.140, at 0°. Unsuccessful attempts have been made to prepare nitrosocreatinine from nitrososarcosine and cyanamide, and from nitrous fumes and aqueous creatinine. C. S.

**Constitution of Morphine.** Conversion of the Methyl Ethers of  $\alpha$ - and  $\epsilon$ -Methylmorphimethine into 3:4:6- and 3:4:8-Trimethoxyphenanthrene respectively. ROBERT PSCHORR [with F. DICKHÄUSER and C. D'AVIS] (*Ber.*, 1912, 45, 2212—2220).—The methyl ether of bromoacetoxydihydro- $\alpha$ -methylmorphimethine when treated with acetic anhydride is transformed into 4-acetoxy-3:6-dimethoxyphenanthrene, whilst, under similar conditions, the methyl ether of bromohydroxydihydro- $\epsilon$ -methylmorphimethine yields 4-acetoxy-3:8-dimethoxyphenanthrene. The proof so obtained that the secondary alcoholic hydroxyl group of  $\psi$ -codeine is attached to the C-atom 8 of the phenanthrene nucleus, considered in conjunction with Knorr's proof of the similar structure of codeine (morphine) and  $\psi$ -codeine, renders the formula for morphine proposed by Pschorr (Abstr., 1903, i, 193) untenable, but supports that advanced by Knorr and Hörlein (Abstr., 1907, i, 789).

*Bromohydroxydihydro- $\alpha$ -methylmorphimethine methyl ether*, m. p. 112° (corr.), was obtained by the bromination of  $\alpha$ -methylmorphimethine methyl ether in chloroform solution and treatment of the reaction product with water and ether. Its *acetyl* derivative, m. p. 126° (corr.), was formed when  $\alpha$ -methylmorphimethine methyl ether was brominated in glacial acetic acid solution in the presence of sodium acetate, and had  $[\alpha]_D^{26} + 108.4^\circ$  in methyl-alcoholic solution. When the latter was boiled with acetic anhydride, it was transformed into 4-acetoxy-3:6-dimethoxyphenanthrene, which was further identified by means of its picrate.

Attempts to brominate  $\epsilon$ -methylmorphimethine methyl ether in glacial acetic acid did not lead to a crystalline product. Bromination in chloroform solution, followed by treatment with water and sodium hydroxide, yielded *bromohydroxy- $\epsilon$ -methylhydromorphimethine methyl ether*, m. p. 127—128°, the *hydriodide* of which, decomposing at 155—156°, was also investigated. When boiled with acetic anhydride and sodium acetate, it formed 4-acetoxy-3:4-dimethoxyphenanthrene, m. p. 196°, the constitution of which follows from its conversion into 3:4:8-trimethoxyphenanthrene and its picrate. As by-product of the action of acetic anhydride, a *substance* was isolated, the *hydriodide*

of which had m. p. 190—195°, and decomposed at 215°. Analyses corresponded with the formula  $C_{24}H_{29}O_6N, HI, 2H_2O$ . Concentrated potassium hydroxide liberated a *base*, which sintered at 78°, evolved gas at 105°, and was completely decomposed at about 125°. H. W.

**Syntheses in the Pyrrole Group. V.  $\alpha$ -,  $\beta$ -, and  $\gamma$ -Pyrrolyl Diketones.** BERNARDO ODDO and CESARINA DAINOTTI (*Gazzetta*, 1912, 42, i, 716—726. Compare Oddo, Abstr., 1911, i, 496).—*Dipyrrolylmethane*,  $CH_2(CO \cdot C_4NH_4)_2$ , is obtained by the action of magnesium pyrrolyl iodide (2 mols.) on malonyl chloride (1 mol.) in ether and decomposing with ice. The compound is extracted by means of boiling water and crystallised from benzene. It forms a *copper* and a *silver* salt.

Dipyrrolylmethane reacts with phenylhydrazine acetate, yielding 1-phenyl-3:5-dipyrrolylpyrazolone,  $C_4NH_4 \cdot C \begin{smallmatrix} \text{N} \cdot \text{NPh} \\ \text{CH} \end{smallmatrix} C \cdot C_4NH_4$ , which separates from a mixture of benzene and light petroleum in pale yellow crystals, m. p. 166° (decomp.). It is reduced to the pyrazoline compound by sodium and alcohol.

*Dipyrrolylisooxazole*,  $C_4NH_4 \cdot C \begin{smallmatrix} \text{N} \cdot \text{O} \\ \text{CH} \end{smallmatrix} C \cdot C_4NH_4$ , prepared by the action of hydroxylamine on dipyrrolylmethane, forms yellow crystals, m. p. 167°. Concentrated potassium hydroxide converts dipyrrolylmethane into pyrrolyl methyl ketone.

*s-Dipyrroylethane*,  $C_2H_4(CO \cdot C_4NH_4)_2$ , is prepared in similar manner from succinyl chloride, and forms pearly crystals, m. p. 234—235° (decomp.). The *dioxime*,  $C_{12}H_{14}O_2N_4$ , is a white powder, m. p. 175° (decomp.).

*Dipyrrolylmonoxime*,  $C_{10}H_9O_3N_3$ , forms pale yellow crystals, m. p. 147°. C. H. D.

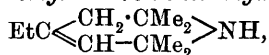
**Syntheses in the Pyrrole Group. VI. Action of Organic Anhydrides on Magnesium Pyrrolyl Compounds.** BERNARDO OTTO and CESARINA DAINOTTI (*Gazzetta*, 1912, 42, i, 727—730. Compare Oddo, Abstr., 1910, i, 426; 1911, i, 496).—It has been shown that acyl chlorides and magnesium pyrrolyl compounds yield ketones instead of tertiary carbinols. It is now found that acid anhydrides react in a similar manner, giving a still better yield. Thus magnesium pyrrolyl iodide and acetic anhydride form pyrrolyl methyl ketone, whilst benzoic anhydride yields phenyl pyrrolyl ketone.

C. H. D.

**Some Derivatives of Triacetonamine.** CHARLES HUGH CLARKE and FRANCIS FRANCIS (*Ber.*, 1912, 45, 2060—2065).—Triacetonalkamine (4-hydroxy-2:2:6:6-tetramethylpiperidine), obtained by reduction of triacetonamine (2:2:6:6-tetramethyl-4-piperidone, E. Fischer, Abstr., 1884, 1290), is converted by the action of benzoyl chloride and alkali into the *dibenzoyl* derivative, m. p. 200°; benzoylation in pyridine solution gives a quantitative yield of the *monobenzoate* (O-derivative), needles, m. p. 97—98°; *hydrochloride*, m. p. 240°; the physiological effect was examined with the easily soluble *lactate*, m. p.

100° (compare Vinci, Abstr., 1899, ii, 316). *Nitrosotriacetonealkamine*, obtained by the action of potassium nitrite on the sulphate of the base, forms pale yellow needles, m. p. 93°.

The action of magnesium ethyl iodide on an ethereal solution of anhydrous triacetoneamine gives a poor yield of 4-*hydroxy-2:2:6:6-tetramethyl-4-ethylpiperidine*, m. p. 62°; *platinichloride*, m. p. 218°; the *hydriodide*, colourless prisms, m. p. 195°, when fused loses a molecule of water with the formation of the *hydriodide* of 4-*ethyltriacetone* (2:2:6:6-*tetramethyl-4-ethyl-1:2:5:6-tetrahydropyridine*),



a liquid of odour resembling piperidine; *hydriodide*, needles, m. p. above 270°; *nitrate*, m. p. 195° (decomp.).

4-*Hydroxy-4-phenyl-2:2:6:6-tetramethylpiperidine*, obtained in poor yield by the action of magnesium phenyl bromide on triacetoneamine, has m. p. 130°.

Nitrosotriacetoneamine (Heintz, this Journ., 1877, i, 592) when reduced by an acid alcoholic solution of stannous chloride gives *triacetoneamineoxime*, m. p. 153°. In a similar manner the nitrosoamine of vinylacetoneamine (nitroso-2:2:6-trimethyl-4-piperidone), m. p. 58°, is converted into vinylacetoneamineoxime (4-oximino-2:2:6-trimethylpiperidine), m. p. 150°. Nitrosotriacetonealkamine, however, under similar treatment yields triacetonealkamine. It is probable that in the first two cases the nitroso-group is first reduced and then split off as hydroxylamine, which then reacts with the ketonic group. A suggestion is made that a substance obtained in small amount by Heintz from the treatment of nitrosotriacetoneamine with acids may have been the above triacetoneamineoxime.

D. F. T.

**Equilibrium in Systems Consisting of Lead Halides and Pyridine.** GEORGE W. HEISE (*J. Physical Chem.*, 1912, 16, 373—381).—Various molecular compounds of pyridine with lead chloride, bromide, and iodide have been described from time to time, but the solubility curves have not been investigated. As a result of these measurements of the solubilities over a wide temperature range it is shown that none of the compounds previously mentioned exists, except the substance  $\text{PbBr}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ , but on the other hand a number of new compounds are described.

The substance,  $\text{PbI}_2 \cdot 3\text{C}_5\text{H}_5\text{N}$ , is stable below +6°, and forms an eutectic with solid pyridine at -43.5°. Between +6° and the boiling point of pyridine the substance,  $\text{PbI}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ , is the stable form. Both of these substances separate in minute chalk-white crystals, which may be dried in the air and analysed very readily by volatilising the pyridine at 150°.

The solubility curve of lead bromide in pyridine has a well defined minimum at the transition point (+19°). From -26° to +19° the substance,  $\text{PbBr}_2 \cdot 3\text{C}_5\text{H}_5\text{N}$ , with a negative temperature-coefficient of solubility, is the stable form. From +19° upwards, the substance  $\text{PbBr}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ , previously described by Goebbels, separates.

These substances are both very unstable, losing pyridine rapidly in the air.

Lead chloride forms only one compound with pyridine between  $-20^{\circ}$  and  $+110^{\circ}$ , namely, the *substance*,  $\text{PbCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ ; this separates in needles which lose pyridine rapidly in the air, and are, therefore, difficult to obtain in a suitable condition for analysis.

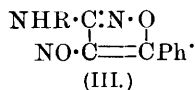
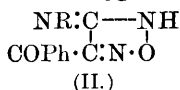
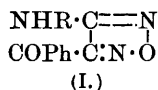
R. J. C.

**Synthesis of 4-Phenyl-2-methylquinoline and 2:4-Diphenylquinoline.** ROSARIO SPALLINO and G. SALIMEI (*Gazzetta*, 1912, 42, i, 607—612).—A mixture of 2 parts of acetanilide, 1 part of acetophenone, and 2 parts of fused zinc chloride is heated in a sealed tube at  $250$ — $300^{\circ}$  for four days, the product is extracted with chloroform, and the portion dissolved is recovered and distilled. The fraction passing over between  $250^{\circ}$  and  $350^{\circ}$ , yields an abundant precipitate with alcoholic picric acid, from which the base is obtained. 4-Phenyl-2-methylquinoline (compare Geigy and Konigs, *Abstr.*, 1885, 1236) forms transparent tablets, m. p.  $98$ — $99^{\circ}$ ; the sulphate has m. p.  $235^{\circ}$ , and the hydrochloride, m. p.  $219^{\circ}$  (both decomp.); the picrate has m. p.  $206$ — $207^{\circ}$ . The base condenses with chloral, and the resulting compound,  $\text{C}_9\text{H}_5\text{Ph} \cdot \text{CH} : \text{CH} \cdot \text{CCl}_3$ , forms white needles, m. p.  $198^{\circ}$ .

If benzanilide is used in place of acetanilide, the product is 2:4-diphenylquinoline,  $\text{C}_{11}\text{H}_{15}\text{N}$ , forming white crystals, m. p.  $106$ — $107^{\circ}$ . The *platinichloride* decomposes at  $200^{\circ}$  without melting; the picrate has m. p.  $198^{\circ}$ .

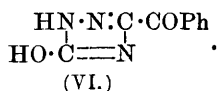
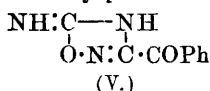
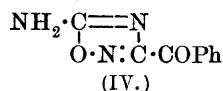
C. H. D.

**Action of Primary Amines on the Dinitrosoacyls (Glyoxime Peroxides or Diacylfuroxans).** III. JACOB BÖESEKEN and D. P. ROSS VAN LENNEP (*Rec. trav. chim.*, 1912, 31, 196—205).—The product of the action of any amine on dibenzoylglyoxime peroxide is an aminodioxime, which easily loses water and gives a coloured compound, for which three formulæ have been suggested:



Formula III is put forward by Wieland and Gmelin (*Abstr.*, 1909, i, 610), since they have succeeded in replacing an oxygen atom by two hydrogen atoms, so destroying the colour and giving a compound with the properties of a primary aromatic amine.

The authors have studied the original reaction with ammonia as the amine, and from their results they put forward three other formulæ:



On adding dibenzoylglyoxime peroxide to an excess of ammonia, it dissolves to a deep yellow solution, from which, on warming, there separates a mass of crystals, which by repeated crystallisation can be separated into benzamide and 5-imino-3-benzoylfurazan (formula V), m. p.  $135^{\circ}$  (compare Holleman, *Abstr.*, 1893, i, 205). This substance

is not acted on by thionyl chloride, but with phosphorus pentachloride it gives a dichloride, reconvertible by water into the original compound. It is destroyed by warming with alcoholic potassium hydroxide, does not form salts with acids, cannot be diazotised, and does not combine with potassium isocyanate, all of which properties eliminate formulæ IV and VI.

On agitating a suspension of iminobenzoylfurazan with alcoholic potassium hydroxide in the cold, it gives the *potassium* salt of 5-keto-

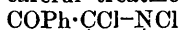
3-benzoyl- $\psi$ -furazan, 
$$\begin{array}{c} \text{O}:\text{C}—\text{NH} \\ | \quad | \\ \text{O}:\text{N}:\text{C}:\text{COPh} \end{array}$$
 giving a neutral aqueous solution,

from which hydrochloric acid precipitates the *ketofurazan* as a white compound, which is decomposed by water on attempting crystallisation. Determination of its conductivity showed it to be a fairly strong acid ( $K=3\cdot3$ ). It yields a *silver* salt, soluble in ammonia, from which it separates in brilliant crystals,  $\text{C}_6\text{H}_5\text{CO}\cdot\text{C}_2\text{N}_2\text{O}_3\text{Ag}+\text{NH}_3$ . On heating the potassium salt with an excess of alkali, it yields potassium benzoate, cyanamide, and carbonate.

W. G.

**Configuration of the Dinitrosoacyls (Diacylglyoxime Peroxides).** JACOB BÖESEKEN and M. C. BASTET (*Rec. trav. chim.*, 1912, 31, 206—220).—The authors have studied the behaviour of dibenzoylglyoxime peroxide towards phosphorus pentachloride and potassium hydroxide with the idea of elucidating the constitution of the compound. Difficulties arose in separating the products of the successive stages of the reaction with the second reagent.

On gradually adding the glyoxime peroxide to an excess of phosphorus pentachloride at  $110^\circ$ , a viscid oil is formed, which, on careful treatment with ice, gives 2:3-dichloro-3:4-dibenzoylfurazan,



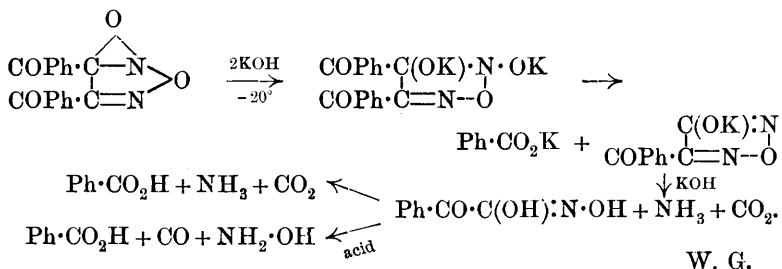
$\text{COPh}\cdot\text{C}:\text{N}:\text{O}$ , white needles, m. p.  $124-125^\circ$ . It is stable

towards boiling acetic acid and reducing agents in acid solution. With alkali hydroxides or ammonia, it is decomposed, giving benzoic acid and a hydroxamic acid.

Wieland and Semper (*Abstr.*, 1908, i, 108) obtained by the action of sodium hydroxide on phenylglyoxime peroxide at  $0^\circ$  a compound, which they named hydroxyphenylfurazan, and to which they gave the constitution 
$$\begin{array}{c} \text{HO}\cdot\text{C}:\text{N}:\text{O} \\ | \\ \text{CPh}:\text{N} \end{array}$$
 the triatomic ring of the glyoxime peroxide

being opened. At this temperature, dibenzoylglyoxime peroxide, when similarly treated, is decomposed, giving benzoic and hydroxamic acids. Working in acetone solution at  $-20^\circ$ , the authors have, however, been able to divide the decomposition into several stages. One molecule of potassium hydroxide is immediately neutralised, benzoic but not hydroxamic acid being formed. A similar result is obtained using two molecules of the alkali. On acidifying, glyoxime peroxide is regenerated. With more than two molecules of the alkali at  $-20^\circ$ , or with less alkali at  $0^\circ$ , a hydroxamic acid is formed, and the pentatomic ring is opened, benzoic acid, ammonia, and carbon dioxide being generated in two stages. If, however, at the end of the first stage the liquid is boiled with phosphoric or hydrochloric acids, the nitrogen is

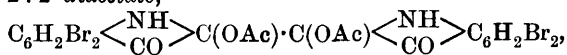
then eliminated as hydroxylamine. The complete course of the reaction is as follows :



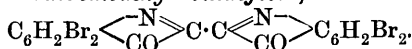
Leuco-bases and Dyes Derived from Diphenylethylene ; Preparation of Two *cyclo*Hexylidene Bases. PAUL LEMOULT (*Compt. rend.*, 1912, 155, 217—219).—Schmidlin and Escher (this vol., i, 437) having questioned the author's preparation of tetramethyldiaminodiphenylcyclohexylenemethane from Michler's ketone and magnesium cyclohexyl bromide (Abstr., 1911, i, 399) on account of lack of detail, a full detailed account of the preparation is now given, and the author claims that it is an improvement on their method, since he reduces the time of heating from sixty to six hours, and obtains a yield of 82%. The corresponding *tetraethyl* compound can be similarly prepared, and is obtained in pale yellow prisms, m. p. 74°.

W. G.

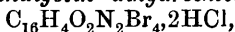
Dehydroindigotin. IV. Additive Compounds. LUDWIG KALB (*Ber.*, 1912, 45, 2136—2149).—5 : 7 : 5' : 7'-Tetrabromodehydroindigotin 2 : 2'-diacetate,



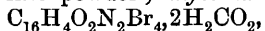
yellow prisms or leaflets, is obtained by heating a finely divided suspension of 5 : 7 : 5' : 7'-tetrabromindigotin in glacial acetic acid with powdered potassium permanganate on the water-bath. The substance does not dissociate in boiling chloroform or benzene, but when heated in carbon tetrachloride and a little pyridine is converted into 5 : 7 : 5' : 7'-tetrabromodehydroindigotin,



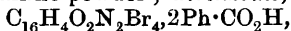
This substance forms violet-brown crystals with a copper lustre, is decomposed by boiling pyridine, develops a blue coloration with sulphuric acid, and is stable in boiling water and concentrated hydrochloric acid. Tetrabromodehydroindigotin is converted into the following derivatives by warming with benzene and the requisite acid ; tetrabromodehydroindigotin dihydrochloride,



yellowish-green, crystalline powder ; diformate,

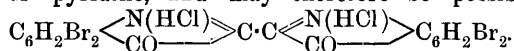


yellowish-green, crystalline powder ; dibenzoate,

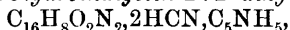


yellowish-green leaflets.

Reasons are given for regarding the preceding additive compounds, except the dihydrochloride, as  $CC'$ -derivatives (formulae correspond with that of the diacetate given above). The dihydrochloride, unlike the other additive compounds, is decomposed very easily by water or pyridine, and may therefore be possibly an  $NN'$ -derivative,



*Dehydroindigotin 2:2'-diformate*,  $C_{16}H_8O_2N_2 \cdot 2\frac{1}{2}H_2CO_2$ , yellowish-green needles, is obtained from dehydroindigotin and anhydrous formic acid in chloroform. *Dehydroindigotin 2:2'-dihydrocyanide*,



green, quadratic plates containing pyridine, is obtained by shaking a suspension of dehydroindigotin in cold pyridine with anhydrous hydrogen cyanide. The substance, from which the pyridine cannot be removed without decomposition, is dissociated by boiling alcohol or toluene, and is reduced to indigo-white by alkaline sodium hyposulphite.

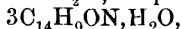
*Dehydroindigotin 2:2'-diphenolate*,  $C_{16}H_8O_2N_2 \cdot 2PhOH$ , yellow needles, and *dehydroindigotin phenolate*,  $C_{16}H_8O_2N_2 \cdot PhOH$ , are obtained by shaking dehydroindigotin with a well-cooled mixture of chloroform, phenol, and pyridine; the two additive compounds are separated by acetone, in which the phenolate is easily soluble. The constitution of the phenolate is unknown; the substance has not been converted into a derivative of indigotin or of dehydroindigotin. C. S.

**2-Phenylindolone and Phenylindoxyl.** LUDWIG KALB and JOSEPH BAYER (*Ber.*, 1912, 45, 2150—2162).—The abnormal reactions of the azomethine group in dehydroindigotin and the uncertainty of the constitution of its dihydrochloride (preceding abstract) led the authors to examine the behaviour of similarly constituted, but less complex, compounds.

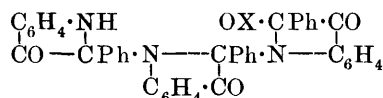
3-Amino-2-phenylindole, which is best obtained by the reduction of 3-oximino-2-phenylindole by alkaline sodium hyposulphite, is suspended in benzene, and the hot mixture is treated with lead peroxide. The resulting 3-imino-2-phenylindole,  $C_6H_4 \left\langle \begin{array}{c} N \\ \diagup \quad \diagdown \\ C(:NH) \end{array} \right\rangle CPh$ , m. p.  $114.5^\circ$ , glistening, orange-yellow leaflets, is hydrolysed by ethereal oxalic acid to 2-phenylindolone,  $C_6H_4 \left\langle \begin{array}{c} N \\ \diagup \quad \diagdown \\ CO \end{array} \right\rangle CPh$ , dark red crystals, m. p.  $102^\circ$ , and is converted by concentrated hydrochloric acid into 2-phenylindolone  $N$ -hydrochloride,  $C_6H_4 \left\langle \begin{array}{c} N(HCl) \\ \diagup \quad \diagdown \\ CO \end{array} \right\rangle CPh$ , reddish-brown needles, which is converted into 2-phenylindolone very conveniently by boiling benzene and a little calcium oxide.

Whilst resembling dehydroindigotin in its property of forming abnormal additive compounds, 2-phenylindolone also exhibits distinctly basic properties, and forms true salts with mineral acids. The additive compounds are pale yellow, and in their behaviour correspond with the similar derivatives of dehydroindigotin. The *methyl alcoholate*,  $C_6H_4 \left\langle \begin{array}{c} NH \\ \diagup \quad \diagdown \\ CO \end{array} \right\rangle CPh \cdot OMe$ , quadratic leaflets, and the analogously constituted additive compounds with ammonia, m. p.

168°, with aniline, m. p. about 134°, and with potassium hydrogen sulphite are described. The *acetate*,  $3C_{14}H_9ON, CH_3 \cdot CO_2H$ , m. p. 168°, *propionate*,  $3C_{14}H_9ON, CH_2Me \cdot CO_2H$ , m. p. 204°, and *hydrate*,



m. p. 168°, are stable to boiling water or toluene, are dissociated by boiling acetic acid, benzaldehyde, or nitrobenzene, and receive the annexed formula (in which X is H,

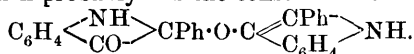


OAc, or  $O \cdot CO \cdot CH_2Me$ ), which are similar to those of the simple additive compounds. The additive compounds of 2-phenylindolone with formic, trichloroacetic, hydrochloric,

sulphuric, and other strong acids are deeply coloured, and are easily dissociated in indifferent solvents or by water or alcohol. These phenomena of dissociation and of halochromy indicate, therefore, that the additive compounds of 2-phenylindolone with strong acids are true salts; consequently they receive constitutions similar to that of the hydrochloride given above. The fact that the dihydrochloride of dehydroindigotin does not exhibit halochromy is strong evidence of its constitution as a  $CC'$ -derivative (preceding abstract).

By reduction with hydrochloric acid and stannous chloride, 2-phenylindolone hydrochloride yields 2-phenylindoxyl,  $C_6H_4 \cdot \begin{smallmatrix} \text{NH} \\ \text{CO} \end{smallmatrix} \cdot CPh$ , which partly melts and decomposes at 140—145°, and is obtained in colourless leaflets by crystallisation from dry boiling carbon tetrachloride in an atmosphere of carbon dioxide; the compound is quite different from the various substances described as 2-phenylindoxyl in the literature.

When 2-phenylindoxyl is dissolved in boiling benzene, autoxidation occurs, and 2-phenylindolone is produced. The two substances react to form an additive compound, m. p. 180—181°, reddening at 178°, yellow needles, which probably has the constitution:

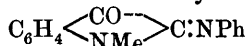


It is also obtained as an intermediate product in the reduction of 2-phenylindolone or the oxidation of 2-phenylindoxyl.

When 2-phenylindolone or 3-imino-2-phenylindole is boiled with dilute sodium hydroxide and a little alcohol, the solution yields 3-phenyldioxindole by acidification. Migration of the phenyl group from position 2 to 3 must have occurred. C. S.

**N-Methyl Derivatives of Indigotin.** LEO ETTINGER and PAUL FRIEDLÄNDER (*Ber.*, 1912, 45, 2074—2080. Compare A. von Baeyer, *Abstr.*, 1884, i, 76).—3-Acetyl-1-methylindoxyl (compare Vorländer and Mumme, *Abstr.*, 1902, i, 451, 454), tablets, m. p. 57°, is obtained by boiling methylantranilic acid with excess of chloroacetic acid in alkaline solution, and heating the product with a mixture of acetic anhydride and anhydrous sodium acetate. When it is dissolved in dilute alcohol to which ammonia has been added, and oxidised by a current of air, 1:1'-dimethylindigotin,  $C_6H_4 \cdot \begin{smallmatrix} \text{CO} \\ \text{NMe} \end{smallmatrix} \cdot C : C \cdot \begin{smallmatrix} \text{CO} \\ \text{NMe} \end{smallmatrix} \cdot C_6H_4$ , separ-

ates in needles with a coppery lustre. The same dimethylindigotin is also obtained by the reduction of 1-methylisatin-2-anil,



(Pummerer, Abstr., 1911, i, 231), in aqueous alcohol containing a little ammonia by hydrogen sulphide. It forms needles, m. p. 182°, and sublimes at a higher temperature; it is generally much more soluble than indigotin, and the benzene solution possesses a colour resembling that of malachite-green; alkaline hyposulphite reduces it to a pale yellow vat (which is only slightly absorbed by the fibre), from which on the addition of an alkali hydrogen carbonate, the *leuco*-compound separates in pale yellow needles. Dimethylindigotin is more strongly basic than indigo, and can be completely extracted from its benzene solution by hydrochloric acid, D 1·19.

1-Methylindigotin can be obtained by atmospheric oxidation of a mixture of indoxyl and 1-methylindoxyl in ammoniacal solution, and also by warming in acetic acid solution a mixture of indoxyl, 1-methylisatin-2-anil, and acetic anhydride; in the latter preparation a considerable quantity of another *substance*, crystallising in brownish-red needles, is obtained. In either method of preparation the methylindigotin is best isolated by extraction with sulphuric or hydrochloric acid and reprecipitating by the addition of water; it forms coppery needles (from benzene), which, on heating, sublime with partial decomposition; the colour of its solutions approaches more closely that of the above dimethylindigotin than that of indigotin, the maximum absorption in xylene solution for dimethylindigotin, methylindigotin, and indigotin occurring at  $\lambda$  644·5,  $\lambda$  639·4, and  $\lambda$  590·9 respectively.

5-Chloroisatin-*p*-chloroanil can be obtained by Sandmeyer's method from *p*-chloroaniline; it forms violet-black needles, m. p. 205—206°, and by treatment with methyl sulphate and sodium ethoxide gives 5-chloro-1-methylisatin-*p*-chloroanil, brownish-red needles, m. p. 165—166°; this can be converted into 5:5'-dichloro-1:1'-dimethyl-

indigotin,  $\text{C}_6\text{H}_5\text{Cl} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{NMe} \end{array} \text{C:C} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{NMe} \end{array} \text{C}_6\text{H}_5\text{Cl}$ , needles, which are insoluble in aqueous hydrochloric acid. The solutions in benzene hydrocarbons show maximum absorption at  $\lambda$  665.

In a similar manner, *p*-toluidine can be converted into 1:5-dimethylisatin-*p*-toluidide, red needles (from alcohol), m. p. 185—186°, which can be further converted into 1:1':5:5'-tetramethylindigotin,

$\text{C}_6\text{H}_5\text{Me} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{NMe} \end{array} \text{C:C} \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{NMe} \end{array} \text{C}_6\text{H}_5\text{Me}$ , deep blue needles, giving solutions of maximum absorption at  $\lambda$  665.

For the preparation of 6:6'-dibromo-1:1'-dimethylindigotin, 2-nitro-4-aminobenzoic acid by diazotisation and the Sandmeyer reaction was converted into 4-bromo-2-nitrobenzoic acid, which by reduction gave 4-bromoanthranilic acid; this was methylated by the action of methyl sulphate on its solution in aqueous sodium carbonate, and the product purified by conversion into 4-bromo-2-nitrosoamino-methylbenzoic acid, needles, m. p. 160°, by reduction of which the

pure 4-bromo-2-methylaminobenzoic acid,  $\text{NHMe} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CO}_2\text{H}$ , needles, m. p.  $189^\circ$ , was obtained. From this, the action of chloroacetic acid in the usual way gave 2-bromo-6-carboxyphenylmethylaminoacetic acid,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , prisms, m. p.  $188^\circ$ , which by boiling with acetic anhydride and sodium acetate was converted into 6-bromo-3-acetyl-1-methylindoxyl,  $\text{C}_6\text{H}_3\text{Br} \left\langle \begin{smallmatrix} \text{COAc} \\ \text{NMe} \end{smallmatrix} \right\rangle \text{CH}$ , grey needles, m. p.  $95^\circ$ ; this was cautiously hydrolysed to 6-bromo-1-methylindoxyl, and the action of potassium ferricyanide on an alkaline solution of this produced 6:6'-dibromo-1:1'-dimethylindigotin, coppery needles, which gave a solution in xylene showing maximum absorption at  $\lambda$  638, whereas maximum absorption by 6:6'-dibromoindigotin is at  $\lambda$  587.5.

The substitution of methyl groups into the imino-groups of indigotin is therefore of greater influence on the colour than is substitution in the benzene rings.

D. F. T.

**6:6'-Dibromoindirubin.** LEO ETTINGER and PAUL FRIEDLÄNDER (*Ber.*, 1912, 45, 2081—2083).—The 6:6'-dibromoindigotin obtained from *Murex brandaris* (Friedländer, *Abstr.*, 1909, i, 262) is not accompanied by 6:6'-dibromoindirubin.

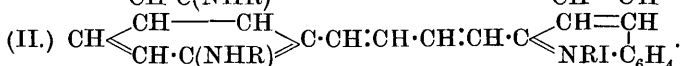
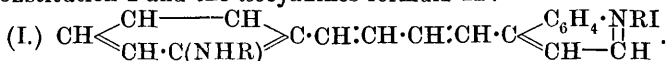
6:6'-Dibromoindirubin can be synthesised from 6-bromoisatin and 6-bromoindoxyl; the latter is already known, whilst the necessary 6-bromoisatin can be obtained by Sandmeyer's method.

*m*-Bromoaniline can be converted through the thiocarbamide derivative into bromoisatinbromoanil,  $\text{C}_6\text{H}_3\text{Br} \left\langle \begin{smallmatrix} \text{CO}^- \\ \text{NH} \end{smallmatrix} \right\rangle \text{C} \cdot \text{N} \cdot \text{C}_6\text{H}_4\text{Br}$ ; the product, violet-brown needles, m. p.  $205\text{--}206^\circ$ , proves to be a mixture of 6-bromoisatin-2-*m*-bromoanil with the isomeric 4-bromo-compound. The mixture when warmed with diluted sulphuric acid dissolves, and then a crystalline deposit of a mixture of two isomeric bromoisatins forms; this can be separated by alcohol into 6-bromoisatin, needles, m. p.  $263\text{--}264^\circ$  (decomp.), and 4-bromoisatin, tablets, m. p.  $258\text{--}259^\circ$  (uncorr.); the identity of these is proved by converting each into the corresponding dibromoindigotin, as all the symmetrical dibromoindigotins have been described.

If equivalent amounts of 6-bromoisatin and 6-bromoacetylindoxyl are warmed in glacial acetic acid solution with a little fuming hydrochloric acid, 6:6'-dibromoindirubin is obtained as a deposit of brown needles. It is sparingly soluble in most solvents, but easily in quinoline; alkaline hyposulphite reduces it to a yellow vat, which dyes cotton cherry-red. The xylene solution shows two absorption bands with maxima at  $\lambda$   $567\mu\mu$  and  $\lambda$   $520\mu\mu$ . D. F. T.

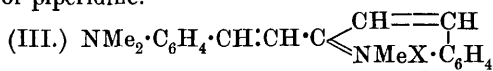
**Constitution of the Cyanine Dyes.** WALTER KÖNIG (*J. pr. Chem.*, 1912, [ii], 86, 166—174. Compare *Abstr.*, 1906, i, 207; Kaufmann, *Abstr.*, 1911, i, 328).—The author discusses the various formulæ which have been assigned to the cyanine dyes, and shows that the properties and behaviour of these substances are most

satisfactorily represented by Kaufmann's formulæ, the cyanines having the constitution I and the *isocyanines* formula II :



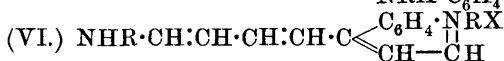
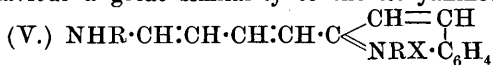
The formulæ explain the analogies existing between the pyridine and cyanine dyes, and also the formation of yellowish-white nitrosoamines by treating both the cyanines and *isocyanines* with nitrous acid.

Further support is given to these formulæ by the synthesis of *dyes* (formula III and IV) resembling the cyanines by the condensation of 2- and 4-methylquinoline salts with *p*-dimethylaminobenzaldehyde in the presence of piperidine.

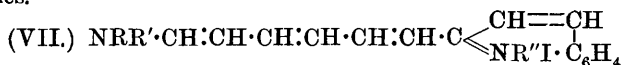


These dyes are bluish-red to violet in colour, and show the characteristic behaviour of the cyanines of being almost completely decolorised by dilute acids.

It is also mentioned that salts of  $\beta$ -hydroxyacraldehydedianilide condense with 2- and 4-methylquinoline salts in the presence of piperidine, yielding dyes (formulæ V and VI) which exhibit in their chemical behaviour a great similarity to the *isocyanines*, whilst the



condensation of aldehydes of the type  $\text{NRR}' \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CH} \cdot \text{CHO}$  (where R = aryl and R' = alkyl) with salts of 2- and 4-methylquinoline results in the formation of dyes (VII and VIII) resembling the cyanines.



F. B.

**Electrochemical Reductions. II. Reduction of Secondary Nitroamines to Hydrazines.** H. J. BACKER (*Rec. trav. chim.*, 1912, 31, 142—195. Compare this vol., i, 339).—Up to the present secondary nitroamines have only been reduced by zinc and acetic acid, the yield of the corresponding hydrazines being in all cases very poor. Alkyl nitroamides have not, as yet, been reduced to hydrazines. The author has reduced a number of secondary nitroamines and one alkyl-nitroamide by electrochemical methods, and has, in general, obtained much better yields. The best results were produced by employing a cathode of copper, coated with tin, and dilute sulphuric acid as the

electrolyte. To promote solution it was sometimes necessary to add acetic acid. The hydrazines, etc., were identified by preparation of hydrazones or analogous compounds with a number of aromatic aldehydes, or by interaction with cyanates, giving semicarbazides. The yield of hydrazine was determined either by titration in alkaline solution with mercuric chloride solution, or by weighing the tetrazone formed in this reaction.

Dimethylnitroamine is best reduced by using the copper cathode and 10% sulphuric acid as electrolyte. After reduction the solution is evaporated with hydrochloric acid, made alkaline with potassium hydroxide, and fractionated over barium oxide. *as*-Dimethylhydrazine gives an oxalyl derivative (compare Renouf, Abstr., 1881, 151) and a *picryl* derivative, m. p. 136.5°. *N*-Nitropiperidine gives a better yield of *N*-aminopiperidine by reduction with zinc and acetic acid than by electrochemical methods, using a nickel cathode and a 10% solution of sodium acetate as electrolyte.

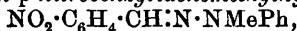
For dinitropiperazine the best electrolyte is 50% acetic acid. The author has condensed the resulting diaminopiperazine with a number of aldehydes. The derivatives so obtained are all colourless, and are decomposed on warming with dilute sulphuric acid. Salicylaldehyde gives 1:4-*disalicylideneaminopiperazine*,  $C_4N_2H_8(N\cdot CH\cdot C_6H_4\cdot OH)_2$ , white needles, m. p. 226°, which retains its phenolic character. With *o*-methoxybenzaldehyde there is produced 1:4-*di-o-methoxybenzylidenaminopiperazine*,  $C_4N_2H_8(N\cdot CH\cdot C_6H_4\cdot OMe)_2$ , m. p. 207°. The corresponding derivative from anisaldehyde has m. p. 246.5°. Diaminopiperazine and potassium isocyanate when mixed in aqueous solution give 1:4-*dicarbamidopiperazine*,  $C_4N_2H_8(NH\cdot CO\cdot NH_2)_2$ , colourless crystals, m. p. 286°, which in hydrochloric acid solution reacts with sodium nitrite, giving a *dinitroso*-compound, which is very unstable and decomposes at 74°, or on exposure to light or moisture. It is decomposed by alkalis, giving nitrous oxide, carbon dioxide, ammonia, and piperazine.

Ethylenebismethylnitroamine, as prepared by Franchimont and Klobbie (Abstr., 1889, 492) from ethylenediurethane by nitration, treatment with ammonia, and subsequent methylation, using, however, methyl sulphate instead of the iodide is best reduced by suspension in dilute acetic acid containing sodium acetate, the copper cathode being employed. The resulting hydrazine condenses with anisaldehyde, giving a *dianisylidenedimethylethylenedihydrazine*,



long, white needles, m. p. 147.5°. With *p*-nitrobenzaldehyde, *di-p-nitrobenzylidenedimethylethylenedihydrazine*, orange-red needles, m. p. 192.5°, is obtained, which on the addition of concentrated hydrochloric acid is converted into a pale yellow compound,  $C_{13}H_{20}O_4N_6\cdot 2HCl$ .

Phenylmethylnitroamine, which with concentrated nitric acid gives trinitrophenylmethylnitroamine (compare Franchimont, Abstr., 1880, i, 616), is electrically reduced in dilute acetic acid solution containing sodium acetate, giving *as*-phenylmethylhydrazine. On mixing this with *p*-nitrobenzaldehyde in alcoholic solution, the liquid is turned red, and deposits *phenyl-p-nitrobenzylidenemethylhydrazine*,

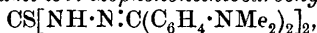


as small, red needles, m. p. 135°. This red modification on trituration with petroleum or ether passes readily into a yellow modification, which has m. p. 130·5—131°. These two enantiotropic modifications are mutually transformable at different temperatures, the red being the more stable at higher temperatures. Phenylmethylhydrazine condenses with cinnamaldehyde to form *cinnamaldehyde-as-phenylmethylhydrazone*, m. p. 112·3°, and with phenyl isocyanate it gives *diphenylmethylsemicarbazide*,  $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{NMePh}$ , white needles, m. p. 158·5°.

Methyl methylnitroaminoformate is best reduced in dilute sulphuric acid solution, and yields methyl methylhydrazinoformate, which is identified by boiling its solution with sodium hydroxide for several hours, when it is decomposed into methylhydrazine, methyl alcohol, and carbon dioxide. On oxidation by bromine water the hydrazine gives a tetrazone, m. p. 187·5° (compare Klobbie, *Abstr.*, 1891, 292). With benzaldehyde it gives a *hydrazone*, m. p. 77·5°, and with *o*-nitrobenzaldehyde a *hydrazone*, m. p. 105·5°. W. G.

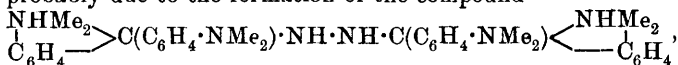
**Reduction of the Ketonehydrazines and Ketazines of Tetramethyldi-*p*-aminobenzophenone and Fluorenone.** THEODOR CURTIUS and KARL KOF (*J. pr. Chem.*, 1912, [ii], 86, 113—132).—Tetramethyldi-*p*-aminobenzophenonehydrazone (Wieland and Roseau, *Abstr.*, 1911, i, 571) is readily hydrolysed by cold concentrated sulphuric acid into its components, and on treatment with bromine vapour in acid solution yields successively brownish-red and dark green *dyes*. Towards iodine in alcoholic solution the hydrazone behaves similarly, the final product consisting of a dark blue, crystalline *substance*, of a metallic lustre, m. p. 240°, with previous softening at 209°.

*Bistetramethyldi-p-aminobenzophenonethiocarbohydrazone*,



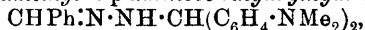
prepared by heating the hydrazone for six hours with carbon disulphide in benzene solution, crystallises in citron-yellow needles, m. p. 233°; if the period of heating is shortened, a cinnabar-red, microcrystalline *substance*, having m. p. 222°, is produced.

When reduced with sodium amalgam and alcohol, or with aluminium amalgam in moist ethereal solution, tetramethyldi-*p*-aminobenzophenonehydrazone yields *s-ditetramethyldi-p-aminobenzhydriylhydrazine*,  $\text{N}_2\text{H}_2[\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2]_2$ , which forms small, white crystals, m. p. 285° (decomp.), dissolves in glacial acetic acid, yielding a blue coloration, probably due to the formation of the compound



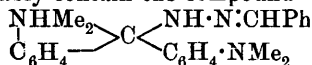
and on treatment with sodium nitrite and acetic acid, yields an orange *nitrosoamine* (?) melting indefinitely about 180°.

*Benzaldehydetetramethyldi-p-aminobenzhydriylhydrazone*,



prepared by reducing tetramethyldi-*p*-aminobenzophenonebenzylidenehydrazone,  $\text{CHPh}\cdot\text{N}\cdot\text{N}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$  (Wieland and Roseau, *loc. cit.*), with sodium amalgam and alcohol, crystallises in lustrous, colourless

needles, m. p. 143°, and dissolves in glacial acetic acid, yielding blue solutions which probably contain the compound



It is hydrolysed by cold dilute hydrochloric acid to benzaldehyde and the above mentioned *s*-ditetramethyl-di-*p*-aminobenzhydrazyl-hydrazine.

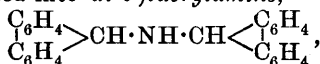
When heated with zinc and dilute acetic acid, tetramethyl-di-*p*-aminobenzophenonehydrazone is hydrolysed to Michler's ketone, which then undergoes further reduction to tetramethyl-di-*p*-aminodiphenylmethane.

The azine of Michler's ketone is obtained by heating the ketone with either hydrazine hydrate or tetramethyl-di-*p*-aminobenzophenonehydrazone and alcohol at 170° (compare Wieland and Roseeu, *loc. cit.*).

Oxidation of fluoronehydrazone with mercuric oxide in benzene solution gives rise to diphenyleneazomethylene (Staudinger and Kupfer, *Abstr.*, 1911, i, 751), together with an amorphous, brick-red substance, m. p. 243°.

Fluorenonebenzylidenehydrazone crystallises in short, orange-red needles, m. p. 91—94°; Staudinger and Kupfer give 82—84°.

When reduced with sodium amalgam and alcohol, fluorenonehydrazone is converted into *di*-9-fluorylamine,



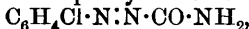
which crystallises in short, yellow needles, and melts at 167° to a green liquid.

The azine of fluorenone is obtained in violet-red crystals, m. p. 265°, by heating fluorenone with hydrazine hydrate or fluorenonehydrazone (compare Wieland and Roseeu, *loc. cit.*). On reduction with zinc dust and acetic acid it yields 9-acetylaminofluorene.

The compound described by Sorge (*Abstr.*, 1902, i, 379) as *p*-tolyl methyl ketonehydrazone is found by the authors to consist of *p*-tolyl-methylketazine,  $\text{N}_2(\text{:CMe}\cdot\text{C}_6\text{H}_4\text{Me})_2$ , which has m. p. 136°, and is best obtained by heating the ketone with hydrazine hydrate and alcohol at 140°. All attempts to prepare the hydrazone proved unsuccessful.

F. B.

**Unusual Oxidation of an Azo-compound.** EUGEN BAMBERGER and OSCAR BAUDISCH (*Ber.*, 1912, 45, 2054—2059. Compare *Abstr.*, 1909, i, 977)—The oxidation of *syn*-*p*-chlorodiazobenzene cyanide in ethereal solution with hydrogen peroxide in the presence of magnesium carbonate follows an unusual course. The ethereal liquid when extracted with barium hydroxide solution gives a precipitate (leaflets) of the barium salt of *p*-chloronitrosophenylhydroxylamine, which on treatment with cold hydrochloric acid yields the free *p*-chloronitrosophenylhydroxylamine,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{N}(\text{NO})\cdot\text{OH}$  (m. p. 73.5—74.5°). The residual ethereal solution on evaporation leaves orange-red crystals of *p*-chlorophenylazoformamide,

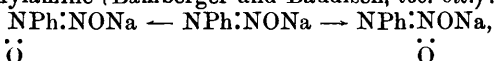


m. p. 181—182° (compare Hantzsch and Schultze, Abstr., 1895, i, 658).

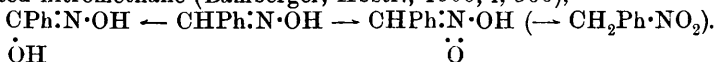
On oxidation in a similar manner, but in the presence of sodium hydroxide solution in place of magnesium carbonate, *syn-p*-chlorodiazobenzene cyanide gives *p*-chlorophenylazoformamide with a very small quantity of nitrosophenylhydroxylamine.

*iso*-(*anti*)-*p*-Chlorodiazobenzene cyanide when treated as above with hydrogen peroxide in the presence of magnesium carbonate is chemically unaffected.

The first-named of the authors in a footnote states that he now accepts the analogy between the steric behaviour of the diazo-compounds and the oximes; he points out the similarity of the oxidation of the normal (*syn*)-diazotates to a benzenediazoic acid and a nitrosophenylhydroxylamine (Bamberger and Baudisch, *loc. cit.*):



with the oxidation of the oximes to a hydroxamic acid and a substituted nitromethane (Bamberger, Abstr., 1900, i, 500),



D. F. T.

**Heat Coagulation of Proteins. III. The Influence of Alkali on Reaction Velocity.** HARRIETTE CHICK and CHARLES J. MARTIN (*J. Physiol.*, 1912, 45, 61—69. Compare Abstr., 1911, i, 822).—The denaturation rate of egg-albumin in alkaline solutions is increased by increased concentration of hydroxyl ions, just as it is by hydrogen ions in acid solution. As denaturation proceeds, hydroxyl ions are continuously removed, but if the alkalinity is kept constant by the presence of excess of solid magnesium oxide, denaturation proceeds as a reaction of the first order, as was also shown in the case of acid.

The influence of acids and alkalis on this phenomenon is compared with their effect on the viscosity and precipitability by alcohol of protein solutions, and on the imbibition of water by protein. It is suggested that protein in the form of salts is in more intimate association with water.

W. D. H.

**The Precipitation of Suspensoid Protein by Various Ions.** W. NEVILL HEARD (*J. Physiol.*, 1912, 45, 27—38).—The power of an electrolyte to precipitate negatively-charged suspensoid protein is primarily dependent on the valency of the cation, but this is greatly modified by the relation of the latter to the OH-group and its capacity to reduce the ionisation of that group.

Positively charged suspensoid protein being kept in solution by the charge given it by the H ion, the power of the anion to precipitate is due to its capacity to reduce the ionisation of the compound of acid and protein. Although the cation is the principal element in the precipitation of alkaline protein, and the anion in the precipitation of acid protein, the accompanying ion is probably never without some effect.

W. D. H.

**The Conditions for the Complete Hydrolysis of Proteins.** DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1912, 12, 295—300).—The percentage of amino-nitrogen reaches a definite maximum when acid hydrolysis of a protein is complete, and this maximum is the same whether the hydrolysis occurs at 100° or 150°. The ammonia does not reach a definite maximum, but increases the longer the hydrolysis continues. W. D. H.

**Complex Compounds of Ferrous Salts, Hydrogen Peroxide, and Proteins; On the Part Played by Iron in Biological Oxidation Processes.** FRANZ RÖHMANN and T. SHAMINE (*Biochem. Zeitsch.*, 1912, 42, 235—249).—Iron by itself, in colloidal or protein solutions, is not capable of causing oxidation by molecular oxygen to the extent at which oxidative processes take place in the organism. Dyad- or triad-iron (the latter probably only after preliminary reduction) forms compounds with hydrogen peroxide which have a strong oxidative capacity. In solutions of certain proteins (egg-white, sodium nucleate, and proteoses from Witte's peptone), ferrous salts can remain in solution, which in conjunction with hydrogen peroxide can bring about energetic oxidation. If suitable proportions of protein, iron salts, and hydrogen peroxide be chosen, precipitates can be produced, several of which are described by the authors under the name of oxyferrous-protein compounds. Such substances have the property of blueing guaiacum tincture, and in the presence of excess of hydrogen peroxide, oxidising substances like pyrogallol and quinol. They can thus act as oxygenases or peroxydases. It is suggested that similar compounds can play an active part in the oxidative processes in the cell.

S. B. S.

**Compounds of Ferric Salts with Albumoses.** FRANZ RÖHMANN and T. SHAMINE (*Biochem. Zeitsch.*, 1912, 42, 250—254).—On addition of simple ferric salts, such as the sulphate to a solution of Witte's peptone, a precipitate containing both iron and sulphate is obtained. The substance has the properties of an acid insoluble in water, as it dissolves in alkalis giving a solution which is neutral to turmeric paper. If such a solution is treated with excess of alkali, the iron is precipitated as hydroxide. If barium hydroxide is used, barium compounds of albumose pass into solution. On treatment of the solution with the theoretical quantity of sulphuric acid necessary to combine with the barium, a part of the albumoses is separated with the barium sulphate as a substance insoluble in water, which is, however, soluble both in acids and alkalis. It is suggested that these reactions might be employed for separating certain constituents from digestion mixtures.

S. B. S.

**Fibrinogen. I. The Biological Differentiation of the Three Proteins of Blood Plasma.** JULIUS BAUER and ST. ENGEL (*Biochem. Zeitsch.*, 1912, 42, 399—402).—Just as caseinogen can be differentiated from lactoglobulin and lactalbumin (which according to the authors are identical with serum-globulin and serum-albumin), so

fibrinogen can be differentiated from the other blood proteins. The methods of differentiation employed were those of the precipitation reaction and the deviation of the complement. The fibrinogens from different species of animals could also be differentiated in a similar way. S. B. S.

**Distribution of Salts between Saturated Aqueous and Moist Gluten.** ALB. J. J. VANDEVELDE and L. BOSMANS (*Bull. Soc. chim. Belg.*, 1912, 26, 249—254).—Saturated solutions of salts (40 c.c.) and moist gluten (5 grams, containing 3·4 grams of water) were kept at 37° for one, two, and three weeks, and the amounts of salts in the solution and in the gluten estimated. The dry matter of the gluten remained unchanged. The weight of the moist gluten diminishes, the absorption of salt being coincident with loss of water.

By dividing the percentages of salt in solution by the percentages in the moist gluten, it is shown that chlorides and nitrates of alkalis give higher coefficients than those of the alkaline earths. With potassium salts the coefficient of the nitrate is lower than that of the chloride, and the sulphate lower than the nitrate. In the case of sodium salts, the relations are reversed. The chlorides and nitrates of barium, strontium, and calcium show only slight differences. The highest coefficients obtained are those of ammonium and magnesium sulphates, both of which are important in the fractional precipitation of proteins. N. H. J. M.

**Constitution of the Colouring Matter of Blood. III.** OSCAR PILOTY and SIEGFRIED J. THANNHAUSER (*Annalen*, 1912, 390, 191—209).—The determination of the constitution of the colouring matter of the blood is rendered difficult by the fact that by the degradation of the substance, whilst one half of the molecule is obtained in well-defined compounds (pyrroles and their carboxylic acids), the other half is obtained in the form of the amorphous, ill-defined hæmatopyrrolidinic acid. It is fortunate, therefore, that bilirubin (obtained from the gall-stones of the ox) yields by its degradation a substance, bilic acid, which is quite analogous to hæmatopyrrolidinic acid, but is crystalline and well-defined. Since it is extremely probable that the colouring matter of the bile is directly produced in the liver from the colouring matter of the blood, the authors hope, by determining the constitution of bilic acid, to secure a tool whereby the constitution of hæmatopyrrolidinic acid, and ultimately that of the colouring matter of the blood, may be fashioned with certainty.

By fusion with potassium hydroxide and a little water at 200° and finally at 370°, bilirubin yields an oil which is shown to contain *bis*-2 : 3-*dimethylpyrrole*,  $C_{12}H_{18}N_2$ , m. p. 84—85°, colourless crystals (*picrate*, m. p. 148°), and 2 : 3 : 4-*trimethylpyrrole*, which has only been isolated as the *picrate*,  $C_7H_{11}N, C_6H_2(NO_2)_3 \cdot OH$ , m. p. 140°, on account of lack of material. The synthesis of these two pyrrole derivatives will be described in a future communication.

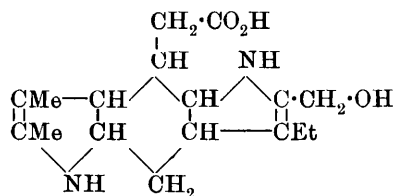
By reduction on the water-bath with hydriodic acid (D 1·96) and

phosphonium iodide in the presence of glacial acetic acid, bilirubin yields, in addition to a very small quantity of a base (unexamined), which is volatile with steam, *bilic acid*, and an acid which, being isomeric with phonopyrrolecarboxylic acid, is called *isophonopyrrole-carboxylic acid*.

*Bilic acid*,  $C_{17}H_{26}O_3N_2$ , m. p.  $187^\circ$ , colourless plates, does not respond to the pine-shaving test, and does not develop a red coloration with *p*-dimethylaminobenzaldehyde. The acid is moderately soluble in water, forming a solution which foams on shaking, liberates carbon dioxide from sodium carbonate, and forms an amorphous picrate.

*Bilic acid* yields hæmatic acid and methylethylmaleimide by oxidation with chromic and dilute sulphuric acids at  $50$ – $60^\circ$ , or by treatment with nitrous acid in warm dilute sulphuric acid. This fact, taken in conjunction with the fact that *bilic acid* yields, by fusion with potassium hydroxide, a mixture of pyrroles which does not contain hæmopyrrole (thereby showing that an oxygen atom in *bilic acid* must be present in a hydroxyl group in the  $\alpha$ -position to an

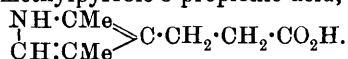
imino-group) is strong evidence in favour of the annexed formula of *bilic acid*.



The authors show that zinc hæmatopyrrolidinate also yields hæmatic acid and methylethylmaleimide by oxidation with chromic and dilute sulphuric acids at about  $50^\circ$ . Conse-

quently, the constitution of hæmatopyrrolidinic acid previously suggested is to be replaced by one differing from that of *bilic acid* only by containing a methyl group in place of the  $\text{CH}_2 \cdot \text{OH}$ .

*isoPhonopyrrolecarboxylic acid*,  $C_9H_{13}O_2N$ , m. p.  $126$ – $127^\circ$ , colourless, prismatic needles, responds to the pine-shaving test, forms a *picrate*, m. p.  $146^\circ$ , and is converted by sodium nitrite and dilute sulphuric acid at about  $50^\circ$  into the semi-oxime of hæmatic acid, decomp.  $210^\circ$ , identical with that obtained from xanthopyrrolecarboxylic acid; the semi-oxime yields hæmatic acid by hydrolysis with boiling dilute sulphuric acid. *isoPhonopyrrolecarboxylic acid*, therefore, is 2:4-dimethylpyrrole-3-propionic acid,



C. S.

**A Comparison of Paranuclein Split off from Caseinogen with a Synthetic Paranuclein based on Immunity Reactions.** FREDERICK P. GAY and T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1912, 12, 233–238).—Paranuclein and synthetic paranuclein-A (Robertson) derived from the products of complete peptic digestion of caseinogen and synthesised by the action of pepsin at  $36^\circ$  are interchangeable, as tested by reactions of anaphylaxis and of alexin fixation with an anti-caseinogen serum. They have identical and specific antigenic properties that are not present in the original peptic digestion product.

W. D. H.

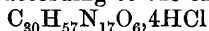
**Electrochemistry of Proteins. VIII. The Dissociation of Solutions of the Sulphate and Chloride of Protamine (Salmine).** THORBURN BRAILSFORD ROBERTSON (*J. Physical Chem.*, 1912, 16, 382—394. Compare Abstr., 1911, i, 933).—The proteins hitherto investigated by the author have been either predominantly acidic (caseinogen, serum-globulin) or feebly basic (ovimucoid). The protein salmine here considered is of the predominantly basic type.

Salmine sulphate was prepared from the sperm of Pacific salmon by Kossel's method (Abstr., 1898, i, 715). The chloride was obtained from it by interaction with barium chloride. The author's products were not analysed.

The dissociation of these salts obeys Ostwald's law for a binary electrolyte in the special form devised by the author. The number of ions is therefore two or a multiple of two.

In the case of the sulphate no further evidence could be obtained because the substance separates as an oily phase on cooling and does not lend itself to cryoscopic measurements.

According to the conductivity, a  $\frac{1}{2}\%$  solution of salmine chloride is almost completely ionised. The freezing point of this solution indicates a concentration (molecular + ionic) of  $M/46$ . The amount of hydrochloric acid present according to the empirical formula



(Kossel) is  $N/45$ . Hence one ion is produced for every molecule of hydrogen chloride in the compound. The author argues that one molecule of salmine chloride must yield four ions, and as it behaves as a binary electrolyte, these ions must be capable of combining in pairs. From the value of the conductivity constant ( $\rho = 4$  approximately), it is deduced that each ion must be quadrivalent.

Accepting the suggestion of Kossel and Dakin that there are twelve arginine radicles and twelve hydrogen chloride molecules in a salmine hydrochloride molecule, the author supposes that half the arginine radicles combine with the acid to form the anions, whilst the remainder of the arginine radicles form the corresponding cations. In other words, salmine hydrochloride dissociates into twelve quadrivalent protein ions.

The dissociation is formulated on the same lines as that of ovimucoid hydrochloride (*loc. cit.*). R. J. C.

**Nature of Animal Lactase.** MARJORY STEPHENSON (*Bio.-Chem. J.*, 1912, 6, 250—254).—E. F. Armstrong showed that there are two kinds of lactase, one, galacto-lactase, inhibited only by galactose, and the other, gluco-lactase, inhibited only by dextrose. The lactase in the intestine of animals belongs to the latter class. W. D. H.

**Syntheses of Alkyl Glucosides by means of Emulsin:**  $\beta$ -Methyl Glucoside,  $\beta$ -Ethyl Glucoside, and  $\beta$ -Propyl Glucoside. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1912, 155, 86—88. Compare this vol., i, 522, 672).—Emulsin acting on a solution of dextrose in 85% methyl alcohol in the course of thirty-four days converts 79% of the sugar into  $\beta$ -methylglucoside, m. p. 102—104°,  $[\alpha]_D - 32.06^\circ$ , which in aqueous solution is completely re-hydrolysed by emulsin.

The authors have succeeded in obtaining  $\beta$ -ethyl glucoside in a crystalline form (compare Königs and Knorr, *Abstr.*, 1901, i, 369) from the syrupy product obtained by a similar reaction by dissolving it in cold pure acetone and keeping the solution. It crystallises in white, felted masses, m. p.  $73^{\circ}$ ,  $[\alpha]_D - 33.38^{\circ}$ . It is very hygroscopic, but its aqueous solution does not reduce Fehling's solution.

$\beta$ -Propyl glucoside similarly prepared crystallises in silky tufts,  $[\alpha]_D - 34.9^{\circ}$ . W. G.

**The Supposed Specific Action of Phenolase.** ALEXIS BACH and (Mlle.) V. MARYANOVITCH (*Arch. Sci. phys. nat.*, 1912, [iv], 33, 483—497; *Biochem. Zeitsch.*, 1912, 42, 417—431).—The influence exercised by salts (calcium chloride and acetate, zinc sulphate and acetate, manganese sulphate and acetate, aluminium sulphate) on phenolase when acting on different substrates (guaiacol, quinol, pyrogallol, orcinol,  $\alpha$ -naphthol +  $p$ -phenylenediamine) varies with the nature of the substrate. Thus calcium chloride retards the oxidation of guaiacol and of pyrogallol and accelerates oxidation of the other phenols mentioned. Zinc sulphate accelerates the oxidation of guaiacol and of the mixture  $\alpha$ -naphthol +  $p$ -phenylenediamine, but retards action in all other cases. There is no direct relation between the hydrolysis of the salts and their action.

The salts have a similar specific influence on the oxidation of the phenols by themselves in the absence of phenolase. It is therefore unnecessary to attribute the varying behaviour of phenolase to the presence in it of several specific ferments. All attempts to isolate such specific enzymes have failed, and the specific differences observed are to be attributed to the formation of complexes between the salt and the phenol which are more or less readily oxidised, as the case may be, than the original phenol.

The inability of the oxydase of the potato to act on guaiacol is due, not to the absence of a specific oxydase, but to the ease with which the products of oxidation of guaiacol are reduced by a reducing enzyme also present in the potato. The products of oxidation of quinol or of pyrogallol are not so easily reduced.

The inability of certain preparations of phenolase to oxidise orcinol is to be attributed to the absence of salts of alkaline reaction, the presence of which is essential for the spontaneous oxidation of orcinol.

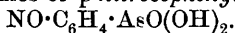
There is thus no evidence that phenolase is in any way specific, or that a different oxydase is required to oxidise polyhydroxyphenols than for monohydroxyphenols. E. F. A.

**Relations of Isomorphism in Organometallic Compounds. II. Derivatives of Tervalent Elements.** PAUL PASCAL (*Bull. Soc. chim.*, 1912, [iv], 11, 595—602. Compare this vol., i, 524).—The author has studied the elements of the nitrogen family by means of their compounds corresponding with triphenylamine, and his results bear out the facts already known as to the subdivision of this family, nitrogen and phosphorus going together, then arsenic and antimony, whilst bismuth stands somewhat apart.

Triphenylamine and triphenylphosphine both crystallise in the monoclinic system, triphenylarsine and triphenylstibine in the triclinic, whilst triphenylbismuthine crystallises in the monoclinic system, but in forms fundamentally different from the amine and stibine. A study of their molecular volumes groups them in the same way. Further, the author has studied the solidification temperatures of mixtures of these substances and plotted the corresponding curves, and the results of this thermal analysis are in accord with the chemical study of this group of elements.

W. G.

**Aromatic Arsenic Compounds. I. *p*-Nitrosophenylarsinic Acid.** P. KARRER (*Ber.*, 1912, 45, 2065—2068).—If a neutral or feebly alkaline solution of atoxyl is oxidised with a neutralised solution of permonosulphuric acid, the resultant liquid on acidifying deposits pale yellow needles of *p*-nitrosophenylarsinic acid,



This substance shows all the typical nitroso-reactions; on heating it turns brown at 180°, and chars without melting, but when rapidly heated it explodes; it has no medicinal value. Sodium hyposulphite reduces it to *pp'*-diaminoarsenobenzene (Ehrlich and Berthelm, *Abstr.*, 1911, i, 593), whilst milder reducing agents, such as sulphurous acid reduce it to *p*-aminophenylarsenic oxide.

Clauser's method for the estimation of nitrogen (*Abstr.*, 1901, ii, 422) gives satisfactory results with *p*-nitrosophenylarsinic acid.

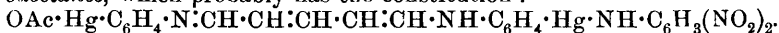
D. F. T.

**Action of the Acetal of Propargaldehyde on Mercuriated Amines.** FRITZ REITZENSTEIN and GOTTLIEB BONITSCH (*J. pr. Chem.*, 1912, 86, [ii], 73—81).—The authors have attempted to prepare the compound,  $\text{OAc} \cdot \text{Hg} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{Hg} \cdot \text{OAc}$ , by the condensation of *p*-aminophenylmercuric acetate with the acetal of propargaldehyde, but these attempts have not met with success.

When heated on the water-bath with the acetal of  $\beta$ -ethoxyacetaldehyde, *p*-aminophenylmercuric chloride yields an orange-red substance, probably  $\text{HgCl} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH} : \text{CH} \cdot \text{CH}(\text{OEt})_2$ , which darkens at 160° and has m. p. 190°.

Diazotised 3''-amino-4:4'-tetramethyldiaminotriphenylmethane combines with phenol dissolved in aqueous sodium hydroxide, yielding a dark yellow sodium salt of 4:4'-tetramethyldiaminotriphenylmethane-3''-azophenol,  $\text{ONa} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ , and with *o*-hydroxyphenylmercuric chloride to form a dark green substance, possibly  $\text{HgCl} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{C}_6\text{H}_4 \cdot \text{NMe}_2)_2$ .

The interaction of *o*-aminophenylmercuric acetate and dinitrophenylpyridinium chloride in acetone solution yields a reddish-brown substance, which probably has the constitution:



F. B.

## Organic Chemistry.

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**Action of Ultraviolet Rays on Gaseous Hydrocarbons.** DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1912, 155, 521—522).—A claim for priority over Landau (*ibid.*, 403) in the study of the action of light on saturated hydrocarbons. The authors briefly recapitulate the results previously recorded by them (compare *Rev. gén. des Sciences*, 1911, 330). W. G.

**Optical Investigation of Hungarian Naphtha.** MICHAEL A. RAKUSIN and E. LASLO (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1076).—A sample of Hungarian naphtha,  $D^{15}_D$  0.8348, gave a carbonisation constant,  $K$ , greater than 0.25%. Seven fractions showed rotations of 0—1.6 saccharimetric divisions, and gave the ordinary coloration with Tschugaëff's cholesterol reagent. T. H. P.

**Decomposition of Methylene Iodide and its Bearing on the Constitution of Steel.** EDWARD D. CAMPBELL and HENRY S. RAWDON (*J. Amer. Chem. Soc.*, 1912, 34, 1159—1168).—The hypothesis recently advanced by Sargent (this vol., i, 674), that the mixture of hydrocarbons obtained on dissolving steel in hydrochloric acid may be explained by the decomposition of a single carbide of iron,  $CFe_3$ , into methylene which polymerises into the olefines, is strongly criticised with regard to its originality and its truth. The old assumption that methylene, if liberated in acid solution in presence of nascent hydrogen, would either be completely reduced to methane or, if polymerisation took place, this would not proceed beyond the formation of ethylene, which latter might be reduced to methane, is now confirmed. Methylene iodide was reduced by means of a zinc-copper couple, and found to yield no hydrocarbon with more than two carbon atoms, even in the presence of ferrous chloride. In one experiment, 16.798 grams of methylene iodide and hydrochloric acid acting on an excess of zinc until all action had ceased, yielded 16.15 litres of gas, which contained 64.6 c.c. of ethylene and 1033.6 c.c. of methane, leaving 17.4% of the carbon in the form of ethyl and ethylene haloids.

The authors plead for the recognition of the possibility of there being many complex carbides of iron in which the property of carbon to link up with carbon is preserved. Their experience shows that the conception that in steel the main part of the iron holds in solution a number of carbides the constitution of which depends on the carbon concentration and heat treatment, is not contrary to fact. J. C. W.

**Preparation of  $\beta\gamma$ -Dimethyl- $\Delta^{\alpha\gamma}$ -butadiene.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.P. 246660, 249030, 250086).—The preparation of  $\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene from pinacone can be effected by dehydration with potassium hydrogen sulphate or acid salts of di- or poly-sulphonic acids; pinacone (500 parts) is intimately mixed with the salt (750 parts), the mixture heated at 140—150°, and the product

separated by fractional distillation. Toluidine hydrogen sulphate or other hydrogen salts of sulphuric acid can be employed for this reaction, as can also neutral salts having an acid reaction such as the alums, the sulphates of copper, iron, aluminium, etc. F. M. G. M.

**Preparation of Isoprene.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 246241. Compare Abstr., 1906, i, 394).—When methylisopropenylcarbinol,  $\text{CH}_2\text{:CMe}\cdot\text{CHMe}\cdot\text{OH}$ , is heated slowly to 130–150° with 10 parts of anhydrous oxalic acid, water is eliminated and isoprene formed. The oxalic acid can be replaced by zinc chloride, hydrogen potassium sulphate, or similar dehydrating agents. F. M. G. M.

**Preparation of Erythrene and Isoprene.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 247145. Compare Abstr., 1911, i, 598).—When the quaternary halogen ammonium bases of general formula  $\text{CH}_3\cdot\text{CHX}\cdot\text{CHY}\cdot\text{CH}_2\cdot\text{NMe}_3\text{X}$  (where X is a halogen atom and Y hydrogen or methyl) are distilled with either alkaline hydroxides or alkaline earths, they furnish erythrene or isoprene according to the equation:  $\text{CH}_3\cdot\text{CHX}\cdot\text{CHY}\cdot\text{CH}_2\cdot\text{NMe}_3\text{X} + 2\text{KOH} = 2\text{KX} + \text{CH}_2\text{:CH}\cdot\text{CY}\cdot\text{CH}_2 + \text{NMe}_3 + 2\text{H}_2\text{O}$ .

The compound,  $\text{HO}\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{NMe}_3\text{Br}$ , is a colourless, crystalline mass, whereas the halogenated bases are usually viscid, brown syrups. F. M. G. M.

**A Method for the Exact Determination of the Position of the Hydroxyl Groups in Polyhydroxy-compounds.** JACOB BÖESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 216–223).—The experiments of Böeseken and van Rossem (this vol., ii, 147) have shown that, of the polyhydroxybenzenes, only the ortho-derivatives exert a very great positive influence on the conductivity of boric acid.

Simple glycols do not increase the conductivity, and it is assumed that the hydroxyl groups repel one another, a similar condition occurring in sucrose.  $\alpha$ -Dextrose increases the conductivity at first, the value then falling, whilst  $\beta$ -dextrose has little influence at first, the conductivity then increasing until the same final value is reached. This behaviour gives a clue to the configuration of the two isomerides.

C. H. D.

**Ethoxides of Calcium and Barium.** ROBERT DE FORCRAND (*Ann. Chim. Phys.*, 1912, [viii], 26, 209–227).—A more detailed account of work published already (this vol., i, 67).

Calcium ethoxide, prepared by Doby's method (Abstr., 1903, i, 546), develops 40.27 Cal. on neutralisation by hydrochloric acid, whence its heat of formation is 93.93 Cal. That of its molecular compound with 2 mols. of ethyl alcohol is 102.48 Cal., whilst solution of calcium in excess of alcohol develops 101.04 Cal. The last figure is very close to Guntz's result for the solution of calcium in water, namely, 101.12 Cal.

T. A. H.

**Oxidation of Propylene Glycol. I. The Action of Alkaline Permanganate Giving Carbonic, Acetic, and Oxalic Acids.** WILLIAM LLOYD EVANS and EDGAR J. WITZEMANN (*J. Amer. Chem. Soc.*, 1912, 34, 1086—1104).—The paper commences with a brief résumé of the results of previous investigations under various conditions.

The action of an alkaline solution of potassium permanganate on aqueous propylene glycol at room temperature gives as sole end products, carbon dioxide, acetic and oxalic acids; an increase in the proportion of alkali raises the ratio of oxalic to acetic acid (compare Cochenhausen, *Abstr.*, 1899, i, 251); raising the temperature increases the proportion of carbon dioxide. The authors conclude that there must be at least three reactions (exclusive of any intermediate ones), namely: (a)  $\text{HO}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH} + 4\text{O} \rightarrow \text{AcOH} + \text{CO}_2 + 2\text{H}_2\text{O}$ ; (b)  $\text{HO}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH} + 7\text{O} \rightarrow \text{C}_2\text{O}_4\text{H}_2 + \text{CO}_2 + 3\text{H}_2\text{O}$ ; (c)  $\text{HO}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH} + 8\text{O} \rightarrow 3\text{CO}_2 + 4\text{H}_2\text{O}$ .

Similar experiments on the oxidation of lactic and pyruvic acids yielded like results; acetic and oxalic acids and carbon dioxide are formed, the last again being in excess of that expected from one carbon atom of each oxidised molecule.

These results are discussed in the light of Nef's dissociation theory (*Abstr.*, 1905, i, 3). Attention is also drawn to the fact that the oxidation of lactic acid is not as simple a process as is assumed by Ulzer and Seidel (*Abstr.*, 1897, ii, 389) in their process for the estimation of this acid.

D. F. T.

**Preparation of Glycols from Dihalogenbutanes and their Homologues.** CHEMISCHE FABRIK AUF ACTIEN VORM. E. SCHERING (D.R.-P. 246572. Compare *Abstr.*, 1876, 64; 1878, 845, 850).—Various methods of preparing glycols have been previously described; the following procedure is now advocated.

$\beta\gamma$ -Dibromoisopentane (23 parts) is added to a solution of sodium hydroxide (10 parts in 500 parts of water) and allowed to remain several days at the ordinary temperature with frequent stirring; the solution is neutralised, a "salting out" agent introduced, and the glycol (8.5 parts) isolated by extraction with ether.

$\beta\gamma$ -Butanediol (7 to 8 parts) is obtained when  $\beta\gamma$ -dichlorobutane (12.7 parts) is added to a mixture of calcium hydroxide (10 parts) with water (500 parts) and heated at about 75° until the reaction is complete.

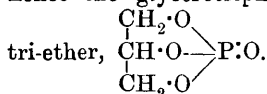
F. M. G. M.

**Action of Concentrated Phosphoric Acid on Glycerol. II.** ANGELO CONTARDI (*Gazzetta*, 1912, 42, ii, 270—282).—Consideration of previous results (compare Carré, *Abstr.*, 1904, i, 133, 215; 1905, i, 184; 1911, i, 263; Contardi, *Abstr.*, 1910, i, 157, 609) would lead to the conclusion that in the esterification of polyhydric alcohols with phosphoric acid, when the number of hydroxyls is sufficiently large and no dehydration intervenes, the reaction occurs preferably between 1 mol. of alcohol and 1 mol. of the acid. The reaction between glycerol or other polyhydric alcohol and phosphoric acid seems, however, to be more complicated than is generally assumed; thus, when

equimolecular proportions of glycerol and phosphoric acid are mixed, esterification does not proceed solely molecule for molecule, the tri-phosphoric ester,  $C_3H_5(PO_4H_2)_3$ , being always formed in considerable amount; this ester alone is obtained when 1 mol. of glycerol or triacetin is esterified with 3 mols. of phosphoric acid.

When an equimolecular mixture of anhydrous glycerol and phosphoric acid is heated at  $130^\circ$  for ten to twelve hours and under 18—20 mm. pressure, one-half of the phosphoric acid is transformed into glycerotriphosphoric acid, and the other half, in the first phase, into ordinary  $\alpha$ - and  $\beta$ -glycerophosphoric acid,

$[OH \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot PO_4H_2]$  and  $OH \cdot CH_2 \cdot CH(PO_4H_2) \cdot CH_2 \cdot OH$ ; one-third of the glycerol takes no part in the reaction, which may be represented thus:  $6C_3H_8O_3 + 6H_3PO_4 = C_3H_{11}O_{12}P_3 + 2C_3H_8O_3 + 3C_3H_9O_6P + 6H_2O$ . This result does not seem to agree with Carré's observation that an equimolecular mixture of glycerol and phosphoric acid is transformed quantitatively into the neutral tri-ester in the vacuum of a mercury pump. It is found that esterification of 1 mol. of glycerol with 3 mols. of phosphoric acid, and treatment of the final glycerotriphosphoric acid obtained with 2 mols. of anhydrous glycerol under the conditions employed by Carré, gives an almost quantitative yield of the solid, neutral ether; hence the glycerotriphosphoric acid loses 2 mols.  $H_2O$ , giving the



T. H. P.

**Preparation of Epichlorohydrin from Dichlorohydrin.** CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 246242).—It is found that the potassium hydroxide usually employed in the preparation of epichlorohydrin (from dichlorohydrin) can be replaced by either alkali carbonates or alkaline earth hydroxides. The distillation of dichlorohydrin at  $80^\circ$  and 135 mm. with twice the quantity of calcium hydroxide indicated by theory furnished a 95% yield of epichlorohydrin, whilst with sodium carbonate an 85% yield was obtained.

F. M. G. M.

**The Lecithin of Egg-Yolk.** J. D. RIEDEL (*Chem. Zentr.*, 1912, i, 1794; from *Riedel's Ber.*, 1912, 24—33).—A purified lecithin has been obtained from egg-yolk, free from cholesterol and foreign albumin, by extraction with cold methyl alcohol. The formula:  $OR \cdot CH_2 \cdot CR'(OH) \cdot CH_2 \cdot PO_3(OH) \cdot C_2H_4 \cdot NMe_3 \cdot OH$ , is proposed for lecithin, R and R' being aliphatic acyl groups, of which palmitic, stearic, oleic, and linoleic acids have been recognised.

C. H. D.

**Purification of Ether to be Used as an Anæsthetic.** GABRIEL GUÉRIN (*J. Pharm. Chim.*, 1912, [vii], 6, 212—213).—Commercial ether is shaken repeatedly with 3% by volume of Deniges' mercuric acid sulphate reagent, until on addition of a fresh quantity of the reagent no precipitate, or only a white precipitate, is formed. The separated ether is filtered and then allowed to remain, with frequent agitation, in contact with excess of quicklime and ground calcium chloride, and

finally redistilled. The purified ether should be kept in full, well-corked bottles. T. A. H.

**Methyl Thiomethyl Ether and the Corresponding Thioethers.** JEAN DE LATTRE (*Bull. Soc. chim. Belg.*, 1912, 26, 323—336).—*Methyl thiomethyl ether*,  $\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\cdot\text{SH}$ , was prepared by the action of methyl chloromethyl ether on potassium hydrogen sulphide ( $4\text{KHS}, \text{H}_2\text{O}$ ) at the ordinary temperature. Anhydrous potassium hydrogen sulphide and methyl chloromethyl ether react very slowly in the absence of solvent or in the presence of ether. The thiol has b. p.  $52^\circ/15$  mm., m. p.  $-52.4^\circ$ ,  $D_0^0$  1.1018,  $D_{12}^{12}$  1.0738,  $n_D^{20}$  1.4909, mol. wt. (in benzene or glacial acetic acid solution) 154. Water and alkalis decompose it with the formation of thiomethylene. When heated at the boiling point of aniline, it forms trithiomethylene, m. p.  $215^\circ$ , and methyl alcohol. Gaseous hydrogen chloride and hydrogen iodide transform it into trithiomethylene, methyl chloride, and methyl iodide respectively. Addition of an alcoholic solution of mercuric chloride precipitates the compound,  $\text{OMe}\cdot\text{CH}_2\text{S}, \text{HgCl}$ , which decomposes when heated, whilst yellow mercuric oxide converts it in alcoholic solution into the *mercaptide*,  $(\text{CH}_3\cdot\text{O}\cdot\text{CH}_2\cdot\text{S})_2\text{Hg}$ . Benzoylation in pyridine solution yields the corresponding *benzoyl* derivative, b. p.  $146^\circ/15$  mm.,  $D_0^0$  1.2171,  $D_{21.6}^{21.6}$  1.2007,  $n_D^{21.6}$  1.5760. Application of the Schotten-Baumann method yields principally trithiomethylene with small quantities of the above compound, whilst, when boiled with benzoyl chloride, the thiol yields trithiomethylene and methyl benzoate. Acetyl chloride in the presence of pyridine converts the thiol into the corresponding *acetyl* derivative, b. p.  $94^\circ/15$  mm.,  $D_0^0$  1.1978,  $D_{27}^{27}$  1.1860,  $n_D^{27}$  1.5178.

An attempt to prepare methyl thiomethyl ether by the action of methyl chloromethyl ether on an alcoholic solution of potassium hydrogen sulphide led to the isolation of a *thiomethylene*,  $(\text{CH}_2\text{S})_n$ , m. p.  $123-124^\circ$ .

*Dimethyl ether sulphide*,  $(\text{CH}_3\cdot\text{O}\cdot\text{CH}_2)_2\text{S}$ , prepared by the action of methyl chloromethyl ether on potassium sulphide ( $2\text{K}_2\text{S}, \text{H}_2\text{O}$ ) at the ordinary temperature, has b. p.  $62^\circ/15$  mm.,  $D_0^0$  1.0671,  $D_{21.5}^{21.5}$  1.0418,  $n_D^{12.5}$  1.4575. When heated with methyl iodide, at the ordinary temperature or at  $80^\circ$ , it forms trimethylsulphonium iodide and oxymethylene.

*Dimethyl ether disulphide*,  $(\text{CH}_3\cdot\text{O}\cdot\text{CH}_2)_2\text{S}_2$ , is formed simultaneously with some monosulphide and *trisulphide* by cautiously heating methyl chloromethyl ether with potassium disulphide ( $2\text{K}_2\text{S}_2, \text{H}_2\text{O}$ ). It has b. p.  $115^\circ/15$  mm.,  $D_0^0$  1.2086,  $D_{22}^{22}$  1.1881,  $n_D^{22}$  1.5290. When the above substances are allowed to react in the cold, only the monosulphide,  $(\text{CH}_3\cdot\text{O}\cdot\text{CH}_2)_2\text{S}$ , is obtained. The latter substance, at its boiling point, does not react with sulphur. If, however, potassium sulphide ( $2\text{K}_2\text{S}, \text{H}_2\text{O}$ ) is added, it combines with the sulphur, giving excellent yields of disulphide.

*Phenyl methoxymethyl sulphide*,  $\text{C}_6\text{H}_5\cdot\text{S}\cdot\text{CH}_2\cdot\text{OMe}$ , obtained by the action of magnesium phenyl bromide on dimethyl ether disulphide (compare Wuyts, *Abstr.*, 1906, i, 257), is a colourless liquid, b. p.  $108^\circ/12$  mm.,  $D_0^0$  1.1214,  $D_{16}^{16}$  1.1047,  $n_D^{16}$  1.5707. H. W.

**The Hydrolytic Action of Glycine on Ethyl Butyrate.** S. LIEBOWITZ (*J. Amer. Chem. Soc.*, 1912, 34, 1111—1113. Compare Falk and Nelson, this vol., i, 522).—Experiments at temperatures from 20° to 40° indicate that glycine exerts a marked hydrolytic effect on aqueous solutions of ethyl butyrate; there is a rough parallelism between the amount of action and the amounts of ester or of glycine used, the extent of the hydrolysis being measured when far from completion. The replacement of water by *N*-sodium chloride solution as medium had no effect. D. F. T.

**Preparation of Carbonic Ester of Tertiary Alcohols.** VEREINIGTE CHININFABRIKEN ZIMMER & Co. (D.R.-P. 246298).—It is found that amylene carbamate (this vol., i, 541) or similar esters can be readily prepared by treating the sodium derivative of the alcohol with carbamyl chloride in dry benzene, or by employing the free alcohol in the presence of an acid eliminating agent, such as dimethylaniline. F. M. G. M.

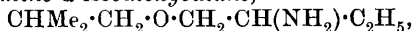
**Action of Alcoholic Ammonia on  $\alpha\beta$ -Dibromopropionic Acid.** WILLIAM H. WARREN (*J. Amer. Chem. Soc.*, 1912, 34, 1082—1086).—The action of ammonia on  $\alpha\beta$ -dibromopropionic acid is known to yield  $\alpha\beta$ -diaminopropionic acid (Klebs, Abstr., 1894, i, 439) and  $\beta$ -amino- $\alpha$ -hydroxypropionic acid (*isoserine*: Neuberg and Ascher, Abstr., 1907, i, 1014). If, however, a 12.5% solution of ammonia in absolute alcohol is allowed to react in the cold with an alcoholic solution of  $\alpha\beta$ -dibromopropionic acid, the sole organic product appears to be ammonium  $\alpha$ -bromoacrylate; this was separated from the mixture obtained after evaporation by treating with silver sulphate to convert the ammonium bromide into the sulphate, from which the ammonium  $\alpha$ -bromoacrylate, plates, m. p. 148° (decomp.), is easily separable by alcohol; the identity of this substance was confirmed by conversion into the silver salt and into the free acid, which from its m. p. (69°) must be the  $\alpha$ -isomeride (Wagner and Tollens, this Journ., 1874, 680).

When the interaction of alcoholic ammonia and dibromopropionic acid is assisted by heat, no ammonium  $\alpha$ -bromoacrylate is obtained, but some  $\alpha\beta$ -diaminopropionic acid. The formation of the former compound in the above reaction may explain the poor yields of  $\alpha\beta$ -diaminopropionic acid obtained by earlier investigators, as  $\alpha$ -bromoacrylic acid decomposes exceedingly readily, giving a gelatinous product. D. F. T.

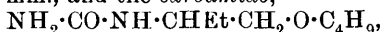
**Action of the Chlorides of  $\alpha$ -Alkyloxy-acids on Organo-Metallic Derivatives of Zinc.** II. EDMOND E. BLAISE and L. PICARD (*Ann. Chim. Phys.*, 1912, [viii], 26, 258—288).—In the previous memoir (this vol., i, 332) it was shown that the products of this reaction may be either alkyloxy-ketones or ethers, and the influence on the reaction of the radicle in the organo-metallic compound used was investigated. The present paper deals with the influence of the alkyloxy-residue of the acid chloride.

*iso*Butoxyacetic acid,  $C_4H_9 \cdot O \cdot CH_2 \cdot CO_2H$ , b. p. 118—119°/16 mm. or 105—106°/8 mm., prepared by the action of *isobutyl* chloroacetate

on sodium *isobutoxide*, is a viscous liquid, readily soluble in water. The *ethyl ester*, b. p.  $69^{\circ}/10$  mm., is a mobile liquid with a fruity odour. The *chloride*, b. p.  $48^{\circ}/10$  mm., is a mobile liquid of suffocating odour produced along with some *chloromethyl isobutyl ether*, b. p.  $26^{\circ}/12$  mm., and a little *isobutyl isobutoxyacetate*, b. p.  $89-90^{\circ}/10$  mm., by the action of thionyl chloride on the acid. The *amide*, m. p.  $78^{\circ}$ , crystallises from a mixture of benzene and light petroleum in needles. The *anilide*, m. p.  $45^{\circ}$ , forms colourless needles from light petroleum. The *p-toluidide*, m. p.  $43^{\circ}$ , crystallises from alcohol, and the *phenylhydrazide*, m. p.  $92^{\circ}$ , separates from ether on addition of light petroleum in slender needles. The condensation of the chloride with zinc ethyl iodide has been described already (Abstr., 1911, i, 175); the resulting *isobutoxymethyl ethyl ketone* on reduction with sodium yields the corresponding *alcohol*,  $C_4H_9O \cdot CH_2 \cdot CH(OH) \cdot C_2H_5$ , b. p.  $72-73^{\circ}/14$  mm., whilst the *ketoxime* (*loc. cit.*) is reduced by sodium amalgam, giving ammonia, *isobutyl alcohol* (phenylurethane, m. p.  $85.5-86^{\circ}$ ), *sec.-butylamine* (*di-sec.-butyloxamide*, needles, m. p.  $160^{\circ}$  approx.), and  $\beta$ -amino- $\alpha$ -isobutoxybutane,



b. p.  $167^{\circ}/760$  mm. The last-mentioned substance is a viscous liquid, sparingly soluble in water, and has an odour recalling that of piperidine. The *sulphate* forms colourless spangles, and the *picrate*, m. p.  $101^{\circ}$ , lemon-yellow spangles. The *benzoyl* derivative has m. p.  $40^{\circ}$ , b. p.  $206^{\circ}/19$  mm., and the *carbamide*,

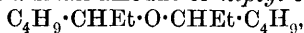


m. p.  $92^{\circ}$ , forms brilliant spangles from a mixture of benzene and light petroleum. On addition of hydrochloric acid, *aminoisobutoxybutane* gives *aminobutyl alcohol hydrochloride*,  $C_2H_5 \cdot CH(CH_2 \cdot OH) \cdot NH_2 \cdot HCl$ , deliquescent needles, the *platinichloride* of which forms yellow lamellæ, m. p.  $189-190^{\circ}$  (decomp.).

Phenoxymethyl ethyl ketone, the product of the action of zinc ethyl iodide on phenoxyacetyl chloride (*loc. cit.*), gives with hydrazine hydrate the corresponding *azine*, m. p.  $72^{\circ}$ , crystallising in needles. With hydroxylamine only a small yield of the *ketoxime*, m. p.  $69^{\circ}$ , needles, is obtained, due to partial decomposition of the ketone, with the liberation of phenol, and on reduction the oxime yields *sec.-butylamine* and phenol.

Ethyl  $\alpha$ -bromohexanoate reacts with sodium ethoxide to form ethyl  $\alpha$ -ethoxyhexanoate as chief product, with a small amount of a second ester,  $C_{16}H_{30}O_4$ , b. p.  $149^{\circ}/7$  mm., yielding on hydrolysis a liquid acid, which readily gives an *anhydride*, b. p.  $175-180^{\circ}/9$  mm., from which an *anilide*, m. p.  $154^{\circ}$ , in brilliant crystals may be obtained; this acid is probably *aa-di-n-butylsuccinic acid*.  $\alpha$ -Ethoxyhexoic acid, b. p.  $124.5^{\circ}/10$  mm., prepared from the *ethyl ester*, b. p.  $93^{\circ}/16$  mm. (see above), yields crystalline *copper* and *calcium* salts, and with thionyl chloride furnishes the acid chloride (Abstr., 1911, i, 260), from which the corresponding *amide*, brilliant spangles, m. p.  $78^{\circ}$ , *anilide*, needles, m. p.  $57^{\circ}$ , and *p-toluidide*, m. p.  $34^{\circ}$ , b. p.  $185^{\circ}/9$  mm., were prepared. On treating  $\alpha$ -ethoxyhexoyl chloride with zinc ethyl iodide no ketone is produced, the only condensation product being  $\gamma$ -ethoxyheptane (*loc. cit.*), which, on treatment with hydriodic acid, yields  $\gamma$ -iodoheptane,

$C_2H_5 \cdot [CH_2]_2 \cdot CHI \cdot C_2H_5$ , b. p.  $64.5^\circ/8.5$  mm. The latter with moist silver oxide furnishes a small amount of *heptyl ether*,



b. p.  $106^\circ/10$  mm., with  $\gamma$ -*hydroxyheptane*, b. p.  $156.5$ — $157^\circ/760$  mm. as the chief product. The *acetate* of this, b. p.  $53$ — $54^\circ/8$  mm., is a pleasant-smelling liquid.

T. A. H.

**Solubilities of the Lead Salts of the Higher Fatty Acids in Ether and in Light Petroleum.** G. B. NEAVE (*Analyst*, 1912, 37, 399—400).—Whereas lead oleate is readily soluble in both liquids, 100 c.c. of ether at  $20^\circ$  dissolve of lead heptate 0.2397, of lead octate 0.0938, of lead nonate 0.1115, and of lead decoate only 0.0290 gram; lead myristate, lead laurate, lead palmitate, and lead stearate are practically insoluble. At the boiling point is dissolved of lead decoate 1.3640, of lead heptate 1.4900, of lead octate 0.5460, of lead nonate 0.2404, of lead decoate 0.4285, of lead myristate 0.0555, of lead laurate 0.0205, and of lead palmitate 0.0261 gram; lead stearate is insoluble.

In light petroleum (b. p.  $40$ — $60^\circ$ ) at  $20^\circ$  they are practically insoluble, except the heptate, which dissolves to the extent of 0.0200 gram. [The solubility of lead decoate at  $20^\circ$  in either solvent is not recorded.] At the boiling point the solubilities are as follows: lead decoate 0.0608, lead heptate 0.0528, lead octate 0.0384, lead nonate 0.0450, lead decoate 0.0170, lead myristate 0.0210 (lead laurate and palmitate are practically insoluble), and lead stearate 0.017 gram per 100 c.c.

L. DE K.

**The Formation of *d*-Lactic Acid in Incubated Hen's Eggs.** KINZUCHI ANNO (*Zeitsch. physiol. Chem.*, 1912, 80, 237—240).—After three days' incubation an abundant formation of *d*-lactic acid occurs in the white of the hen's egg, whereas only a small quantity can be detected in the yolk.

W. D. H.

**A Biochemical Method of Preparation of *l*-Tartaric Acid.** JACOB BÖESEKEN and H. J. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 212—216).—*l*-Tartaric acid is conveniently prepared by the action of *Aspergillus niger* on racemic acid; the solution after six days at  $33$ — $34^\circ$  gives a maximum *l*-rotation, after which the *l*-acid is slowly consumed. The variety of *Penicillium glaucum* employed had very little selective power, and therefore differed from that used by Pasteur.

C. H. D.

**Relation between the Iodine Number and the Structure with Acids of the Oleic Series.** GIACOMO PONZIO and C. GASTALDI (*Gazzetta*, 1912, 42, ii, 92—95).—The values of the iodine number for undecenoic acid, determined by the Hübl, Wys and Hanuš methods, are very close to the theoretical number, whilst those for crotonic,  $\Delta^{\beta}$ -hypogæic, and  $\Delta^{\beta}$ -oleic acids are very considerably lower than the theoretical ones. These results are not due to any abnormality in the interaction with iodine of double linkings near to the carboxyl group, but merely to the low velocities with which such

double linkings react. Thus, with  $\Delta^8$ -oleic acid, it is found that increase of the duration of the tests is accompanied by marked increase of the iodine number obtained by all three methods; for instance, the Wys method gave 18.0 after 30 minutes, 37.7 after 3 hours, 76.2 after 12 hours, 84.2 after 24 hours, and 86.8 after 70 hours, the theoretical value being 89.7.

The suggestion is made that the determination of the iodine number may serve as a good method of establishing the position of the double linking in an unsaturated acid.  
T. H. P.

**Degradation of Cholic Acid. III. The Capacity of Cholic Acid Derivatives for Combining with Ozone.** OTTO VON FÜRTH and HIROMU ISHIHARA (*Biochem. Zeitsch.*, 1912, 43, 323—334. Compare Abstr., 1910, i, 606).—The oils obtained by distillation of cholic acid can combine with ozone. If Pregl's formulæ is accepted, the principal distillation product forms an ozonide of the formula  $C_{17}H_{24}O_7$ . A similar product was obtained by the action of ozone on the product obtained by the fusion of bilianic acid with sodium hydroxide. These ozonides or perozonides show great resistance to various chemical reagents, and have the characteristics of the ozonides of hydroaromatic rather than of aliphatic character. In the substance called dehydrocholon by Pregl, the action of ozone revealed the presence of several double bonds.  
S. B. S.

**Catalytic Hydrogenation of Ketones.** GUSTAVE VAVON (*Compt. rend.*, 1912, 155, 286—288. Compare this vol., i, 628).—Ketones can be readily reduced, by a current of hydrogen in the presence of platinum black, to the corresponding secondary alcohols. Aliphatic, cyclic, aromatic, ethylenic and terpenic ketones, ethyl acetoacetate, and a diketone, acetylacetone, have all been experimented on. Reduction is best carried out in the presence of a solvent varying with the ketone to be reduced. The method is very general, and in most cases the corresponding secondary alcohols are the products, although with some ketones the reduction, if allowed to go on, will proceed to further stages.  
W. G.

**Higher Ketones and Secondary Alcohols Derived from the Amides of Palmitic and Stearic Acids.** HUGH RYAN and THOMAS NOLAN (*Proc. Roy. Irish Acad.*, 1912, 30, B, 1—7). The authors have prepared a series of ketones by the action of Grignard's reagents on the amides of palmitic and stearic acids. Reduction by sodium and alcohol transforms these ketones into the corresponding secondary alcohols.

Methyl pentadecyl ketone,  $CH_3 \cdot CO \cdot C_{15}H_{31}$ , m. p.  $48^\circ$ , is obtained by the action of magnesium methyl iodide on palmitamide. Similarly, magnesium phenyl bromide and palmitamide yield *phenyl pentadecyl ketone*, m. p.  $59^\circ$ , the *oxime* of which has m. p.  $73$ — $74^\circ$ . *p*-Tolyl pentadecyl ketone, prepared in an analogous manner, has m. p.  $60^\circ$ ; its *phenylhydrazone*, m. p.  $54$ — $55^\circ$ , and its *semicarbazone*, m. p.  $114.5^\circ$ . *α*-Naphthyl pentadecyl ketone has m. p.  $48^\circ$ .

The following ketones were obtained from stearamide: *ethyl hepta-*

decyl ketone, m. p.  $57^{\circ}$ ; phenyl heptadecyl ketone, m. p.  $64^{\circ}$  (phenylhydrazone, m. p.  $54^{\circ}$ ); p-tolyl heptadecyl ketone, m. p.  $66-67^{\circ}$ ;  $\alpha$ -naphthyl heptadecyl ketone, m. p.  $53-54^{\circ}$ . An attempt to prepare the phenylhydrazone of the latter was unsuccessful.

p-Tolylpentadecylcarbinol,  $\text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}(\text{OH}) \cdot \text{C}_{15}\text{H}_{31}$ , prepared in good yield by the reduction of p-tolyl pentadecyl ketone by sodium and alcohol, has m. p.  $44-45^{\circ}$ . Its phenylurethane, m. p.  $44^{\circ}$ , and its somewhat impure acetate were also examined.

Phenylpentadecylcarbinol and phenylheptadecylcarbinol have m. p.'s  $53^{\circ}$  and  $59^{\circ}$  respectively. The latter substance, when heated with sodium acetate and acetic anhydride, yields an impure acetate.

H. W.

**The Photochemical Synthesis of Carbohydrates.** WALTHER LÖB (*Biochem. Zeitsch.*, 1912, 43, 434-437).—The author contends that the experimental results of Stoklasa, Sebor, and Zdobnický in their work on the photochemical synthesis of carbohydrates (this vol., i, 606) do not justify the conclusions they have drawn from them.

S. B. S.

**Reducing Power of Sugars.** NICOLAAS SCHOORL (*Chem. Weekblad*, 1912, 9, 678-694).—The author gives a summary of work on reduction by the aid of various sugars. He considers that the reduction of alkaline copper solutions by sucrose is a property of the sucrose molecule.

A. J. W.

**Reducing Power of Sugars (Monosaccharides) and its Bearing on the Definition of these Substances.** NICOLAAS SCHOORL (*Chem. Weekblad*, 1912, 9, 706-711).—The author had found that introduction of a non-oxidised carbon atom between the CO- and CH(OH)-groups in a compound containing the group  $\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot$  materially diminishes its power of reducing a weakly alkaline copper solution. He considers that the term "sugars" should include all substances with the group  $\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot$ , whether polyhydric alcohols or not.

A. J. W.

**Enzymatic Phosphate Union.** HANS EULER and DAVID JOHANSSON (*Zeitsch. physiol. Chem.*, 1912, 80, 205-211).—During the alcoholic fermentation, dextrose, lævulose, galactose, and mannose yield intermediate substances which form compounds with phosphates. The hexoses themselves do not form these esters, but dihydroxyacetone, one of the intermediate substances, does. A similar material is formed from dextrin by the action of dilute alkali.

W. D. H.

**Photolysis of Ketoses by Solar and Ultra-violet Light.** DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1912, 155, 401-403. Compare Abstr., 1910, ii, 813, 114; this vol., ii, 715).—The sugars dihydroxyacetone, erythrulose, lævulose, sorbose, and perseulose are decomposed when their aqueous solutions are exposed in quartz tubes to sunlight. Carbon monoxide with a little carbon dioxide is evolved, and the corresponding alcohol containing one carbon atom less

than the sugar used is formed. The decomposition is slow and more feeble the more complex the sugar used.

On exposure to ultra-violet light from a mercury lamp the same fundamental decomposition occurs, but there are also accessory reactions which result in the evolution of a little hydrogen and sometimes of methane, and in the formation of formaldehyde and non-volatile acids in the solutions. Similar changes occur when the solid sugars are exposed to ultra-violet light.

T. A. H.

**Hydrolysis of Maltose by Dilute Acids.** LADISLAS KOPACZEWSKI (*Bull. Soc. chim.*, 1912, [iv], 11, 850—853).—The existing statements regarding the rate of hydrolysis of maltose by dilute acids being conflicting, the author has re-investigated the question and finds that (1) the hydrolytic activity of acids towards maltose depends on their electrolytic dissociation, and (2) the rate of hydrolysis (*a*) increases rapidly when the concentration of the acid rises above  $N/4$ , (*b*) increases with the temperature in the case of dilute acids, and (*c*) increases with the concentration of maltose, especially for sulphuric acid.

T. A. H.

**Influence of Different Acids on the Hydrolysis of Maltose by Maltase.** LADISLAS KOPACZEWSKI (*Zeitsch. physiol. Chem.*, 1912, 80, 182—193).—The effect of various acids varies considerably, which shows that concentration of hydrogen ions is not the only important factor in influencing enzymatic activity; the nature of the anions is important also.

W. D. H.

**Products of the Interaction of Mercuriammonium Chloride and Methyl Iodide.** MÁRTON LÖW (*Zeitsch. Kryst. Min.*, 1912, 51, 138—142).—By heating a mixture of 1 mol. of mercuriammonium chloride and 3 mols. of methyl iodide in a sealed glass tube in a water-bath, S. Hajnóci (*Magyar Chem. Foly.*, 1911, 17, 91) obtained the following three substances: (1) methylamine mercuri-iodide as pale yellow prisms and plates; these are orthorhombic with  $a:b:c = 0.5793:1:0.5164$ . (2) Dark yellow plates and pyramids, also orthorhombic,  $a:b:c = 0.6168:1:0.7704$ , but of unknown composition. (3) Pale yellow crusts and spherical aggregates with probably the composition  $\text{NH}_4\text{I}_2\text{HgI}_2$ . The three substances differ in their degree of solubility in an aqueous solution of potassium iodide, in nitrobenzene, alcohol, etc., and they also show differences in their behaviour when heated.

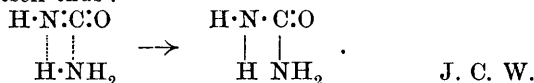
L. J. S.

**Composition of Different Kinds of Silk.** XIV. Total and Partial Hydrolysis of the Cocoon of the Ailanthus Spinner and of Tailung Silk. EMIL ABDERHALDEN and RYNGO INOUE (*Zeitsch. physiol. Chem.*, 1912, 80, 198—204. Compare Abstr., 1911, i, 1050).—Analytical data are given similar to those in the previous papers of the series in reference to the two kinds of Chinese silk mentioned.

W. D. H.

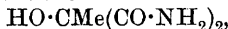
**Transformation of Ammonium Cyanate into Carbamide.** ALVIN S. WHEELER (*J. Amer. Chem. Soc.*, 1912, 34, 1269—1270).—The author points out that the transformation of ammonium cyanate

into carbamide has been explained for some time, by Willstätter among others, in a simpler way than that proposed by Chattaway (Trans., 1912, 101, 170). The salt decomposes into cyanic acid and ammonia, and, introducing the idea of partial valency, the latter is assumed to attach itself thus :



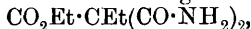
**The Constitution of the Bimolecular Cyanides of the Fatty Acids.** WILHELM BARDROFF (*Monatsh.*, 1912, 33, 859—871).—Two different structures have been proposed for the bimolecular cyanides of organic acids, namely,  $\text{RCO}_2 \cdot \text{CR}(\text{CN})_2$  (Brunner, Abstr., 1895, i, 335, etc.) and  $\text{RC}(\text{CN}) < \text{O} > \text{CR} \cdot \text{NC}$  (Diels and Pillow, Abstr., 1908, i, 535). To aid decision between these two formulæ the author has investigated the intermediate products in the hydrolysis of these cyanides to homologous tartronic acids (compare Brunner, *loc. cit.*) ; the results are entirely in favour of the first structure.

If bimolecular acetyl cyanide is cautiously introduced into sulphuric acid (D 1.57) in a freezing mixture and the mixture kept cold for twenty hours, about 50% of the cyanide undergoes conversion into a substance, forming columnar crystals (from alcohol), m. p. 192°. From the molecular weight in aqueous solution and the elementary analysis, the formula is  $(\text{C}_3\text{H}_5\text{O}_2\text{N})_2$  ; as hydrolysis causes the formation of one molecule of acetic acid and two of ammonia, the structure is probably  $\text{OAc} \cdot \text{CMe}(\text{CO} \cdot \text{NH}_2)_2$ , *acetylmethyltartrondiamide*. If this substance is carefully hydrolysed in the cold by potassium hydroxide solution, the acetyl group is removed with formation of a new amide,



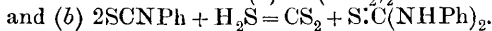
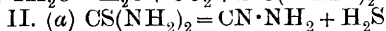
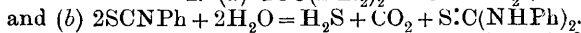
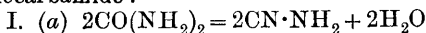
*methyltartrondiamide*, m. p. 203.5°, which yields two molecules of ammonia on further hydrolysis.

When bimolecular propionyl cyanide is treated as above with sulphuric acid, there is formed the analogous substance



*propionylethyltartrondiamide*, tablets, m. p. 168° ; it was found impossible to remove the propionyl radicle from this in the manner described for the corresponding acetyl compound. D. F. T.

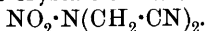
**Action of Phenylthiocarbimide on Carbamide and on Thiocarbamide.** A. PIERONI (*Gazzetta*, 1912, 42, ii, 183—185).—The products of both of these reactions consist of cyanamide and diphenylthiocarbamide :



T. H. P.

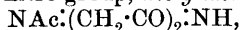
**The Direct Nitration of Aliphatic Imino-compounds.** ANTOINE P. N. FRANCHIMONT and J. V. DUBSKY (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 207—212. Compare Abstr., 1907, i, 395).—Nitric acid and iminodiacetonitrile,  $\text{NH}(\text{CH}_2 \cdot \text{CN})_2$ , yield a

crystalline *nitrate*, m. p. 138—140°. If dissolved in absolute nitric acid and evaporated in a vacuum, the product, crystallised from benzene, forms snow-white crystals of *nitroiminodiacetonitrile*,



Heating iminodiacetic acid with nitric acid to boiling forms *nitroiminodiacetic acid*,  $\text{NO}_2 \cdot \text{N}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$ , which crystallises from ethyl acetate in broad, flat needles, decomp. 153°. The *potassium* salt explodes at 195°. Methyl iminodiacetate forms a *nitrate*, m. p. 198—199°, which is converted by cold nitric acid into the *nitro*-compound,  $\text{NO}_2 \cdot \text{N}(\text{CH}_2 \cdot \text{CO}_2\text{Me})_2$ , m. p. 63·5°. Iminodiacetamide,  $\text{NH}(\text{CH}_2 \cdot \text{CO} \cdot \text{NH}_2)_2$ , forms a *nitrate*, m. p. 206° (decomp.), which is decomposed by absolute nitric acid, yielding nitroiminodiacetic acid.

Iminodiacetamide,  $\text{NH}(\text{CH}_2 \cdot \text{CO})_2 \cdot \text{NH}$ , forms a *hydrochloride*, decomp. above 180°, and a *nitrate*, both of which contain 1 mol. of acid. Evaporation with nitric acid in a vacuum yields colourless crystals of nitroiminodiacetamide,  $\text{NO}_2 \cdot \text{N}(\text{CH}_2 \cdot \text{CO})_2 \cdot \text{NH}$ . In order to determine the position of the nitro-group, *acetyliminodiacetamide*,



has been prepared by subliming the corresponding diamide, and also by direct acetylation. It has m. p. 167—168°.

Methyliminodiacetic acid,  $\text{NMe}(\text{CH}_2 \cdot \text{CO}_2\text{H})_2$ , yields the *diamide*, m. p. 162—163°, from which the *imide*,  $\text{NMe}(\text{CH}_2 \cdot \text{CO})_2 \cdot \text{NH}$ , is obtained by sublimation under reduced pressure, and has m. p. 106°. It yields a crystalline *hydrochloride* and *nitrate*, decomposing above 235° and 130° respectively. It has not been found possible to isolate a nitro-derivative.

The phenyl group does not have the same effect as the carboxyl or nitrile groups, as dibenzylamine does not yield a nitroamine.

C. H. D.

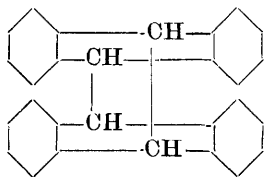
**The Formula of Organo-magnesium Derivatives: Magnesium Hydride.** PIERRE JOLIBOIS (*Compt. rend.*, 1912, 155, 353—355).—For various reasons the author considers that Grignard's formula,  $\text{EtMgI}$ , for his reagent must be abandoned in favour of the formula  $\text{MgEt}_2 \cdot \text{MgI}_2$ . If a concentrated solution of the Grignard reagent is submitted to the action of an electric current, with a high potential difference, for a short time until the liquid becomes hot, magnesium is deposited at the cathode, but no gas can be detected at the anode. On heating the reagent gradually by electrical means, under reduced pressure, so that the gaseous products are withdrawn without being able to react on the solid products, the ether is first completely eliminated at 95°, this stage in the reaction being reversible. At 175° an irreversible reaction occurs, almost pure ethylene being evolved to the extent of two molecules for every atom of magnesium. The solid residue at this stage is a grey powder, which must be represented either as  $\text{HMgI}$  or  $\text{MgH}_2$ . From it practically all the iodine can be removed by washing with dry ether, and on heating it to 280° it evolves hydrogen to the extent of one molecule per atom of magnesium. The author considers that these results support his formula  $\text{MgEt}_2 \cdot \text{MgI}_2$ .

W. G.

**Preparation of Carboxylic Acid Esters Containing Mercury and the Products of their Hydrolysis.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 246207).—Complex mercury salts of unsaturated carboxylic acids have previously been prepared (this vol., i, 596); it is now found that similar compounds can be obtained from the mono- and poly-carboxylic acids of the acetylene series which are of therapeutic value.

An alcoholic solution of mercuric acetate when treated with an equal weight of ethyl behenolate and allowed to remain at the ordinary temperature during twenty-four hours furnishes a *product* which, after hydrolysis with cold sodium hydroxide, contains about 35% mercury. The analogous compound from ethyl stearolate contains 30% of mercury. F. M. G. M.

**1-Methylantracene and Some Anthracene Derivatives.** OTTO FISCHER and HUGO ZIEGLER (*J. pr. Chem.*, 1912, [ii], 86, 289—297).—A continuation of previous work on 1-methylantracene (Abstr., 1911, i, 279), together with an account of the polymerisation of a number of anthracene derivatives by exposure to sunlight in benzene solution. It is found that dihydroanthracene, methyl-dihydroanthracene, and anthraquinone, which do not contain a para-linkage, undergo no change, whereas 1-methylantracene, 1-chloro-4-methyl-



anthracene, 9-bromoanthracene, and 1-chloro-9(or 10)-bromoanthracene, in which the para-bond remains intact, readily polymerise to dianthraces. From these observations the conclusion is drawn that the polymerisation is due to the rapture of the para-linkage, followed by the union of two molecules as shown in the annexed formula. Further,

since the dianthraces do not combine with picric acid, the basic properties of anthracene derivatives, and also their halochromism, must be referred to the presence of the para-bond.

1-Methyl-9:10-dihydroanthracene, prepared by reducing 1-methylantracene with sodium and amyl alcohol, distils at 314—315°/740 mm., and solidifies in colourless, transparent needles, m. p. 30°.

1-Chloro-4-methylantracene forms a *picrate*, crystallising in dark red needles, m. p. 118°, and combines with bromine in carbon disulphide solution, yielding 1-chloro-9:10-dibromoanthracene, pale green prisms (decomp. 139°). On treatment with hydrogen iodide in glacial acetic acid solution, it is reduced to 1-chloro-4-methyl-9:10-dihydroanthracene, which crystallises in long, white needles, m. p. 47—48°, gives blue fluorescent solutions, and dissolves in strong sulphuric acid with a reddish-yellow coloration.

1-Chloro-4-methylantranol, prepared by passing hydrogen iodide into a boiling solution of 1-chloro-4-methylantraquinone in glacial acetic acid solution, forms long, light yellow needles, m. p. 145—146°.

When gently warmed with strong nitric acid, 1-methoxy-4-methylantraquinone is converted into *nitro-1-hydroxy-4-methylantraquinone*,

$C_{15}H_9O_5N$ , which crystallises in lustrous, orange prisms, m. p.  $182^\circ$ , and dissolves in aqueous alkalis, yielding reddish-violet salts.

*Nitro-1-methylantraquinone*, prepared by nitrating 1-methylantraquinone with strong nitric acid, forms lustrous, light yellow needles, m. p.  $252^\circ$ , and is oxidised by dilute nitric acid at  $200^\circ$  to *nitroanthraquinone-4-carboxylic acid*, crystallising in stellar aggregates of brownish-yellow needles (decomp.  $270^\circ$ ).

1-Chloroanthraquinone is reduced by zinc dust and strong aqueous ammonia to 1-chloroanthracene. This forms white leaflets, m. p.  $79^\circ$ , yields a *picrate*, crystallising in red needles, m. p.  $101-102^\circ$ , and combines with bromine (1 mol.) in carbon disulphide solution to form an unstable *additive* compound, which rapidly loses hydrogen bromide, yielding 1-chloro-9(or 10)-bromoanthracene. The latter compound crystallises in long, slender, sulphur-yellow needles, m. p.  $143-144^\circ$ .

*Bis-1-methylanthrancene*, prepared by exposing a benzene solution of 1-methylanthrancene to direct sunlight for three to four days, crystallises in lustrous, colourless plates containing benzene, which is lost on exposing the crystals in air; it has m. p.  $246^\circ$ , and on distillation is reconverted into 1-methylanthrancene.

*Bis-1-chloroanthracene*, obtained in a similar manner, forms white, well-developed crystals of a rhombic habit, m. p.  $235^\circ$ .

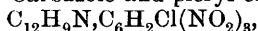
*Bis-1-chloro-4-methylanthrancene* separates in stout, white, efflorescent crystals, m. p.  $231^\circ$ , containing benzene.

*Bis-9-bromoanthracene* crystallises in clusters of greenish-yellow needles, m. p.  $274^\circ$ .

*Bis-1-chloro-9(or 10)-bromoanthracene* forms stout, white prisms, m. p.  $220^\circ$ . F. B.

**Additive Products of Trinitrobenzene: Derivatives with Certain Aromatic Nitrogen Compounds.** ROBERTO CIUSA and L. VECCHIOTTI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 161—166).—The following *additive* compounds have been obtained by interaction of the components, either alone or in boiling alcoholic solution:

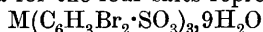
2-Methylindole and *s*-trinitrobenzene,  $C_9H_9N, C_6H_3(NO_2)_3$ , red needles, m. p.  $152^\circ$  (compare Sudborough and Beard, *Trans.*, 1910, 97, 773). 2-Methylindole and trinitrotoluene,  $C_9H_9N, C_6H_2Me(NO_2)_3$ , yellow needles, m. p.  $110^\circ$ . 2-Methylindole and trinitroaniline, brick-red needles showing metallic lustre, m. p.  $166^\circ$ . 2-Methylindole and picryl chloride,  $C_9H_9N, C_6H_2Cl(NO_2)_3$ , red needles, m. p.  $115^\circ$ . 3-Methylindole and picryl chloride, red needles, m. p.  $120^\circ$  (compare Ciusa and Agostinelli, *Abstr.*, 1907, i, 553). 2:3-Dimethylindole and *s*-trinitrobenzene,  $C_{10}H_{11}N, C_6H_3(NO_2)_3$ , red needles, m. p.  $175^\circ$ . 2:3-Dimethylindole and trinitrotoluene,  $C_{10}H_{11}N, C_6H_2Me(NO_2)_3$ , red needles, m. p.  $118^\circ$ . 2:3-Dimethylindole and picryl chloride,  $C_{10}H_{11}N, C_6H_2Cl(NO_2)_3$ , dark red needles, m. p.  $140^\circ$ . Tetrahydrocarbazole and picryl chloride, chocolate-brown needles, m. p.  $121^\circ$ . Carbazole and trinitrotoluene give two compounds: (1)  $2C_{12}H_9N, 3C_6H_2Me(NO_2)_3$ , yellow needles, m. p.  $160^\circ$ , and (2)  $C_{12}H_9N, C_6H_2Me(NO_2)_3$ , dark yellow needles, melting at  $140-200^\circ$ . Carbazole and picryl chloride,



dark red crystals softening at  $140^{\circ}$ , m. p.  $155^{\circ}$ . Phenylindole and trinitrotoluene,  $2C_{14}H_{11}N, 3C_6H_3Me(NO_2)_3$ , yellow needles, m. p.  $97^{\circ}$ . Phenylindole and picryl chloride,  $C_{14}H_{11}N, C_6H_2Cl(NO_2)_3$ , carmine-red needles, m. p.  $119^{\circ}$ . T. H. P.

**Morphological Studies of Benzene Derivatives. III.** *p*-Dibromobenzenesulphonates (Isomorphous) of the "Rare Earth" Elements—a means of Determining the Directions of Valency in Tervalent Elements. HENRY E. ARMSTRONG and ERNEST H. RODD (*Proc. Roy. Soc.*, 1912, A, 87, 204—217. Compare *Trans.*, 1910, 97, 1578; Colgate and Rodd, *ibid.*, 1585).—Lanthanum, neodymium, praseodymium, and cerium form *p*-dibromobenzenesulphonates, which crystallise from water at the ordinary temperature with 18 molecules of water. The crystals are monoclinic, and the four salts appear to be isomorphous. At about  $35^{\circ}$  they are converted into salts containing 9 molecules of water, which crystallise in well-formed rhombic prisms. In the case of samarium, the higher hydrate only has been obtained, but this also appears to be isomorphous with the corresponding salts of the other four metals. The gadolinium salt crystallises with 12 and 7 molecules of water. Both hydrates crystallise out from solution at  $37^{\circ}$ , but at  $50^{\circ}$  the lower hydrate only is obtained. These observations indicate that, as the atomic weight of the metal increases, peculiarities are exhibited which are not evident in the case of the lower members of the series.

Crystallographic data for the four salts represented by



are recorded, and these show that the salts are closely isomorphous, the approximation of the neodymium, praseodymium, and lanthanum salts being much closer than that ordinarily observed between members of an orthorhombic isomorphous series. The pseudotrigonal character of the salts indicates that the crystal structure is derived from the benzene structure of cubic origin typified by *p*-di-iodobenzene, and by reference to the values of the axial ratios, it is shown that the relationships required by theory are satisfied in a quantitative manner. This quantitative correspondence between the crystal structure of *p*-di-iodobenzene and the rare earth salts described affords strong evidence of the correlation of crystalline form with chemical composition and constitution.

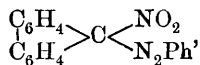
The agreement in question shows, further, that the valency directions of the trivalent elements of the rare earth series are symmetrically disposed, the metal occupying the central position in a plane containing three benzene groups. A new method is thus indicated by means of which, the directions in which valency acts, may be determined.

H. M. D.

**Preparation of  $\omega$ -2-Dinitrotoluene, its Homologues and Derivatives.** SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (D.R.-P. 246381. Compare this vol., i, 176).—When *o*-nitrotoluene (2000 parts) is heated at  $130$ — $140^{\circ}$  during three hours with the vapour of nitric acid (1000 parts) it yields 400—500 parts of  $\omega$ -2-dinitrotoluene.

F. M. G. M.

**Migration of the Nitro-group.** GIACOMO PONZIO (*Gazzetta*, 1912, 42, ii, 55—57).—When treated with benzenediazonium chloride, 9-nitrofluorene, which is capable of giving salts corresponding with the formula:  $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{C}:\text{NO}_2\text{H}$ , yields an unstable product,



which undergoes intramolecular rearrangement with formation of fluorenone-*p*-nitrophenylhydrazone,  $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{smallmatrix} > \text{C}:\text{N}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ . This behaviour of 9-nitrofluorene is similar to that previously observed with  $\omega$ -dinitrotoluene,  $\omega$ -nitrophenylacetonitrile, and  $\omega$ -nitrodiphenylmethane (Abstr., 1910, i, 192, 194; this vol., i, 547). T. H. P.

**Preparation of Four Dicyclohexylpropanes.** PAUL SABATIER and MARCEL MURAT (*Compt. rend.*, 1912, 155, 385—388. Compare this vol., i, 617).—The authors have applied their method of direct hydrogenation to the preparation of dicyclohexylpropanes.

$\alpha\gamma$ -Dicyclohexylpropane,  $D_0^0$  0.8874,  $D_0^{21}$  0.8701,  $n_D$  1.475, b. p. 289—290° (corr.), was obtained by direct hydrogenation with nickel at 175° of dibenzyl ketone, the latter being prepared by catalysis of phenylacetic acid over thoria at 400° (compare Frézouls, this vol., i, 629).

$\alpha\beta$ -Dicyclohexylpropane,  $D_0^0$  0.8891,  $D_0^{21}$  0.8725,  $n_D$  1.479, b. p. 272—273° (corr.), was prepared from phenylbenzylmethylcarbinol, b. p. 289—292°, as a starting point, by dehydrating this over thoria at 300°, and reducing the  $\alpha\beta$ -diphenylpropylene thus formed (Klages, Abstr., 1902, i, 668) to  $\alpha\beta$ -diphenylpropane,  $D^{23}$  0.9745,  $n_D$  1.455, b. p. 280—282° (corr.), and this in turn to the substance required.

Diphenylethylcarbinol,  $\text{HO}\cdot\text{CPh}_2\cdot\text{Et}$ , m. p. 95° (Masson, Abstr., 1903, i, 28), on distillation yields (1) *aa*-diphenyl- $\Delta^a$ -propylene,  $D^{23}$  1.0076,  $n_D$  1.593, m. p. 51.5°, b. p. 284.5° (corr.), which separates from alcohol in pearly leaflets, and (2) a small amount of *aa*-diphenyl- $\Delta^b$ -propylene,  $D^{24}$  1.0038,  $n_D$  1.587, b. p. 279—281° (corr.), which is liquid. These two isomerides on direct hydrogenation over partly spent nickel yield the same *aa*-diphenylpropane,  $D_0^0$  0.9881,  $n_D$  1.569 (Klages and Heilmann, Abstr., 1904, i, 487). This on being passed twice over nickel at 175° is quantitatively converted into *aa*-dicyclohexylpropane,  $D_0^0$  0.9038,  $D_0^{23}$  0.8887,  $n_D$  1.485, b. p. 270—271° (corr.).

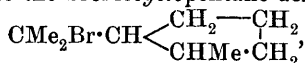
$\beta\beta$ -Diphenylpropane (Silva, Abstr., 1880, 259),  $D_0^{25}$  0.9958,  $n_D$  1.570, m. p. 29°, b. p. 282—283° (corr.), prepared by Friedel and Craft's method is reduced, with some decomposition, by nickel at 175°, yielding  $\beta\beta$ -dicyclohexylpropane,  $D_0^0$  0.9158,  $D_0^{23}$  0.9002,  $n_D$  1.490, b. p. 273—274° (corr.). T. A. H.

**Decomposition of Pyrazoline Bases as a means of Obtaining Derivatives of cycloPropane.** NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 849—865. Compare Abstr., 1911, i, 1028; this vol., i, 245).—The action of hydrazine on camphorone yields a pyrazoline base which, when distilled with alkali, decomposes into a bicyclic hydrocarbon,  $\text{C}_9\text{H}_{16}$ , containing a cyclopropane ring. These trans-

formations are completely analogous to those occurring with mesityl oxide and pulegone.

The *pyrazoline base*,  $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 - \text{CH} \cdot \text{CMe}_2 \\ \text{CHMe} \cdot \text{C} = \text{N} \end{smallmatrix} \text{NH}$ , has b. p. 119—120°/37 mm.,  $D_0^{20}$  0.9515,  $n_D$  1.4759, and is transformed into pulegenone when boiled with hydrochloric acid.

2:6:6-*Trimethyl-0:1:3-bicyclohexane*,  $\text{CMe}_2 \begin{smallmatrix} \text{CH} \cdot \text{CHMe} \\ \text{CH} - \text{CH}_2 \end{smallmatrix} \text{CH}_2$ , obtained by distilling the pyrazoline base with potassium hydroxide and platinised porcelain, has b. p. 140.5°/752 mm.,  $D_0^{18.5}$  0.8229,  $D_0^{20}$  0.8223,  $n_D^{18.5}$  1.4465, and resembles light petroleum in odour. When reduced by Sabatier and Senderens' method, it yields 1:1:3-trimethylcyclohexane. By the action of hydrogen bromide, this bicyclic hydrocarbon is converted into the bromocyclopentane derivative,



which loses the elements of hydrogen bromide in two ways: (1) the action of alcoholic potassium hydroxide gives 1-methyl-2-isopropylidene-

cyclopentane,  $\text{CMe}_2 \cdot \text{C} \begin{smallmatrix} \text{CH}_2 - \text{CH}_2 \\ \text{CHMe} \cdot \text{CH}_2 \end{smallmatrix}$ , b. p. 149—151°/755 mm.,  $D_0^{20}$

0.8104,  $n_D$  1.4518, which forms an orange coloration with sulphuric acid in acetic acid solution, yields a blue, oily nitrosochloride, and gives acetone and 1-methylcyclopentanone when oxidised with permanganate; (2) distillation with aniline yields, in addition to 1-methyl-2-iso-propylidenecyclopentane, 1-methyl-2-isopropenylcyclopentane,

$\text{CH}_2 \cdot \text{CMe} \cdot \text{CH} \begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix}$ , b. p. 141—143°/757 mm.,  $D_0^{20}$  0.8006,

$n_D$  1.4455. These two hydrocarbons are interconvertible, (1) into (2) partly by addition of hydrogen bromide and its removal by means of aniline, and (2) into (1) completely by addition of hydrogen bromide and treatment with alcoholic potassium hydroxide. Reduction of either hydrocarbon by Sabatier and Senderens' method yields

1-methyl-2-isopropylcyclopentane,  $\begin{smallmatrix} \text{CHMe} \cdot \text{CH}_2 \\ | \\ \text{CHPr}^{\beta} \cdot \text{CH}_2 \end{smallmatrix} \text{CH}_2$ , b. p. 142.5°/759 mm.,  $D_0^{15}$  0.7833,  $D_0^{20}$  0.7792,  $n_D^{20}$  1.4279.

The interaction of styryl methyl ketone and hydrazine gives 5-phenyl-3-methylpyrazoline,  $\begin{smallmatrix} \text{NH} \cdot \text{CHPh} \\ | \\ \text{N} = \text{CMe} \end{smallmatrix} \text{CH}_2$ , which is a colourless

liquid, b. p. 180°/32 mm.,  $D_0^{20}$  1.0669,  $n_D$  1.5956; its *hydrochloride*,  $\text{C}_{10}\text{H}_{12}\text{N}_2 \cdot \text{HCl}$ , was prepared. When heated with potassium hydroxide and platinised porcelain, the pyrazoline base is converted into 2-phenyl-

1-methylcyclopropane,  $\begin{smallmatrix} \text{CHMe} \\ | \\ \text{CHPh} \end{smallmatrix} \text{CH}_2$ , b. p. 186°/743 mm., 186.3°/747 mm., 186.5°/749 mm.,  $D_0^{20}$  0.9198,  $n_D$  1.5208. The action of

hydrobromic acid on this hydrocarbon gives  $\alpha$ -bromoisobutylbenzene,  $\text{C}_6\text{H}_5 \cdot \text{CHBr} \cdot \text{CHMe}_2$ , a colourless liquid, b. p. 135—137°/37 mm.,  $D_0^{20}$  1.2609,  $n_D$  1.5414, and this, when distilled with quinoline, yields isobutenylbenzene, the nitrosite of which has m. p. 122°.

T. H. P.

**Preparation of *p*-Nitroacetoacetanilide.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 246382).—*p*-Nitroacetoacetanilide, yellow leaflets, m. p. 124°, crystallising from water, is prepared by dissolving acetoacetanilide (177 grams) in 350 c.c. of concentrated sulphuric acid at 0°, slowly adding 250 grams of nitric acid, and meanwhile maintaining the temperature below 3°; on reduction it furnishes *p*-aminoacetoacetanilide. F. M. G. M.

**Decomposition of Diphenylnitrosoamine by Heat.** MARQUEYROL and D. FLORENTIN (*Bull. Soc. chim.*, 1912, [iv], 11, 804—805).—The authors confirm Wieland's observation (Abstr., 1911, i, 569) that diphenylnitrosoamine is decomposed by heat, giving a quantitative yield of nitric oxide. The decomposition takes place at 40° under reduced pressure, but soon slackens unless the nitric oxide is removed as it forms. Heating the nitrosoamine in an oil-bath at 180—190° is a convenient method of preparing nearly pure nitric oxide. T. A. H.

**Preparation of Organic Compounds containing Sulphur.** KNOELL & Co. (D.R.-P. 247186).—The compounds obtained by fusing organic substances with sulphur are (with the exception of diphenylamine derivatives) obtained in a more satisfactory manner if the operation is carried out in the presence of iodine.

The following compounds have been prepared (1) from equal parts of sulphur and phenanthraquinone at 240—260° with about 1% of iodine; (2) the same with anthraquinone; and (3) with quinzarin.

(4) From aminoanthraquinone (1 part), sulphur (3 parts) and 1% of iodine at 260°.

(5)  $\beta$ -Naphthylamine (286 parts), sulphur (64 parts), with 1—2% of iodine at 200° during two and a-half hours, furnished a quantitative yield of *thio*- $\beta\beta$ -dinaphthylamine, m. p. 236°.

(6)  $\alpha$ -Naphthylamine (143 parts), aniline (93 parts), sulphur (32 parts), with 1—2% of iodine at 200° yielded *thiophenyl*- $\alpha$ -naphthylamine, m. p. 137°, whilst (7)  $\beta$ -naphthol under the same conditions furnished *thiophenyl*- $\beta$ -naphthylamine, m. p. 176°. F. M. G. M.

**$\alpha$ -Phenyl-mono- and -di-benzylethylamines.** KNUT PARCK (*J. pr. Chem.*, 1912, [ii], 86, 284—288).— $\alpha$ -Phenyl-N-benzylethylamine,  $\text{CHMePh}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$ , obtained in the form of its *hydrochloride*, short prisms, m. p. 184°, by heating molecular proportions of  $\alpha$ -phenylethylamine and benzyl chloride on the water-bath, is a colourless liquid, b. p. 171°/15 mm.,  $D_{20}^{20}$  1.009, and forms a *nitrate*, lustrous, silky needles, m. p. 124°, a *hydrogen sulphate*,  $\text{C}_{15}\text{H}_{17}\text{N}\cdot\text{H}_2\text{SO}_4$ , m. p. 166°, and a *hydrogen oxalate*, crystallising in small plates, m. p. 193°; the *acetate* and *hydrogen racemate* are also mentioned.

It is accompanied by a small amount of  $\alpha$ -phenyl-N-dibenzylethylamine,  $\text{CHMePh}\cdot\text{N}(\text{C}_7\text{H}_7)_2$ , which forms long, slender needles, m. p. 58°, and yields a *hydrochloride*, crystallising in small plates, m. p. 196°.

The resolution of the monobenzyl compound into its optically active components has been accomplished by the crystallisation of its hydrogen *d*-tartrate from water.

The *hydrogen d-tartrate* of the *l*-base,  $C_{19}H_{23}O_6N \cdot 3H_2O$ , is the less soluble, and separates in long, efflorescent prisms, m. p.  $72^\circ$ , from which *l*- $\alpha$ -phenyl-*N*-benzylethylamine is obtained, having b. p.  $171^\circ/15$  mm., and  $[\alpha]_D^{20} - 39.7^\circ$ .

The optically active monobenzyl compounds are most readily prepared by heating the active  $\alpha$ -phenylethylamines with benzyl chloride, small amounts of the active  $\alpha$ -phenyldibenzylethylamines being produced simultaneously; thus *d*- $\alpha$ -phenylethylamine is converted into *d*- $\alpha$ -phenyl-*N*-benzylethylamine, which has  $[\alpha]_D^{20} + 39.9^\circ$ . The salts of the active monobenzyl compounds resemble those of the inactive base; the *hydrochloride* has m. p.  $177^\circ$ ; the *nitrate*, m. p.  $113^\circ$ . The *hydrogen d-tartrate* of the *d*-base crystallises with  $2H_2O$  in triangular plates, m. p.  $62^\circ$ .

*l*- $\alpha$ -Phenyl-*NN*-dibenzylethylamine has  $[\alpha]_D^{20} - 97.7^\circ$  in alcoholic solution; the *d*-isomeride,  $[\alpha]_D^{20} + 99.3^\circ$ ; both forms have m. p.  $74^\circ$ , and yield *hydrochlorides*, m. p.  $197^\circ$ .  
F. B.

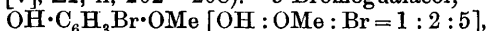
**Action of Tribromophenol and *p*-Bromophenol on Toluene in the Presence of Aluminium Chloride.** MORITZ KOHN and FRIEDRICH BUM (*Monatsh.*, 1912, 32, 923—928).—It has already been shown (Kohn and Müller, *Abstr.*, 1909, i, 567) that in the action of tribromophenol on benzene in the presence of aluminium chloride a transference of bromine occurs from the tribromophenol to the hydrocarbon producing phenol and bromobenzene.

The interaction of tribromophenol, toluene, and aluminium chloride on the water-bath produces phenol and *m*-bromotoluene, the identity of which was proved by oxidation to *m*-bromobenzoic acid. At higher temperatures ( $130$ — $140^\circ$ ) a fair amount of phenol is still obtained, but the yield of bromotoluene is meagre, much resinous matter being formed.

If in the above reaction the tribromophenol is replaced by *p*-bromophenol, *m*-bromotoluene and phenol are obtained.  
D. F. T.

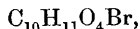
**Preparation of Neutral Phosphoric Acid Esters of Phenols and Naphthols with Their Homologues and Derivatives.** ACTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 246871. Compare *Abstr.*, 1883, 1108; 1894, i, 578).—The neutral esters of phosphoric acid can be obtained in quantitative yield when anhydrous alkali phenoxides or naphthoxides are treated with phosphoryl chloride in the presence of an indifferent anhydrous solvent. The following compounds are described: the tri-*o*-tolyl ester; the tri- $\alpha$ -naphthyl ester, m. p.  $148$ — $149^\circ$  (Autenrieth, *Abstr.*, 1898, i, 14, gives  $145^\circ$ ); the triphenyl ester; the tri-*p*-chlorophenyl ester, m. p.  $112^\circ$  (*loc. cit.*, gives  $99$ — $100^\circ$ ), and the tri-1-chloro-2-naphthyl ester.  
F. M. G. M.

**Bromo- and Chloro-guaiacols.** TEMISTOCLE JONA (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 202—208).—5-Bromoguaiacol,



obtained from 5-aminoguaiacol (Jona and Pozzi, *Abstr.*, 1911, i, 854), forms white crystals, m. p.  $62$ — $65^\circ$ , and gives a bluish-green coloration with ferric chloride. 5-Bromo-1-benzoylguaiacol,  $C_{14}H_{11}O_3Br$ , forms

white needles, m. p. 73—75°. 5-Bromo-1-acetylguaiacol,  $C_9H_9O_3Br$ , separates in white leaflets, m. p. 63—65°. 5-Bromoguaiacol ethyl ether,  $C_9H_{11}O_2Br$ , crystallises in slender, white needles, m. p. 58—60·5°. 5-Bromoveratrole,  $C_8H_9O_2Br$ , forms a straw-yellow liquid, heavier than water, b. p. 239—242°/55 mm. 5-Bromo-1-ethylcarbonatoguaiacol,



crystallises in slender, silky needles, m. p. 46—49°. *o*-Nitrovanillic acid, identical with that obtained by Tiemann and Matsmoto (Abstr., 1876, ii, 524), may be prepared, along with several other products not yet investigated, by oxidising *o*-nitrovanillin (compare Pschorr and Sumuleanu, Abstr., 1900, i, 178). 3-Aminoguaiacol,  $C_7H_9O_2N$ , obtained by reducing *o*-nitrovanillic acid, forms straw-yellow needles, m. p. 97—100°, and 3-acetaminoguaiacol,  $C_9H_{11}O_3N$ , white crystals, m. p. 120—122°. 3-Chloroguaiacol,  $C_7H_7O_2Cl$ , forms white leaflets, m. p. 31·5—33°, and, in aqueous alcoholic solution, gives a greenish coloration with ferric chloride. 3-Chloro-1-benzoylguaiacol,  $C_{14}H_{11}O_3Cl$ , forms white needles, m. p. 36·5—38°, whilst 3-chloro-1-acetylguaiacol,  $C_9H_9O_3Cl$ , is a colourless liquid, b. p. 179—181°/55 mm. (corr.). 3-Chloroguaiacol ethyl ether,  $C_9H_{11}O_2Cl$ , is a colourless liquid, b. p. 162—165°/55 mm. (corr.).

T. H. P.

**Aceteins of Phenol.** ETTORE VASSALLO (*Gazzetta*, 1912, 42, ii, 237—243).—Condensation of phenol with acetic anhydride in presence of sulphuric acid yields a product different from that obtained by Rasinski (Abstr., 1882, 1288) in presence of zinc chloride, namely, *diphenoxymethylcarbinol*,  $OH \cdot CMe(OPh)_2$ , which forms a red, flocculent precipitate, m. p. about 228—232°. The same compound is obtained, but in diminished yield, when acetic acid is used in place of the anhydride. It acts as an indicator and yields the *acetyl* derivative,  $C_{14}H_{15}O_3 \cdot OAc$ , m. p. about 133°.

The mechanism of the action of acetic anhydride on phenol is quite comparable with that of phthalic anhydride (compare Oddo and Vassallo, this vol., i, 792). The only difference is that, with open-chain anhydrides, the acid generated separates and the carbinol function of the molecule is preserved, whilst with cyclic anhydrides the carboxyl and hydroxyl, becoming united to the same molecule at a favourable distance apart, react to form a closed lactonic ring.

T. H. P.

**Di-*p*-hydroxydiphenylisopentane.** A. IVANOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 907—909).—*Di-p-hydroxydiphenylisopentane*,  $CHMe_2 \cdot CH_2 \cdot CH(C_6H_4 \cdot OH)_2$ , prepared by the condensation of phenol with isovaleraldehyde (compare Lunjak, Abstr., 1908, i, 416) in presence of a small proportion of hydrochloric acid, crystallises in needles, m. p. 154°. The *dibenzoyl* derivative,  $C_{21}H_{28}O_4$ , m. p. 146°, and the *dimethyl* ether,  $C_{19}H_{24}O_2$ , b. p. 230—230·5°/11 mm.,  $D_4^{20}$  1·0629,  $D_4^{20}$  1·0506,  $D_4^{20}$  1·0627,  $D_4^{20}$  1·0487, were prepared; oxidation of the latter compound by means of chromium trioxide yields the *dimethyl* ether of di-*p*-hydroxybenzophenone and anisic acid.

T. H. P.

**Two Forms of Decahydro- $\beta$ -naphthol: Peculiar Case of Stereoisomerism.** LUIGI MASCARELLI and GIACOMO RECUSANI (*Gazzetta*, 1912, 42, ii, 35—41).—For decahydro- $\beta$ -naphthol, Leroux

(Abstr., 1905, i, 278) gave m. p.  $75^{\circ}$  and b. p.  $238^{\circ}$ , whilst Ipatieff (*Ber.*, 1907, 40, 1281) gave m. p.  $99-100^{\circ}$  and b. p.  $242-244^{\circ}$ .

On purifying a specimen of the compound supplied to them by Ipatieff, the authors found it to consist of a mixture of the two forms, which possess similar properties and are evidently the racemic modifications corresponding with two pairs of optical isomerides. The complete hydrogenation of  $\beta$ -naphthol renders the carbon atoms in the 2-, 9-, and 10-positions asymmetric, and as the last two of these form part of two different nuclei, theory would indicate the possible existence of two pairs of enantiomorphous compounds (compare Piccinini, Abstr., 1900, i, 249; Aschan, Abstr., 1901, i, 477, and Skraup, Abstr., 1903, ii, 67). T. H. P.

**Phenyldeoxyn of Dextrose.** ALEXANDER M. NASTUKOFF and I. I. KOTUKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1152—1163. Compare Abstr., 1907, i, 413).—Oxidation of the  $\beta$ -phenyldeoxyn of dextrose in glacial acetic acid solution by means of nitric acid yields 50% of a bright yellow, insoluble nitro-product, which was not examined further, together with *o*-nitrobenzoic and 3:5- and 2:4-dinitrobenzoic acids.

When reduced with zinc and acetic acid, the  $\beta$ -phenyldeoxyn yields a product which agrees in elementary composition and chemical properties with the original compound, but is of a purer yellow colour and contains no sulphur. In order to distinguish this product from the sulphur-free  $\beta$ -phenyldeoxyn (Abstr., 1907, i, 413), the authors term it simply desoxyn.

Two formulæ are suggested for desoxyn: (1)  $C_6H_7O_2Ph_3$ , representing the anhydride of dextrose, in which three hydroxyl groups are replaced by phenyl groups; this is termed the "hydroxylic"

formula. (2)  $C_6H_6O_2Ph_2$  or  $\cdot CPh_2 \cdot \overset{O}{\triangle} CH \cdot CH \cdot CH \cdot \overset{O}{\triangle} CH \cdot CH_2 \cdot$ ,

according to which the formation of desoxyn would be represented by the equation:  $C_6H_{10}O_5 + 2C_6H_6 - 3H_2O = C_{18}H_{16}O_2$ ; this formula is termed the "ketonic." The results of analysis of phenyldeoxyn and also the proportion of benzoic acid formed on oxidation with permanganate indicate the ketonic formula to be the more probable. Determinations of the molecular weight of phenyldeoxyn in freezing phenol and in boiling chloroform give unsatisfactory results, the values obtained varying almost proportionally with the concentration.

The principal soluble product formed simultaneously with phenyldeoxyn is found to be benzenesulphonic acid.

When phenyldeoxyn is subjected to prolonged shaking with concentrated sulphuric acid, it is converted into a product soluble in water. This is termed sulphodesoxylic acid of dextrose, and its formula is either  $(C_6H_7O_2)_2(C_6H_5)_3(C_6H_4 \cdot SO_3H)_3$  or  $(C_6H_5 \cdot C_6H_6O_2 \cdot C_6H_4 \cdot SO_3H)_3$ ,

the latter appearing to be the more probable.

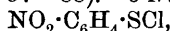
T. H. P.

**Sulphur Aryl Chlorides [Aryl Chlorothiols].** THEODOR ZINCKE (*Annalen*, 1912, 391, 55—56).—The term sulphur aryl chloride is

used by the author to denote substances of the type  $\text{ArSCl}$  [aryl chlorothiols]. Such are produced by the action of chlorine on aromatic mercaptans or their disulphides. They are also obtained by the chlorination of aryl benzyl sulphides, the benzyl group being eliminated in the form of benzylidene chloride.

The corresponding hydroxides,  $\text{ArS}\cdot\text{OH}$ , have not been obtained, but anhydrides,  $\text{ArS}\cdot\text{O}\cdot\text{SAr}$ , and esters,  $\text{ArS}\cdot\text{OR}$ , have been prepared.  
C. S.

**Sulphur *o*-Nitrophenyl Chloride [*o*-Nitrochlorothiolbenzene] and its Transformation Products.** THEODOR ZINCKE and FR. FARR (*Annalen*, 1912, 391, 57—88).—*o*-Nitrochlorothiolbenzene,



m. p.  $75^\circ$ , yellow needles, is readily obtained in more than 90% yield by repeatedly saturating a suspension of finely divided *oo*'-dinitrodiphenyl disulphide in carbon tetrachloride with chlorine in the absence of moisture, until the disulphide has disappeared. The substance is stable and extremely reactive, behaving like an acid chloride in some cases, and like a diazo-compound towards phenols and some aromatic amines. In hot glacial acetic acid, it is converted by nitric acid (D 1.4) into a mixture of *o*-nitrobenzenesulphonic acid and its chloride. Methyl or ethyl alcohol in the cold converts the substance into *oo*'-dinitrodiphenyl disulphide and *oo*'-dinitrodiphenyl disulphoxide, and at the b. p. into the disulphide and the sulphinic acid. When boiled with dilute methyl alcohol, *o*-nitrochlorothiolbenzene undergoes complicated changes, and yields the disulphide, the sulphinic acid, *o*-nitrobenzenesulphonic acid, and aniline-*o*-sulphonic acid. In glacial acetic acid, *o*-nitrochlorothiolbenzene is converted into *o*-nitrophenyl thiocyanate by potassium cyanide.

*o*-Nitrobromothiolbenzene,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SBr}$ , m. p.  $85^\circ$ , obtained in a similar manner as the chloro-derivative, forms long, golden needles.

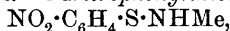
*o*-Nitrothiophenyl oxide,  $\text{O}(\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ , prepared by shaking *o*-nitrochlorothiolbenzene with water for several hours, crystallises in yellow plates, blackens at  $92$ — $93^\circ$ , and explodes; in a capillary tube, explosion does not occur, the blackening at  $92$ — $93^\circ$  being followed by fusion above  $180^\circ$ . The oxide is reconverted into *o*-nitrochlorothiolbenzene by concentrated hydrochloric acid or phosphorus pentachloride. It dissolves in alkalis or aqueous ammonia with a deep blue colour (probably due to a salt of the hydroxide,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{OH}$ ); the colour soon disappears, and the disulphide and the sulphinic acid are obtained.

Esters of *o*-nitrophenylsulphinous acid,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{OR}$ , are obtained by treating a cold alcoholic or ethereal solution of *o*-nitrochlorothiolbenzene with the sodium alkylxide. They are reconverted into the chloride by concentrated hydrochloric acid, and are decomposed by alkalis, yielding the disulphide and the disulphoxide. The *methyl* ester, m. p.  $54^\circ$ , yellow plates or needles; *ethyl* ester, m. p.  $26^\circ$ , yellow needles, and *phenyl* ester, m. p.  $72^\circ$ , yellow plates or needles, are described.

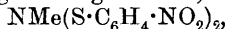
*oo*'-Dinitrodiphenyl disulphoxide,  $\text{O}_2\text{S}_2(\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$ , m. p.  $142$ — $143^\circ$ , colourless leaflets, is obtained, together with the disulphide, by decom-

posing *o*-nitrochlorothiolbenzene by methyl or ethyl alcohol, alkalis, potassium or sodium acetate, or moist silver oxide. *o*-Nitrophenyl-sulphinic acid,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2\text{H}$ , m. p.  $124^\circ$  (methyl ester, m. p.  $106^\circ$ ; ethyl ester, m. p.  $107^\circ$ ), is described.

In ethereal solution, *o*-nitrochlorothiolbenzene behaves like an acid chloride towards ammonia, methylamine, dimethylamine, aniline, and *p*-toluidine, yielding substances called *thiolamines*. *o*-Nitrophenylthiolamine,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{NH}_2$ , m. p.  $124$ — $125^\circ$  (decomp.), yellow needles, behaves in many ways like a primary aromatic amine. It cannot be diazotised, but forms an *acetyl* compound, yellow crystals, m. p.  $179^\circ$ , blackening at  $173$ — $175^\circ$ , *benzylidene* derivative, m. p.  $159^\circ$ , yellow needles, and *isopropylidene* derivative,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{N} : \text{CMe}_2$ , yellow needles, m. p.  $86^\circ$ , stable to alkalis; it yields the disulphide and ammonium iodide when heated with methyl iodide, is reconverted into *o*-nitrochlorothiolbenzene by concentrated hydrochloric acid, and is converted by boiling dilute hydrochloric or acetic acid into *oo'*-dinitrodiphenyldithiolimine,  $\text{NH}(\text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$ , m. p.  $217^\circ$  (decomp.), citron-yellow powder or needles. *o*-Nitrophenylthiolmethylamine,

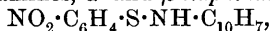


m. p.  $36^\circ$ , forms yellow, glistening needles; the *methylimine*,

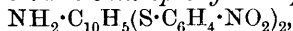


yellow crystals, has m. p.  $204$ — $205^\circ$  (decomp.). *o*-Nitrophenylthiol-dimethylamine,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{NMe}_2$ , m. p.  $63^\circ$ , forms yellow leaflets or needles. Corresponding compounds,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{NHPh}$ , m. p.  $94^\circ$ , red crystals, and  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{NH} \cdot \text{C}_7\text{H}_7$ , m. p.  $133^\circ$ , yellow leaflets or needles, obtained from aniline and *p*-toluidine respectively, are described.

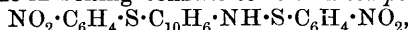
Towards  $\alpha$ - and  $\beta$ -naphthylamines, however, *o*-nitrochlorothiolbenzene behaves like a diazo-chloride, substitution occurring in the naphthalene nucleus. In cold chloroform or ether the reactions are similar to those of the preceding amines,  $\alpha$ - and  $\beta$ -naphthalides,



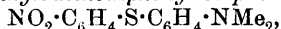
m. p.  $129^\circ$  and  $188^\circ$  respectively, being formed; in boiling acetic acid, however, *o*-nitrochlorothiolbenzene reacts with  $\alpha$ -naphthylamine to form 1-aminonaphthyl 2 : 4-di-*o*-nitrophenyl disulphide,



m. p.  $194^\circ$ , brownish-red, crystalline powder (*acetyl* compound, m. p.  $214$ — $215^\circ$ ), and with  $\beta$ -naphthylamine to form 2-aminonaphthyl 1-*o*-nitrophenyl sulphide,  $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$ , m. p.  $183$ — $184^\circ$  (*acetyl* derivative, m. p.  $183$ — $184^\circ$ ). The *hydrochlorides* of these two substances can be diazotised, and coupled with  $\beta$ -naphthol to form red dyes. The preceding  $\beta$ -naphthylamine derivative reacts with *o*-nitrochlorothiolbenzene in boiling benzene to form a compound,



m. p.  $186$ — $187^\circ$ , yellow, crystalline powder, which is easily decomposed into its generators by glacial acetic and concentrated hydrochloric acids. *o*-Nitro-*p'*-dimethylaminodiphenyl sulphide,



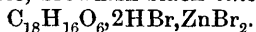
m. p.  $187$ — $188^\circ$ , dark red needles, prepared from *o*-nitrochlorothiolbenzene and dimethylaniline in boiling ether, has basic properties; the *hydrochloride* forms canary-yellow needles.

An ethereal solution of *o*-nitrochlorothiobenzene reacts like a diazo-chloride towards phenols; the hydroxyl group is unattacked, and substitution occurs in the nucleus; thus phenol yields *o*-nitro-*p*'-hydroxy-diphenyl sulphide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , m. p. 130—131°, yellow crystals (*potassium* salt, reddish-brown needles; *acetyl* derivative, m. p. 81—82°, yellow needles);  $\alpha$ -naphthol yields *o*-nitrophenyl-1-hydroxy-naphthyl sulphide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$ , m. p. 186°, brick-red crystals (*potassium* salt, reddish-brown leaflets; *acetyl* derivative, m. p. 125—126°, yellow needles);  $\beta$ -naphthol yields *o*-nitrophenyl-2-hydroxy-naphthyl sulphide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$ , m. p. 179—180°, yellow needles (*potassium* salt, reddish-brown leaflets; *acetyl* derivative, m. p. 101°, citron-yellow needles); resorcinol yields *o*-nitro-*o*'*p*'-dihydroxy-diphenyl sulphide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{C}_6\text{H}_3(\text{OH})_2$ , m. p. 150—151°, yellow crystals (*acetyl* derivative, m. p. 102—103°, yellow plates). *o*-Nitrophenyl acetonyl sulphide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{COMe}$ , m. p. 81°, obtained from *o*-nitrochlorothiobenzene and boiling acetone, crystallises in yellow needles or leaflets, and is not decomposed by concentrated hydrochloric or sulphuric acid. C. S.

**Oxonium Salts of Some Hydroxyanthraquinone Ethers.**  
 OTTO FISCHER and HUGO ZIEGLER (*J. pr. Chem.*, 1912, [ii], 86, 297—305. Compare *Abstr.*, 1911, i, 887).—1 : 2 : 5-Trimethoxyanthraquinone, prepared by heating the potassium salt of hydroxyanthrarufin with methyl sulphate at 140°, crystallises in golden-yellow leaflets, m. p. 203—204°. On treatment with hydrogen bromide in benzene solution, it yields an unstable, bluish-green *hydrobromide*; the *zincibromide*,  $\text{C}_{17}\text{H}_{14}\text{O}_5 \cdot \text{HBr} \cdot \text{ZnBr}_2$ , is obtained as a reddish-violet precipitate by passing hydrogen bromide into a suspension of the trimethyl ether in benzene to which a small amount of a saturated solution of zinc bromide in ethyl acetate has been added.

1 : 2 : 8-Trimethoxyanthraquinone, obtained in a similar manner from hydroxychrysazin, crystallises in clusters of light yellow needles, m. p. 157°, and forms an unstable reddish-brown, crystalline *hydrobromide*.

1 : 4 : 5 : 8-Tetrahydroxyanthraquinone crystallises from boiling naphthalene in feather-like aggregates of bronze-coloured needles, and yields solutions having a fiery-red fluorescence; the *tetra-acetyl* derivative crystallises in light yellow needles (decomp. 250°). Its difficultly soluble, blue *potassium* salt yields, with methyl sulphate, 1 : 4 : 5 : 8-tetramethoxyanthraquinone, which crystallises in lustrous, orange leaflets, m. p. 317°, and forms a very unstable, bluish-green *hydrobromide* and a more stable, brownish-black *zincibromide*,



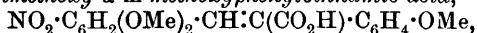
[With HANS GROSS.]—When heated with methyl sulphate at 180—190°, the potassium salt of anthrachrysone (1 : 3 : 5 : 7-tetrahydroxyanthraquinone) yields a *dimethyl ether*,  $\text{C}_{16}\text{H}_{12}\text{O}_6$ , which crystallises from nitrobenzene in columns of a golden-bronze lustre, and forms a *disodium* salt, long, orange-red needles, and a *diacetyl* derivative, long, citron-yellow needles, m. p. 256°. It is accompanied by a small amount of 1 : 3 : 5 : 7-tetramethoxyanthraquinone, crystallising in golden-yellow, flat, lancet-shaped prisms, m. p. 294°. The last-

mentioned compound forms a *perchlorate*,  $C_{18}H_{16}O_6 \cdot HClO_4$ , which forms long, dark red needles, and, on account of its instability, could not be isolated in a pure condition; the unstable, dark red *hydro-bromide* and dark reddish-violet *zincbromide*,  $C_{18}H_{16}O_6 \cdot HBr \cdot Zn \cdot 2$ , are also described.

F. B.

**Synthesis of the 3:4:5-Trimethoxyphenanthrene** obtained from Morphenol. ROLAND PSCHORR (*Annalen*, 1912, 391, 40—55).—By proving the identity of 3:4:5-trimethoxyphenanthrene with the trimethyl ether obtained from morphenol, the author has confirmed Vongerichten's constitution of morphenol.

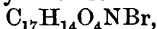
[With F. ZEIDLER and F. DICKHAUSER.]—*m*-Methoxybenzyl alcohol, b. p.  $252^\circ$ , obtained by the action of concentrated alcoholic potassium hydroxide on *m*-methoxybenzaldehyde, is converted by phosphorus trichloride into *m*-methoxybenzyl chloride, b. p.  $124^\circ/13$  mm.; the latter is converted through the nitrile into *m*-methoxyphenylacetic acid, m. p.  $67^\circ$ . This acid is obtained more conveniently by heating *m*-methoxybenzaldehyde, hippuric acid, and anhydrous sodium acetate with acetic anhydride; the resulting lactone of  $\alpha$ -benzoylamino-*m*-methoxycinnamic acid, m. p.  $108^\circ$ , is boiled with 10% sodium hydroxide, treated with 3% hydrogen peroxide, and acidified, whereby a mixture of *m*-methoxyphenylacetic and benzoic acids is obtained, which is separated by the fractional distillation of their esters under 14 mm. pressure. By condensing sodium *m*-methoxyphenylacetate and 2-nitro-3:4-dimethoxybenzaldehyde in acetic anhydride at  $100^\circ$  for three days, 2-nitro-3:4-dimethoxy- $\alpha$ -*m*-methoxyphenylcinnamic acid,



m. p.  $171^\circ$ , is obtained. The corresponding amino-acid, m. p.  $153^\circ$ , obtained by reduction with ferrous sulphate and aqueous ammonia at  $93^\circ$ , is converted by diazotisation and heating into a mixture of 3:4:5-trimethoxyphenanthrene-9-carboxylic acid, m. p.  $234\text{—}235^\circ$ , prisms, and 3:4:7-trimethoxyphenanthrene-9-carboxylic acid, m. p.  $214^\circ$ , long needles, which is separated mechanically. That the former is the chief product is interesting in connexion with the phenomenon of steric hindrance.

[With O. TREIDEL.]—The following compounds have been prepared by reactions similar to the preceding. *o*-Nitro- $\alpha$ -*o*-bromophenylcinnamic acid, obtained from sodium *o*-bromophenylacetate and *o*-nitrobenzaldehyde, has m. p.  $163^\circ$  (corr.). The corresponding amino-acid has m. p.  $205^\circ$ . 8-Bromophenanthrene-9-carboxylic acid, m. p.  $295^\circ$  (corr.), prisms (ethyl ester, m. p.  $93^\circ$ ), is converted by zinc dust and boiling sodium hydroxide into phenanthrene-9-carboxylic acid.

[With W. KOCH.]—When heated in acetic anhydride, hippuric acid, 6-bromo-3-methoxybenzaldehyde, and sodium acetate yield the lactone, m. p.  $175^\circ$ , yellow needles, of 6-bromo- $\alpha$ -benzoylamino-3-methoxycinnamic acid. The lactone yields the corresponding acid,



decomp.  $223^\circ$ , by warming with dilute sodium hydroxide and acidifying, but when boiled with 10% sodium hydroxide it is decomposed, yielding benzoic acid, 6-bromo-3-methoxyphenylpyruvic acid,

$\text{OMe} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CO}_2\text{H}$ , m. p. 159—160°, ammonia, and *p*-bromo-*m*-tolyl methyl ether, b. p. 108·5°/12 mm. By treating its alkaline solution with 1·5% hydrogen peroxide and acidifying, the substituted pyruvic acid yields 6-bromo-3-methoxyphenylacetic acid, m. p. 115°. Its sodium salt and 2-nitro-3:4-dimethoxybenzaldehyde, condensed in acetic anhydride, yield 2-nitro-3:4-dimethoxy- $\alpha$ -6-bromo-3-methoxyphenylcinnamic acid,

$\text{NO}_2 \cdot \text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{CH} : \text{C}(\text{CO}_2\text{H}) \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{OMe}$ ,  
decomp. 209—211°, which is purified through the ammonium salt. The corresponding amino-acid, m. p. 200°, yellow leaflets, yields 8-bromo-3:4:5-trimethoxyphenanthrene-9-carboxylic acid, m. p. 220°, by the usual method. 3:4:5-Trimethoxyphenanthrene-9-carboxylic acid, m. p. 234°, obtained by the prolonged boiling of an alkaline solution of the preceding acid with alcohol and copper-zinc dust, is heated with glacial acetic acid at 210—220° for forty hours, whereby 3:4:5-trimethoxyphenanthrene is obtained. Its picrate, m. p. 167°, brownish-red needles with violet reflex, is shown by direct comparison to be identical with a specimen obtained from morphenol. When heated at about 280°/15 mm., 3:4:5-trimethoxyphenanthrene-9-carboxylic acid is partly converted into methyl 3:4:5-trimethoxyphenanthrene-9-carboxylate, which is isolated as the picrate, m. p. 102°, brick-red needles.  
C. S.

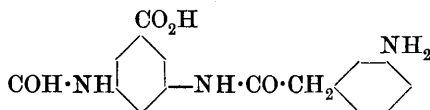
**Catalytic Preparation of Phenolic and Diphenylene Oxides; Mixed Oxides.** PAUL SABATIER and ALPHONSE MAILHE (*Compt. rend.*, 1912, 155, 260—262).—An extension of the study of the catalytic action of thorium oxide on phenols (compare Abstr., 1910, i, 294, 668, 669). By acting on a mixture of phenols, a mixed ether is obtained, together with a certain amount of each simple ether, and in some cases simple or mixed oxides of the type of diphenylene oxide. Mixtures of phenol with each of the three cresols furnish diphenyl ether and the respective tolyl ethers, together with the respective phenyl tolyl ethers, all of which have already been prepared by a different method by Ullmann and Sponagel (compare Abstr., 1907, i, 38). Phenol and  $\alpha$ -naphthol yield phenyl ether and phenyl  $\alpha$ -naphthyl ether (compare Ullmann and Sponagel, *loc. cit.*). Phenol and  $\beta$ -naphthol yield, in addition to phenyl ether, three distinct crystalline compounds, namely, phenyl  $\beta$ -naphthyl ether, m. p. 46° (compare Ullmann and Sponagel, *loc. cit.*),  $\beta\beta$ -dinaphthylene oxide, m. p. 157° (compare Walder, Abstr., 1883, 208), and phenylene- $\beta$ -naphthylene oxide,  $\begin{smallmatrix} \text{C}_6\text{H}_4 \\ \text{C}_{10}\text{H}_6 \end{smallmatrix} > \text{O}$ , m. p. 200°, dissolving in sulphuric acid to a red solution, which on warming becomes first colourless and then deep violet, changing to green on the addition of water. *p*-Cresol and  $\alpha$ -naphthol yield *p*-tolyl ether, *di-p*-tolylene oxide, m. p. 166°, and  $\alpha$ -naphthylene-*p*-tolylene oxide, m. p. 155°. *p*-Cresol and  $\beta$ -naphthol yield *p*-tolyl ether,  $\beta\beta$ -dinaphthylene oxide,  $\beta\beta$ -dinaphthyl ether, m. p. 105°, and  $\beta$ -naphthylene-*p*-tolylene oxide, m. p. 220°, which with sulphuric acid behaves similarly to phenylene  $\beta$ -naphthylene oxide.

W. G.

**Preparation of Acetonechloroform Acetylsalicylate** [*o*-Acetoxybenzoate]. RICHARD WOLFFENSTEIN (D.R.-P. 246383).—The preparation of acetonechloroform *o*-acetoxybenzoate has been previously described (this vol., i, 556); it is now found that the chlorides of other acylated *o*-hydroxybenzoic acids can be employed, and that the tertiary base (quinoline) can be replaced by calcium carbonate in this reaction.

F. M. G. M.

**[Preparation of Derivatives of 3-*m*-Aminophenylacetyl-5-formyldiaminobenzoic Acid.]** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 246668).—When 3-*m*-aminophenylacetyl-amino-5-formylaminobenzoic acid (annexed formula) is diazotised, coupled with



acetyl-*m*-phenylenediamine, and the *aminoazo*-compound thus obtained combined with carbonyl chloride, it furnishes a symmetrical derivative of

carbamide; from this compound the formyl group is eliminated and a *base* obtained, which on subsequent diazotisation and combination with phenylmethylpyrazolone (and other allied compounds) furnishes colouring matters.

A similar reaction with *m*-nitrobenzoyl-2:6-tolylenediamine-4-sulphonic acid and other nitro- and sulphonic derivatives is discussed in the original.

F. M. G. M.

**Action of Heat on *p*-Sulphamido-*o*-toluic Acid.** JOHN W. NOWELL (*Amer. Chem. J.*, 1912, 48, 223—241).—It is found that *p*-sulphamido-*o*-toluic acid, unlike *p*-sulphamidobenzoic acid, does not form any amidine compound on heating (compare Rouiller, this vol., i, 584; Nakaseko, i, 452); this is attributed to the effect of the methyl group in the ortho-position to the carboxyl.

*p*-Sulphamido-*o*-toluic acid,  $\text{NH}_2 \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO}_2\text{H}$ , was obtained from *o*-toluidine-*p*-sulphonic acid by the stages sulphotoluenitrile  $\rightarrow$  cyanotolylsulphonyl chloride,  $\text{SO}_2\text{Cl} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CN}$  (m. p. 52·5—53°)  $\rightarrow$  sulphamidotoluenitrile (m. p. 159—160°)  $\rightarrow$  sulphamidotoluic acid. The potassium, ammonium (m. p. 169—172°), ammonium hydrogen (m. p. 288—289°), and barium hydrogen salts were prepared. No trace of amidine compound was found after fusion of the free acid.

On treating the alcoholic solution of the potassium salt of *p*-sulpho-*o*-toluenitrile with hydrogen chloride, a solution of *p*-sulpho-*o*-toluamide,  $\text{SO}_3\text{H} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO} \cdot \text{NH}_2$ , prismatic crystals, m. p. 276—278°, was obtained, and the barium salt was prepared.

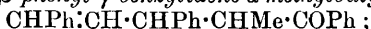
The Sandmeyer reaction applied to 2:6-dibromosulphanilic acid in the hope of obtaining 2:6-dibromosulphobenzonitrile produced an acidic substance, yellow needles; barium salt, plates.

By treating potassium hydrogen *o*-nitro-*p*-sulphobenzoate successively with phosphorus pentachloride and ammonium hydroxide, *p*-sulphamido-*o*-nitrobenzamide, needles, m. p. 226°, was obtained. This substance offers great resistance to hydrolysis.

D. F. T.

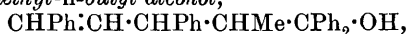
Reaction between Organo-magnesium Compounds and Cinnamylidene Esters. IV. Reactions with Methyl  $\alpha$ -Methylcinnamylideneacetate. MARIE REIMER and GRACE POTTER REYNOLDS (*Amer. Chem. J.*, 1912, 48, 206—223. Compare Reynolds, Abstr., 1911, i, 860; Reimer and Reynolds, Abstr., 1908, i, 988).— $\alpha$ -Cinnamylidenepropionic acid,  $\text{CHPh}:\text{CH}:\text{CH}:\text{CMe}:\text{CO}_2\text{H}$ , prepared by heating at  $160^\circ$  a mixture of cinnamaldehyde and propionyl chloride with excess of sodium propionate (compare Perkin, Trans., 1877, 406), was converted into its methyl ester, m. p.  $91^\circ$ .

The action of magnesium phenyl bromide on this ester produces a mixture of two ketones, which are probably the racemates of stereoisomeric forms of  $\beta$ -phenyl- $\gamma$ -benzylidene- $\alpha$ -methylbutyrophenone,

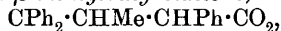


the form of lower m. p. ( $85^\circ$ ), colourless needles, is converted by the action of potassium hydroxide or hydrochloric acid on its alcoholic solution into the other isomeride, needles, m. p.  $112^\circ$ .

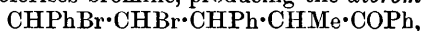
The isomeride of higher m. p. when again treated with magnesium phenyl bromide reacts readily, with formation of  $\alpha\gamma$ -triphenyl- $\delta$ -benzylidene- $\beta$ -methyl-*n*-butyl alcohol,



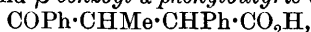
prisms, m. p.  $150^\circ$ , the structure of which is confirmed by oxidation with potassium permanganate in acetone solution to benzoic acid and  $\gamma$ -hydroxy- $\alpha\gamma$ -triphenyl- $\beta$ -methylbutyrolactone,



needles, m. p.  $187^\circ$ . The chloroform solution of the ketone also immediately decolorises bromine, producing the dibromide,



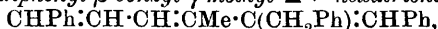
needles, m. p.  $180^\circ$  (decomp.), together with a small quantity of another substance (probably an isomeride), needles, m. p.  $115^\circ$ . The ketone is also oxidised by potassium permanganate in acetone solution, giving benzoic acid and  $\beta$ -benzoyl- $\alpha$ -phenylbutyric acid,



needles, m. p.  $131^\circ$ ; the methyl ester, plates, m. p.  $105^\circ$ , when prepared from the acid, was accompanied by a small quantity of a second ester, m. p.  $87^\circ$ .

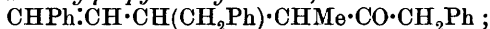
The readily isomerising form of phenylbenzylidenemethylbutyrophenone of low m. p. resists the action of magnesium phenyl bromide, but reacts with bromine, forming the same additive compound (m. p.  $180^\circ$ ) as its isomeride; the formation of the dibromide is probably preceded by the conversion of the ketone into the form of higher m. p. On oxidation it gives a *benzoylphenylbutyric acid* (needles, m. p.  $145^\circ$ ). As the methyl ester of this acid has m. p.  $105^\circ$ , it is suggested that the ester structurally derived from the isomeric acid above (from the ketone, m. p.  $112^\circ$ ) is that (m. p.  $87^\circ$ ) obtained in small quantity, and that the ester, m. p.  $105^\circ$ , was formed after previous isomerisation of the acid, m. p.  $131^\circ$ , into that of m. p.  $145^\circ$ .

Magnesium benzyl bromide converts methyl  $\alpha$ -methylcinnamylideneacetate into  $\alpha\zeta$ -diphenyl- $\beta$ -benzyl- $\gamma$ -methyl- $\Delta^{\alpha\gamma\epsilon}$ -hexatriene,



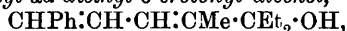
needles, m. p.  $117^\circ$ , which potassium permanganate oxidises into benzoic

and phenylacetic acids. The above product from the Grignard reaction is accompanied by a yellow oil, b. p.  $265^{\circ}/20$  mm., which is  $\beta$ -benzyl- $\gamma$ -benzylidene- $\alpha$ -methylpropyl benzyl ketone,



this is not affected by magnesium ethyl bromide, and although it reacts with bromine no solid product could be separated.

The action of magnesium ethyl bromide on methyl  $\alpha$ -methylcinnamylideneacetate gives a mixture of substances from which  $\delta$ -benzylidene- $\beta$ -methyl- $\alpha\alpha$ -diethyl- $\delta$ -crotonyl alcohol,



a mobile, yellow liquid, b. p.  $200^{\circ}/20$  mm., could be isolated after boiling with alcoholic potassium hydroxide. An ester, m. p.  $185^{\circ}$ , and an acid, m. p.  $207^{\circ}$ , also obtained after this treatment were probably not primary products of the Grignard reaction. D. F. T.

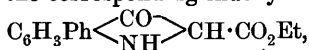
[Preparation of 4:6-Dichloro-*m*-tolylthiolacetic Acid and of 4-Chloro-3:6-dimethyl-1-phenylthiolacetic Acid.] KALLE & Co. (D.R.-P. 246265. Compare this vol., i, 557).—The conversion of  $\psi$ -cumylthiolacetic acid into a dye by the action of fuming sulphuric acid has previously been described; it is now found that if the methyl groups in this compound are replaced by chlorine, variations in colour are produced.

4:6-Dichloro-*m*-tolylthiolacetic acid and 4-chloro-3:6-dimethyl-phenylthiolacetic acid are readily prepared from the corresponding bases by diazotisation, xanthogenation, hydrolysis, and subsequent combination with chloroacetic acid; they form brownish-white powders, which may be crystallised from water. F. M. G. M.

Derivatives of Diphenyl. B. F. FORTINSKY (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 781—787).—The author describes preliminary attempts to prepare an indigotin derivative with a hydrogen atom of the benzene nucleus replaced by phenyl, the method employed by Blank (Abstr., 1898, i, 589) being applied to the aminodiphenyls as starting products.

*o*- and *p*-Aminodiphenyls have the same m. p.,  $49^{\circ}$ , the benzoyl derivatives melting respectively at  $88^{\circ}$  and  $229$ — $229.5^{\circ}$ .

Ethyl *p*-phenylanilinomalonate,  $\text{C}_6\text{H}_4\text{Ph}\cdot\text{NH}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , prepared by the interaction of *p*-aminodiphenyl (2 mols.) and ethyl bromomalonate (1 mol.), forms colourless, acicular crystals, m. p.  $59.5$ — $60^{\circ}$ . Attempts to prepare the corresponding indoxylic ester,



by heating this compound at  $200$ — $210^{\circ}$  did not give a pure product.

T. H. P.

Benzylpyruvic Acid. J. BOUGAULT (*Compt. rend.*, 1912, 155, 477—480).—Fittig's method for the preparation of this acid (Abstr., 1898, i, 196) has been improved by treating  $\alpha$ -hydroxy- $\gamma$ -phenylcrotonamide, instead of the corresponding acid, with alkalis. The products of condensation of the acid with itself and with acetone are described.

In the alkaline hydrolysis of the amide, benzylpyruvic acid is the chief product, but two other substances are formed. The first of these is a *monobasic acid*,  $C_{20}H_{17}O_3N$ , m. p.  $298^\circ$ , very soluble in chloroform, sparingly soluble in ether, and giving alkali salts soluble in hot water. The second is a *dibasic acid*,  $(C_{10}H_{10}O_3)_2 \cdot 1.5H_2O$ , which melts at  $100-105^\circ$ , is dehydrated to a transparent mass, and then re-melts at  $165^\circ$  (approx. decomp.). It is readily soluble in ether or alcohol, but insoluble in chloroform.

Benzylpyruvic acid in presence of cold sodium hydroxide solution undergoes aldol-condensation, forming the *dibasic acid*,

$CH_2Ph \cdot CH_2 \cdot C(CH_2Ph \cdot CH \cdot CO \cdot CO_2H)(OH) \cdot CO_2H$ ,  
m. p.  $168-169^\circ$  (decomp.), soluble in ether, but not in chloroform, and which is hydrolysed by boiling dilute sodium hydroxide solution to benzylpyruvic acid, and with boiling dilute acid forms the *lactone*,  
 $CH_2Ph \cdot CH_2 \cdot \overset{\text{O}}{\underset{\text{O}}{\text{C}}} \text{---} \text{CO}$ , m. p.  $118^\circ$ , very soluble in alcohol or ether, but insoluble in light petroleum.

Benzylpyruvic acid condenses with acetone to form two products. The *first*,  $CH_2Ph \cdot CH_2 \cdot C(CH_2 \cdot COMe)(OH) \cdot CO_2H \cdot H_2O$ , m. p.  $61^\circ$  or  $98^\circ$  (anhydrous), is hydrolysed by hot dilute alkalis to several products, including benzylpyruvic acid, and is dehydrated by hydrochloric acid, forming a new *acid*,  $C_{13}H_{14}O_3$ , m. p.  $95^\circ$ . The *second product*,

$CO_2H \cdot C(OH)(CH_2 \cdot CH_2Ph) \cdot CH_2 \cdot CO \cdot CH_2 \cdot C(OH)(CH_2 \cdot CH_2Ph) \cdot CO_2H$ ,  
m. p.  $178^\circ$ , is soluble in alcohol, but insoluble in chloroform, and yields with hydrochloric acid two dehydration products, the one,  $C_{23}H_{20}O_4$ , m. p.  $124^\circ$ , being neutral and probably an anhydride or a dilactone, and the other a dibasic acid, m. p.  $146^\circ$ , sparingly soluble in ether.

T. A. H.

**Esterification of Unsymmetrical Di- and Poly-basic Acids.**  
**XXVII. Acid Esters of Nitrohemipinic Acid.** RUDOLF WEGSCHEIDER and NOE L. MÜLLER (*Monatsh.*, 1912, **34**, 899—910. Compare this vol., i, 464).—It is now found that of the three supposed isomeric acid esters of nitrohemipinic acid, that of m. p.  $115-117^\circ$  is in reality an eutectic mixture of the other two (compare Wegscheider and von Rušnov, *Abstr.*, 1908, i, 793). This is proved by the possibility of extracting the 2-methyl ester compound (m. p.  $140-142^\circ$ ) from the compound of lower m. p. with water, and also by the fact that a mixture of this ester with the 1-methyl ester compound (m. p.  $147-149^\circ$ ) in the proportion 2:3 forms an eutectic mixture, m. p.  $115-116^\circ$ .

Nitrohemipinic acid, 1-methyl hydrogen nitrohemipinate, and 2-methyl hydrogen nitrohemipinate have electrical conductivities,  $K$  1.986 (for dissociation of the first hydrogen atom), 1.28, and 1.47 respectively. Calculation from the last two numbers as to the conductivity of such a mixture as that suspected in the compound of low m. p. gives a result in good agreement with the experimental.

In one experiment indications of a labile form (m. p.  $128^\circ$ ) of the 2-methyl ester were observed.

D. F. T.

### Induced Molecular Asymmetry in Unsaturated Compounds.

EMIL ERLÉNMYER and G. HILGENDORFF (*Biochem. Zeitsch.*, 1912, 43, 445—452).—By the reduction of optically active phenylbromolactic acid with zinc in the presence of alcohol, one molecule of active phenyl-lactic acid and one of inactive cinnamic acid are formed according to the equation:  $2\text{CHPh}(\text{OH})\cdot\text{CHBr}\cdot\text{CO}_2\text{H} + 2\text{H}_2 = \text{CHPh}\cdot\text{CH}\cdot\text{CO}_2\text{H} + \text{CHPh}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ . In spite of the fact that an inactive cinnamic acid is isolated, the alcoholic solution in which the reaction is carried out shows no diminution (in fact, a slight increase) in optical activity after the reduction. As explanation of this fact, it is assumed that the active phenyl-lactic acid can induce an optical activity in the cinnamic acid, which becomes, however, racemised during the subsequent process of isolation. In support of this explanation, it is shown that when equimolecular proportions of inactive storax cinnamic acid and active phenyl-lactic acid are warmed in alcoholic solution with zinc oxide or zinc bromide, the optical activity is doubled. If bromine is added to such an alcoholic mixture of the zinc salts, the cinnamic acid is converted into the dibromide, and it was found that if bromine is added to the mixture of the zinc salts of *d*-phenyl-lactic acid and cinnamic acid, obtained in the way described, a *l*-dibromocinnamic acid can be isolated. If the *l*-lactic acid is employed instead of the *d*-acid, a *d*-dibromocinnamic acid is obtained. The authors contend that the formation of bromo-derivatives of opposite optical activity to the lactic acids employed is consistent with their former results. S. B. S.

**Preparation of Amides, Carbamides, or Esters of Cinnamic Acids containing Iodine in the Side-chain, Their Homologues, and Substitution Products.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 246165).—When di-iodocinnamic acid (Abstr., 1891, 1483) is treated with phosphorus pentachloride in chloroform solution, it yields a crystalline *chloride*; this furnishes the corresponding *amide*, which crystallises from acetic acid and decomposes violently when heated to about 200°.

The *carbamide*, m. p. 185—186°, is prepared by heating the foregoing chloride with carbamide (2½ mols.) at 100°; if the carbamide is replaced by glycine ethyl ester, it furnishes a *compound*, needles, m. p. 149—150°.

When an acetic acid solution of ethyl phenylpropiolate (Trans., 1884, 45, 174) is treated with iodine (2 parts) at 70—80°, and stirred during twelve to fourteen hours, it yields a crystalline *ester*, m. p. 63°.

*Guaiacyl β-iodocinnamate*, yellow, prismatic crystals, m. p. 131°, is prepared by heating *β-iodocinnamyl chloride* (prepared from the corresponding acid, Abstr., 1902, i, 32) with guaiacol in carbon tetrachloride.

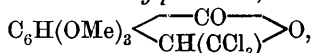
Phenylpropiolamide (Abstr., 1893, i, 163) when treated with iodine furnishes the corresponding *iodoamide* in the form of needles, whilst *ethyl p-nitrodi-iodocinnamate*, yellow, prismatic crystals, m. p. 89°, is prepared by shaking ethyl *p*-nitrophenylpropiolate (Abstr., 1882, 846) with an acetic acid solution of iodine during thirty hours at 80°.

F. M. G. M.

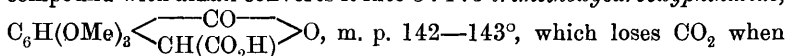
**Constitution of Certain Trimethoxyphthalic Acids.** GUIDO BARGELLINI and OLIMPIA MOLINA (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 146—150).—By the method described below the authors have prepared an acid which must undoubtedly be 3:4:5-trimethoxy-*o*-phthalic acid; this is identical in properties with the acid obtained by Windaus (Abstr., 1911, i, 904) by oxidising colchicine, and regarded by him as 3:4:6-trimethoxy-*o*-phthalic acid, owing to its non-identity with the supposed 3:4:5-trimethoxy-*o*-phthalic acid described by Feist (Abstr., 1908, i, 100); the last-named acid was obtained by etherifying Sennhofer and Brunner's pyrogalloldicarboxylic acid (Abstr., 1881, 267) by means of diazomethane. The conclusion must therefore be drawn that Windaus's acid is 3:4:5-trimethoxy-*o*-phthalic acid, and that the colchicine molecule contains three methoxy-groups arranged vicinally, and not in the 1:2:4-positions, as Windaus assumed.

It is evident, also, that Feist's acid cannot have the constitution attributed to it by this author, and Voswinkel and de Weerth (this vol., i, 472), on other grounds, regard it as 4:5:6-trimethoxy-*iso*-phthalic acid.

3:4:5-Trimethoxytrichloromethylphthalide,



obtained by the action of chloral on methyl trimethylgallate (methyl 3:4:5-trimethoxybenzoate) in presence of concentrated sulphuric acid (compare Fritsch, Abstr., 1898, i, 663), has m. p. 70—71°, and gives the normal molecular weight in freezing benzene. Treatment of this compound with alkali converts it into 3:4:5-trimethoxycarboxyphthalide,



heated, giving 3:4:5-trimethoxyphthalide,  $\text{C}_6\text{H}(\text{OMe})_3 \left\langle \begin{array}{c} \text{CO} \\ \text{CH}_2 \end{array} \right\rangle \text{O}$ , m. p. 134—135°. Oxidation of this by means of permanganate gives 3:4:5-trimethoxy-*o*-phthalic acid, m. p. 174°; the *anhydride* of this acid, m. p. 143°; the *imide*,  $\text{C}_6\text{H}(\text{OMe})_3 \left\langle \begin{array}{c} \text{CO} \\ \text{CO} \end{array} \right\rangle \text{NH}$ , m. p. 180°, giving a fluorescent alcoholic solution, and the anilide were prepared.

3:4:5-Trimethoxyphthalanilic acid,  $\text{C}_6\text{H}(\text{OMe})_3(\text{CO}\cdot\text{NHPh})\cdot\text{CO}_2\text{H}[(\text{OMe})_3\cdot\text{CO}\cdot\text{NHPh}\cdot\text{CO}_2\text{H} = 3:4:5:2:1]$ , has m. p. 187—188°.

All these compounds, including methyl trimethylgallate, dissolve in concentrated sulphuric acid, giving colourless or pale yellow solutions. Addition of increasing quantities of nitric acid to these solutions gives successively intense violet, wine-red, and pale yellow colorations. A sulphuric acid solution of colchicine gives a similar succession of colours with nitric acid.

T. H. P.

**The Phthalyl Cyanides.** GIBBS BLACKSTOCK (*J. Amer. Chem. Soc.*, 1912, 34, 1080—1082).—*Phthalyl*, *isophthalyl*, and *terephthalyl cyanides* can be prepared by (a) the action of hydrocyanic acid on a solution of the acid chloride in anhydrous ether containing some pyridine, when a white substance first precipitates (possibly a com-

pound of acetyl chloride and pyridine), the crude cyanide separating subsequently as a dark oil; (*b*) digesting the acid chloride in acetone solution with mercuric cyanide; (*c*) heating the acid chloride with mercuric cyanide in a sealed tube at 140—160°. Method (*b*) is not very satisfactory, and phthalyl cyanide prepared by method (*a*) is difficult to purify.

The three cyanides are brown powders, which become viscous near 300° with apparent decomposition; they are not hydrolysed when heated with hydrochloric acid in a sealed tube, but when heated with potassium hydroxide solution a little ammonia is formed. D. F. T.

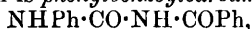
**The Acylation of Amino-acids and Some Ketolactimones.** J. D. RIEDEL (*Chem. Zentr.*, 1912, i, 1773—1774; from *Riedel's Ber.*, 1912, 13—24).—Experiments on the acylation of arylaminoacetates with succinic and camphoric anhydrides show that anthranilic acid is better suited in some cases to the characterisation of dicarboxylic anhydrides than aniline. Phthalic and citraconic anhydrides are less suitable for acylation.

*Chloroacetylanthranilic acid*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , has m. p. 184°. *Hydroxyacetylanthranilolactone*,  $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{NH}\cdot\text{CO} \\ \text{CO}\text{—O}\end{smallmatrix}\right\rangle\text{CH}_2$ , from chloroanthranilic acid and boiling aqueous sodium carbonate, forms red leaflets, m. p. 200°. Solution in sodium hydroxide and precipitation gives *hydroxyacetylanthranilic acid*,

$\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$ , m. p. 181°. *isoValerylanthranilic acid* forms colourless prisms, sintering at 105°, m. p. 114—115°; *α-bromoisovalerylanthranilic acid* is white, m. p. 147—148°, and passes into *α-hydroxyisovalerylanthranilolactone*,  $\text{C}_6\text{H}_4\left\langle\begin{smallmatrix}\text{NH}\cdot\text{CO} \\ \text{CO}\text{—O}\end{smallmatrix}\right\rangle\text{CH}\cdot\text{CHMe}_2$ , m. p. 181°, from which the *hydroxy-acid*, m. p. 175°, is obtained.

*Succinilcarboxylic acid*,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , has m. p. 186°, and behaves as a strong dibasic acid. *Anthranoylcamphoric acid*,  $\text{C}_{17}\text{H}_{21}\text{O}_5\text{N}$ , forms small needles, m. p. 198—199°.

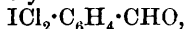
When benzylchloroamide,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NHCl}$ , is used, sufficient alkali must be present to convert it into a salt,  $\text{C}_6\text{H}_5\cdot\text{C}(\text{ONa})\text{NCl}$ , as well as the amino-acid, and the product is then, in the case of anthranilic acid, not *o*-benzoylhydrazinobenzoic acid, but the isomeric *o*-phenylcarbamidobenzoic acid,  $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CO}\cdot\text{NHPh}$ , m. p. 190—192°, from which *phenyldiketotetrahydroquinazoline*,  $\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2$ , m. p. 278—280°, is obtained by heating, or by evaporation with ammonia. A by-product of the acylation is *phenylbenzoylcarbamide*,



m. p. 206—208°.

C. H. D.

***p*-Iodobenzaldehyde and Derivatives with Uni- and Multi-valent Iodine.** CONRAD WILLGERODT and ALEXIS UCKE (*J. pr. Chem.*, 1912, [ii], 86, 276—283).—On treatment with chlorine in chloroform solution, *p*-iodobenzaldehyde yields a stable *iododichloride*,



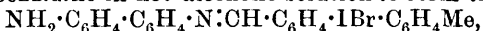
which is converted by aqueous sodium carbonate into *p*-iodosobenzaldehyde.

*hyde*,  $\text{IO} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO}$ . The latter compound reacts with *p*-iodoxytoluene and silver oxide in the presence of water, yielding an alkaline, aqueous solution of *p*-aldehydophenyl-*p*-tolyliodonium hydroxide,



which could not be isolated and, therefore, was characterised by the preparation of the following salts: the *chloride*, prepared by saturating the aqueous solution of the base with sodium chloride, crystallises in small, colourless plates, m. p.  $132^\circ$ ; the amorphous, orange-yellow *platinichloride*,  $(\text{C}_6\text{H}_4\text{Me} \cdot \text{ICl} \cdot \text{C}_6\text{H}_4 \cdot \text{CHO})_2 \text{PtCl}_4$ , decomposes at  $173^\circ$ ; the *bromide* crystallises in small, transparent needles, m. p.  $154-155^\circ$ . The *iodide* forms aggregates of pale yellow, microscopic pyramids, has m. p.  $150-151^\circ$  when slowly heated, and is converted by iodine in alcoholic solution into a *tri-iodide*,  $\text{C}_{14}\text{H}_{12}\text{OI}_4$ , which forms long, brown to black needles, m. p.  $95^\circ$ ; the *acetate*, long, colourless needles, m. p.  $265^\circ$ , and unstable *dichromate* are also described.

*p*-Aldehydophenyl-*p*-tolyliodonium bromide forms a light yellow, amorphous *phenylhydrazone*,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{IBr} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{N} \cdot \text{NHPh}$ , m. p.  $134^\circ$ , and a *semicarbazone*,  $\text{C}_{15}\text{H}_{15}\text{ON}_3\text{BrI}$ , crystallising in short, colourless needles, m. p.  $216^\circ$ . It reacts with aqueous hydrazine sulphate, yielding a pale yellow *azine*,  $\text{N}_2(\text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{IBr} \cdot \text{C}_6\text{H}_4\text{Me})_2$ , m. p.  $185^\circ$ , and with benzidine in hot alcoholic solution to form the *compound*,



an amorphous, yellow powder, m. p.  $155^\circ$ . On account of its instability the oxime could not be isolated.

*Di-p-iodobenzoin*,  $\text{C}_6\text{H}_4\text{I} \cdot \text{CH}(\text{OH}) \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{I}$ , prepared by condensing *p*-iodobenzaldehyde with potassium cyanide in methyl-alcoholic solution, crystallises in colourless needles, m. p.  $122^\circ$ , and on treatment with chlorine in chloroform solution yields on unstable *iododichloride*; the *benzoyl* derivative forms long, colourless, strongly refractive needles, m. p.  $152^\circ$ , and also yields an unstable *iododichloride*.

*Di-p-iodobenzil*,  $\text{C}_6\text{H}_4\text{I} \cdot \text{CO} \cdot \text{CO} \cdot \text{C}_6\text{H}_4\text{I}$ , prepared by oxidising di-*p*-iodobenzoin with nitric acid, crystallises in yellow needles, m. p.  $255^\circ$ .

F. B.

**Bromination of *m*-Hydroxybenzaldehyde, Vanillin, and Homovanillic Acid.** ROLAND PSCHORR (*Annalen*, 1912, 391, 23-39).—The following compounds of definite constitution have been prepared for the synthesis of phenanthrene derivatives.

[With W. SELLE, W. KOCH, H. STOOFF, and O. TREIDEL].—6-Bromo-3-hydroxybenzaldehyde, m. p.  $135^\circ$  (corr.), slender, colourless needles, obtained by the bromination of a 10% chloroform solution of *m*-hydroxybenzaldehyde, yields a *semicarbazone*, m. p.  $253^\circ$  (corr.), and is converted by methyl sulphate and alkali into 6-bromo-3-methoxybenzaldehyde, m. p.  $75-76^\circ$  (*semicarbazone*, m. p.  $251^\circ$  [corr.]). This substance, which is also produced by the bromination of *m*-methoxybenzaldehyde in boiling chloroform, is oxidised in acetone by aqueous potassium permanganate to 6-bromo-3-methoxybenzoic acid, m. p.  $161-162^\circ$  (corr.), the orientation of the substituents in which is known by the formation of the same acid from 6-nitro-3-methoxybenzoic acid. 6-Amino-3-methoxybenzoic acid yields yellow needles, m. p.  $149^\circ$ , by crystallisation, and colourless needles, m. p.  $150^\circ$ , by

sublimation. *2-Amino-3-methoxybenzoic acid*, m. p. 169—170° (corr.), is converted into *2-bromo-3-methoxybenzoic acid*, m. p. 153—155°, by the usual processes.

A 10% solution of protocatechualdehyde in glacial acetic acid yields by bromination *5-bromo-3:4-dihydroxybenzaldehyde*, m. p. 230° (corr.), which forms a *phenylhydrazone*, m. p. 138—140°, *diacetyl* derivative, m. p. 82—84° (corr.), and *dimethyl ether*, m. p. 62—64° (*semi-carbazone*, m. p. 202—203° [corr.]). *5-Bromovanillin*, obtained by the bromination of vanillin in chloroform at 0°, is converted into the preceding dimethyl ether by methyl sulphate and alkali. The position of the halogen atom in these compounds is ascertained by the conversion of the dimethyl ether into *5-bromo-3:4-dimethoxybenzoic acid* by 20% potassium permanganate or by methyl-alcoholic potassium hydroxide; by the latter method, *5-bromoprotocatechuic acid* and *5-bromoveratryl alcohol*, b. p. 190°/12 mm., are also produced. The bromination of vanillin methyl ether in glacial acetic acid at the ordinary temperature yields *6-bromo-3:4-dimethoxybenzaldehyde*, m. p. 149—150° (corr.), the *oxime* of which, m. p. 167—168° (corr.), is converted by boiling acetic anhydride into *6-bromo-3:4-dimethoxybenzonitrile*, m. p. 118—119° (corr.). The nitrile yields Zincke's *6-bromo-3:4-dimethoxybenzoic acid* by treatment with boiling *N/10*-sodium hydroxide. This acid, together with *6-bromo-3:4-dimethoxybenzyl alcohol*, m. p. 88—91°, is also obtained from *6-bromo-3:4-dimethoxybenzaldehyde* and methyl-alcoholic potassium hydroxide.

By bromination in chloroform, *ethyl 4-hydroxy-3-methoxyphenylacetate* (*ethyl α-homovanillate*), b. p. 180—185°/13—15 mm., yields *ethyl 6-bromo-4-hydroxy-3-methoxyphenylacetate*, m. p. 95°, by the hydrolysis of which *6-bromo-4-hydroxy-3-methoxyphenylacetic acid*, m. p. 180—181°, is obtained; its *acetyl* derivative, m. p. 170—171° (corr.), is prepared by the bromination of *acetyl-α-homovanillic acid*. By treating its alkaline solution with methyl sulphate, the preceding brominated ester is converted into *ethyl 6-bromo-3:4-dimethoxyphenylacetate*, by the hydrolysis of which *6-bromo-3:4-dimethoxyphenylacetic acid*, m. p. 115—116° (corr.), is obtained; the same acid is produced, in smaller yield, by the bromination of *3:4-dimethoxyphenylacetic acid*.

The position of the halogen atom in the preceding compounds is deduced as follows. It is not in position-5, because *5-bromo-3:4-dimethoxyphenylacetic acid*, prepared from *5-bromoveratryl chloride*, m. p. 56—59°, through the nitrile, has m. p. 95—98° (corr.). The following experiments show that the bromine is not in position-2. By condensation with *o*-nitrobenzaldehyde, the *bromo-3:4-dimethoxyphenylacetic acid* will yield a *3:4*- or a *2:3*-dimethoxyphenanthrene derivative according as the bromine is in position 6 or 2. The former is obtained; thus *o*-nitrobenzaldehyde and sodium *6-bromo-3:4-dimethoxyphenylacetate*, by heating with acetic anhydride at 100° for sixty hours, yield *o-nitro-α-6-bromo-3:4-dimethoxyphenylcinnamic acid*,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C}(\text{CO}_2\text{H}) \cdot \text{C}_6\text{H}_2\text{Br}(\text{OMe})_2$ , m. p. 199—200° (corr.), yellow crystals. The reduction of the latter by ferrous sulphate and aqueous ammonia at about 93° yields the *amino*-compound, m. p. 194—195° (corr.), which is converted in the usual manner into

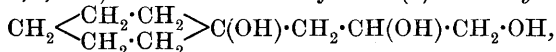
1-bromo-3:4-dimethoxyphenanthrene-10-carboxylic acid, decomp.  $220^{\circ}$ , sintering at  $168-175^{\circ}$ . By eliminating the bromine by boiling alcohol, *N*/1-sodium hydroxide, and copper-zinc dust, the latter is converted into 3:4-dimethoxyphenanthrene-10-carboxylic acid, m. p.  $185-186^{\circ}$ .

[With O. TREIDEL.]—By reactions similar to the preceding, *o*-nitro- $\alpha$ :2:3-dimethoxyphenylcinnamic acid, m. p.  $190^{\circ}$  (corr.), yellow needles, prepared from *o*-nitrobenzaldehyde and sodium  $\alpha$ -homoveratrate, is converted through the amino-acid, m. p.  $173^{\circ}$  (corr.), yellow plates, into 2:3-dimethoxyphenanthrene-10-carboxylic acid, m. p.  $254^{\circ}$  (corr.); the latter yields 2:3-dimethoxyphenanthrene by distillation under 100—150 mm. C. S.

**Preparation of Aldehydes of the Aromatic Series with at least one Hydroxy-group next to the Aldehyde Group.** KALLE & Co. (D.R.-P. 246338).—When “thioindigo scarlet” (prepared by the condensation of isatin with oxythionaphthen) is heated with a 40% solution of sodium hydroxide, it yields *o*-thiolbenzoic acid and oxindolaldehyde,  $C_6H_4 \begin{smallmatrix} \text{C(CHO)} \\ \text{—NH—} \end{smallmatrix} C \cdot OH$ , yellow needles, m. p.  $213^{\circ}$ , which condenses with anthranilic acid to furnish an *azomethine*.

*Acenaphthenonaldehyde*, colourless leaflets, is prepared in a similar manner from the condensation product of 3-oxy-(1)-thionaphthen and acenaphthenquinone. F. M. G. M.

**Action of Zinc on a Mixture of cycloHexanone and Allyl Iodide.** MICHAEL SAYTZEFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1013—1025).—1-Allylcyclohexanol,  $OH \cdot C_6H_{10} \cdot C_3H_5$ , obtained by the action of zinc on a mixture of cyclohexanone and allyl iodide, is a colourless, mobile liquid, b. p.  $188-192^{\circ}$  (compare Matschnevitch, Abstr., 1911, i, 961). On oxidation it yields: (1) the *trihydric alcohol*,



which forms spherical aggregates of acicular crystals, and (2) 1-cyclohexanol-1-acetic acid,  $OH \cdot C_6H_{10} \cdot CH_2 \cdot CO_2H$ , the *calcium*, *lead*, and *zinc* salts of which were analysed.

1-Chloro-1-allylcyclohexane,  $C_6H_{10}Cl \cdot CH_2 \cdot CH : CH_3$ , is a colourless liquid, b. p.  $89-92^{\circ}/21$  mm.,  $D_4^{20}$  1.00275,  $D_{20}^{20}$  0.98744,  $D_4^{20}$  0.98616. When treated with silver carbonate, it is converted into the *hydrocarbon*,  $C_9H_{14}$ , which is a liquid, b. p.  $159-161^{\circ}$ ,  $D_4^{20}$  0.8611,  $D_{20}^{20}$  0.8468,  $D_4^{20}$  0.8457, and combines with bromine, giving the compound,  $C_9H_{14}Br$ , as a yellow, viscous liquid. The positions of the double linkings in the hydrocarbon are being investigated.

T. H. P.

**Action of Sodamide on  $\alpha\delta$ -Dibenzoylbutane.** EDOUARD BAUER (*Compt. rend.*, 1912, 155, 288—291).—Haller and Bauer (Abstr., 1909, i, 108, 654) have studied the action of sodamide on phenyl acyl ketones having at least one atom of hydrogen attached to the carbon atom in the  $\alpha$ -position to the ketonic group. This study has now been extended to the diketones.

$\alpha\delta$ -Dibenzoylbutane (1 mol.) when warmed in benzene solution with sodamide (2 mols.) turns red, and a precipitate is formed. At the end of the reaction (30—45 minutes) the product is decomposed with ice water, and the oil distilled under reduced pressure, a viscid liquid passing over at 218—220°/13 mm. On cooling, this solidifies and can be separated by crystallisation into two substances, one crystallising in slender needles, m. p. 98°, the other in stout, yellow prisms, m. p. 53°. Analysis shows them to be isomerides of the formula  $C_{18}H_{16}O$ , formed by the dehydration of the dibenzoylbutane. On oxidation by potassium permanganate, the isomeride, m. p. 53°, yields  $\gamma$ -benzoylbutyric acid and benzoic acid, whilst the isomeride, m. p. 98°, yields succinic and benzoic acids, thus showing them to be stereoisomerides, 1-benzoyl-2-phenyl- $\Delta^1$ -cyclopentene,  $CH_2 \begin{smallmatrix} \text{CBz} \cdot \text{CPh} \\ | \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix}$ , m. p. 53°, and 1-benzoyl-2-phenyl- $\Delta^2$ -cyclopentene,  $CH_2 \begin{smallmatrix} \text{CHBz} \cdot \text{CPh} \\ | \\ \text{CH}_2 - \text{CH} \end{smallmatrix}$ , m. p. 98°, formed by the elimination of water from the intermediate unstable 1-benzoyl-2-phenylcyclopentan-2-ol.

By prolonging the action of the sodamide for three or four hours the results are very different, benzamide, a substance,  $C_{12}H_{13}ON$ , m. p. 135°, and an unsaturated hydrocarbon,  $C_{11}H_{12}$ , b. p. 110°/13 mm., being obtained in addition to the above cyclopentenenes. W. G.

**Cyclic Hexamethylenic  $\beta$ -Diketones.** GEORGES LESER (*Ann. Chim. Phys.*, 1912, [viii], 26, 227—257).—A connected account of work published already (Abstr., 1899, i, 479, 743; 1900, i, 430; 1901, i, 271; 1902, i, 261, 550; 1910, i, 48. The following new data are recorded.

2-Acetylcylohexanone,  $D_0$  1.075,  $n_D$  1.5138, b. p. 111—112°/18 mm., prepared by condensing cyclohexanone with ethyl acetate in presence of sodium, has a cumin-like odour, yields a copper derivative (steel-grey spangles), a dioxime (m. p. 149°), and a semicarbazone (m. p. 162—163). The diketone dissolves in alkalis, but, on standing, the solution deposits cyclohexanone; in warm alkalis the hydrolysis proceeds further,  $\omega$ -acetylhexoic acid being formed (Kipping and Perkin, *Trans.*, 1889, 55, 338). The potassium derivative of the diketone reacts in the cold with ethyl iodide in alcohol, forming the 2-ethyl derivative, b. p. 238—240°, which is liquid, yields a viscous oxime, and on hydrolysis with hot dilute alkalis yields 2-ethylcylohexanone, b. p. 182—183°.

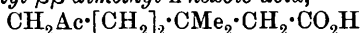
4-Acetyl-1-methylcylohexan-3-one (Abstr., 1900, i, 430),  $n_D$  1.5012, b. p. 230—231°/740 mm., on treatment with ammonia solution gives a crystalline compound,  $C_9H_{15}ON$ , m. p. 102°, which is not decomposed by boiling dilute sodium hydroxide solution. 4-Acetyl-1:4-dimethylcylohexan-3-one (Abstr., 1901, i, 278) has  $n_D$  1.4669,  $D_{13}$  1.007, b. p. 246—247°, and its homologue, 4-acetyl-1-methyl-4-ethylcylohexan-3-one, has b. p. 255—260°; neither reacts with the Grignard reagent.

$\epsilon$ -Acetyl- $\delta\delta$ -dimethyl-*n*-hexoic acid (Abstr., 1899, i, 743) yields an ethyl ester, b. p. 148—150°, and on reduction by sodium in alcohol

gives the corresponding *hydroxy-acid*, m. p.  $61^{\circ}$ , crystallising in silky tufts.

The product formed by the dehydration of 2-acetyl-1:1:3-trimethylcyclohexan-3-ol (Abstr., 1910, i, 48) is now shown to be 2-acetyl-1:1:3-trimethyl- $\Delta^2$ -cyclohexene, since it yields  $\alpha\alpha$ -dimethyladipic acid on oxidation by permanganate. The same product on reduction with sodium furnishes the corresponding unsaturated *alcohol*,  $D^{13}$  0.933,  $n_D$  1.4864, b. p.  $217^{\circ}$ , a liquid having an odour recalling that of ozone and yielding an *acetyl* derivative, b. p.  $231-232^{\circ}$ .

4-Acetyl-1:1-dimethylcyclohexan-3-one (Abstr., 1902, i, 261; 1910, i, 48) on hydrolysis by alkalis yields chiefly the corresponding cyclanone, but also some  $\epsilon$ -acetyl- $\beta\beta$ -dimethyl-*n*-hexoic acid,



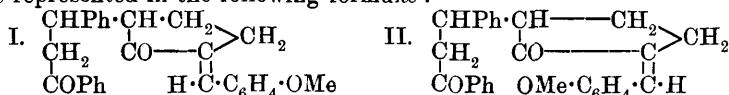
(crystalline *oxime*, m. p.  $93^{\circ}$ ), whilst its potassium derivative reacts with methyl iodide to form 4-acetyl-1:1:4-trimethylcyclohexan-3-one, b. p.  $122-124^{\circ}/20$  mm. or  $229-230^{\circ}/747$  mm., m. p.  $43^{\circ}$ , which does not give the characteristic reactions of the  $\beta$ -diketones, and yields a *monoxime*, m. p.  $159^{\circ}$ , crystallising in voluminous prisms. In this and similar cases it is probably the carbonyl group in the side-chain which does not react with hydroxylamine.

T. A. H.

**Semicyclic 1:5-Diketones of the cyclopentane Series.** HANS STOBBE (*J. pr. Chem.*, 1912, [ii], 86, 209—218. Compare Abstr., 1902, i, 472; 1903, i, 115; 1909, i, 309, and the following abstracts).—Under the influence of alkali hydroxides and secondary amines, cyclopentanone combines with ketones of the type  $\text{CHR}\cdot\text{CH}\cdot\text{COPh}$  (where  $\text{R}=\text{C}_6\text{H}_5$ ,  $p\text{-MeO}\cdot\text{C}_6\text{H}_4$ , or  $mp\text{-CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3$ ), yielding 1:5-diketones,  $\text{COPh}\cdot\text{CH}_2\cdot\text{CHR}\cdot\text{CH}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CO}-\text{CH}_2 \end{smallmatrix}$ , which are decomposed into their components by distillation under ordinary pressure. The diketones readily form disemicarbazones, and react with hydroxylamine, yielding either monoximes or dioximes; when boiled with hydroxylamine hydrochloride in alcoholic solution they are converted into dihydropyridene derivatives,  $\begin{smallmatrix} \text{CH}\cdot\text{CR}\cdot\text{C}\cdot\text{CH}_2 \\ \text{CPh}-\text{N}\cdot\text{C}\cdot\text{CH}_2 \end{smallmatrix} > \text{CH}_2$ , which form stable salts and may also be obtained by the action of hydrogen chloride on solutions of the oximes.

The diketones condense with benzaldehyde, anisaldehyde, and piperonaldehyde to form compounds of the type  $\text{COPh}\cdot\text{CH}_2\cdot\text{CHR}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CO}-\text{C}\cdot\text{CHR} \end{smallmatrix}$ , which often occur in two stereoisomeric forms. The constitution of these condensation products has been established by the behaviour of the isomeric anisylidene compounds (I and II below); on distillation these decompose in two ways, (1) into acetophenone and two stereoisomeric benzylideneanisylidenecyclopentanones,  $\text{CHPh}\cdot\text{C}\begin{smallmatrix} \text{CH}_2-\text{CH}_2 \\ \text{C}\cdot\text{CO}\cdot\text{C}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe} \end{smallmatrix}$  and (2) into phenyl styryl ketone and anisylidenecyclopentanone, which at a higher temperature further decomposes into cyclopentanone and dianisylidenecyclopentanone. Since both isomerides yield the same products, the con-

clusion is drawn that the anisylidene compounds are stereoisomeric, as represented in the following formulæ :

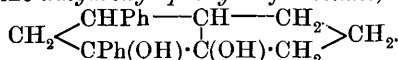


and this view is confirmed by the interconversion of the two forms by exposure to light, or by boiling them with a solution of iodine in benzene. F. B.

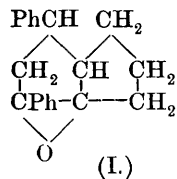
**Optically Active Semicyclic 1:5-Diketones of the cyclo-Hexane Series.** HANS STOBBE (*J. pr. Chem.*, 1912, [ii], 86, 218—225. Compare following abstracts).—*d*-3-Methylcyclohexanone combines with ketones of the type,  $\text{CHR} \cdot \text{CH} \cdot \text{COPh}$  (where  $\text{R} = \text{C}_6\text{H}_5$ ,  $\text{OMe} \cdot \text{C}_6\text{H}_4$ , *mp*- $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3$ ), yielding two stereoisomeric 1:5-diketones,  $\text{COPh} \cdot \text{CH}_2 \cdot \text{CHR} \cdot \text{CH} < \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CO} \text{---} \text{CH}_2 \end{array} > \text{CHMe}$ , of which the less fusible modification is produced in greater quantity. That the two forms are stereoisomeric has been proved by the conversion of each pair of isomerides into one and the same tetrahydroquinoline derivative,  $\begin{array}{c} \text{CH} \cdot \text{CR} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ | \quad | \\ \text{CPh} \cdot \text{N} \cdot \text{C} \cdot \text{CH}_2 \cdot \text{CHMe} \end{array}$ , by boiling with hydroxylamine hydrochloride in alcoholic solution.

The above constitution for the diketone has been confirmed in the case of the condensation products from phenyl styryl ketone and its *mp*-methylenedioxy-derivative by the oxidation of one of the isomerides to  $\beta$ -methylnadipic acid. F. B.

**Semicyclic 1:5-Diketones from cyclopentanone and Phenyl Styryl Ketone.** ROBERT GEORGI [and, in part, with HANS VOLLAND] (*J. pr. Chem.*, 1912, [ii], 86, 232—241. Compare Stobbe and Volland, *Abstr.*, 1903, i, 115).— $\beta$ -Phenyl- $\beta$ -2-cyclopentanonylpropio-phenone is reduced by sodium amalgam in alcoholic or moist ethereal solution to a white, crystalline *dihydroxydiphenylbicyclooctane*,



This has m. p. 142—143°, and gives at first an orange and then a red coloration with sulphuric acid. It discharges the colour from a solution of bromine in chloroform, but the decolorised solution rapidly becomes brown again, owing to the liberation of bromine. It forms a *monobenzoyl* derivative, crystallising in prisms, m. p. 91—92°, and a *mono-m-nitrobenzoyl* derivative, m. p. 127—128°; attempts to prepare the corresponding diacyl derivatives proved fruitless. The action of phenylcarbamide leads to the formation of a *monophenylurethane*,  $\text{C}_{27}\text{H}_{27}\text{O}_3\text{N}$ , m. p. 140—142°, together with a light yellow substance, m. p. 120—122°.



When heated with hydriodic acid and phosphorus at 180—190°, the dihydroxy-compound is converted into a yellow oil, the greater part of which dissolves

in a mixture of alcohol and ether, leaving a small amount of a solid substance,  $C_{20}H_{20}O$ , m. p. 126—130°.

If the action is carried out at lower temperatures, solid substances of still lower m. p. may be isolated from the product. Both the oily and solid products have the same composition, and probably represent anhydrides of constitution (I).

$\beta$ -Phenyl- $\beta$ -2-cyclopentanonylpropio-phenone is reduced by hydriodic acid and phosphorus at 140—150° to a compound,  $C_{20}H_{20}O_2$ , isomeric with the above dihydroxydiphenylbicyclooctane. On treatment with hydrogen chloride in alcoholic solution, the diketone loses water with the formation of a *diphenylbicyclooctenone* (annexed formula). This crystallises in needles, m. p. 122°, and forms a *semicarbazone*,  $C_{21}H_{21}ON_3$ , m. p. 202—203° (decomp.).

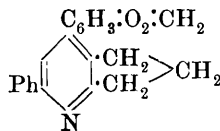
Under the influence of sodium hydroxide in aqueous alcoholic solution, the diketone condenses with benzaldehyde, yielding two stereoisomeric  $\beta$ -phenyl- $\beta$ -3-benzylidenecyclopentan-2-onylpropio-phenones,  $COPh \cdot CH_2 \cdot CHPh \cdot CH \begin{smallmatrix} CH_2 \cdot CH_2 \\ CO \cdot C \cdot CHPh \end{smallmatrix}$ , which are separated by fractional crystallisation from alcohol. The more readily soluble isomeride is light yellow in colour, m. p. 104—106°, dissolves in sulphuric acid with a red coloration, and is transformed by exposure to light into the less soluble, colourless isomeride, which has m. p. 143—144°, and gives an orange-yellow coloration with sulphuric acid; the interconversion of the two forms has been effected by boiling with a 0.01% solution of iodine in benzene.

The diketone also condenses with piperonaldehyde, yielding two stereoisomeric  $\beta$ -phenyl- $\beta$ -3-piperonylidene-cyclopentan-2-onylpropio-phenones,  $COPh \cdot CH_2 \cdot CHPh \cdot CH \begin{smallmatrix} CH_2 \cdot CH_2 \\ CO \cdot C \cdot CH \cdot C_6H_3 \cdot O_2 \cdot CH_2 \end{smallmatrix}$ , of which one is pale yellow, and has m. p. 118—120°, whilst the other isomeride is dark yellow, and has m. p. 143—144°. F. B.

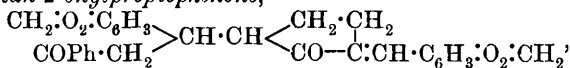
**Semicyclic 1:5-Diketones Prepared by the Addition of cyclopentanone to Phenyl Methylenedioxy-styryl Ketone and Phenyl *p*-Methoxystyryl Ketone.** CURT STRIEGLER (*J. pr. Chem.*, 1912, [ii], 86, 241—250).— $\beta$ -m-*p*-Methylenedioxyphenyl- $\beta$ -2-cyclopentanonylpropio-phenone,  $COPh \cdot CH_2 \cdot CH \begin{smallmatrix} CH_2 \cdot CH_2 \\ CO \cdot CH \cdot C_6H_3 \cdot O_2 \cdot CH_2 \end{smallmatrix}$ , prepared by the condensation of phenyl *mp*-methylenedioxy-styryl ketone with cyclopentanone by means of piperidine or diethylamine, and purified by means of its disemicarbazone, crystallises in clusters of needles, m. p. 120—121°, and is resolved by hot alcoholic potassium hydroxide into its components. It is accompanied by a small quantity of a substance,  $C_{37}H_{32}O_7$ , crystallising in needles, m. p. 275°.

The *disemicarbazone*,  $C_{20}H_{26}O_4N_6$ , crystallises with alcohol (1 mol.) in white, felted needles, m. p. 214—215° (decomp.), which lose their alcohol at 100—110° and then have m. p. 215—216°. The *monoxime* crystallises in needles, m. p. 133—134°; the *dioxime*,  $C_{21}H_{22}O_4N_2$ , in hexagonal leaflets, m. p. 193—194°.

When warmed with hydroxylamine hydrochloride in alcoholic solution the diketone is converted into 5-phenyl-7-*mp*-methylenedioxyphenyl-2:3-dihydro-4-pyridene (annexed formula), which crystallises from alcohol in long, yellow needles, m. p. 124—125°, and forms a yellow, crystalline *hydrochloride*, m. p. 260°, a *hydrogen sulphate*,  $C_{21}H_{17}O_2N \cdot H_2SO_4$ , m. p. 215°, and a *picrate*, m. p. 189—190° (decomp.).



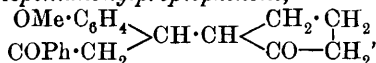
$\beta$ -*mp*-Methylenedioxyphenyl- $\beta$ -3-piperonylidene-cyclopentan-2-onylpropiofenone,



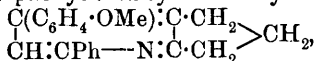
prepared by condensing the diketone with piperonaldehyde by means of aqueous sodium hydroxide at 0°, crystallises in yellow, pointed prisms, m. p. 178—180°, instantly decolorises bromine, gives with sulphuric acid a yellow coloration which gradually becomes darker, and when heated with 20% alcoholic potassium hydroxide decomposes into acetophenone and dipiperonylidene-cyclopentanone (Mentzel, Abstr., 1903, i, 497).

The *anisylidene* derivative,  $C_{29}H_{26}O_5$ , obtained in a similar manner from the diketone and anisaldehyde, forms white needles, m. p. 140—142°, and resembles the preceding compound in its chemical behaviour; the *benzylidene* derivative,  $C_{28}H_{24}O_2$ , crystallises in pale yellow prisms, m. p. 128—130°.

$\beta$ -*Anisyl*- $\beta$ -2-cyclopentanonylpropiofenone,

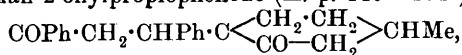


obtained in an impure condition as an oil by condensing phenyl *p*-methoxystyryl ketone and cyclopentanone with piperidine or diethylamine, forms a *disemicarbazone*,  $C_{23}H_{28}O_3N_6$ , m. p. 235—236° (decomp.), and is converted by the action of hydroxylamine, or, better, its hydrochloride, into 5-phenyl-7-anisyl-2:3-dihydro-4-pyridene.



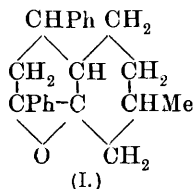
which is pale yellow, has m. p. 144—145°, and forms a *hydrochloride*, m. p. 218°, and a *picrate*, yellow needles, m. p. 185—186°. In one instance the oily product of the condensation deposited a substance,  $C_{22}H_{28}O_4$ , crystallising in white needles, m. p. 191—192°. F. B.

**Stereoisomeric Semicyclic 1:5-Diketones from 3-Methylcyclohexanone and Phenyl Styryl Ketone.** ARTHUR ROSENBERG (*J. pr. Chem.*, 1912, [ii], 86, 250—256).—The condensation of *d*-3-methylcyclohexanone and phenyl styryl ketone by means of sodium hydroxide in alcoholic solution yields, in addition to the  $\beta$ -phenyl- $\beta$ -4-methylcyclohexan-2-onylpropiofenone (m. p. 149—151°),

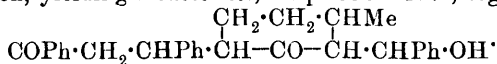


previously described (Abstr., 1902, i, 472; 1903, i, 115), a *stereoisomeric* of m. p. 135—137°, which is separated from the former compound by taking advantage of its greater solubility in carbon tetra-

chloride. If the condensation is effected by means of piperidine,  $\beta$ -piperidyl- $\beta$ -phenylpropiophenone is formed as an intermediate product (compare Georgi and Schwyzer, this vol., i, 787). The diketone of m. p. 149—151° has  $[\alpha]_D^{20} - 20.12^\circ$ , gives at first a yellow and then a red coloration with sulphuric acid, and decomposes at 230° under ordinary pressure, yielding 3-methylcyclohexanone; the *monosemicarbazone*,  $C_{23}H_{27}O_2N_3$ , crystallises in white needles, m. p. 202—204° (decomp.),  $[\alpha]_D + 84.10^\circ$ ; the monoxime has m. p. 215—216°,  $[\alpha]_D^{15} + 34.22^\circ$ , and cannot be transformed into a dioxime by the further action of hydroxylamine, but, when warmed with semicarbazide in alcoholic solution, yields an *oxime-semicarbazone*,  $C_{23}H_{28}O_2N_2$ , crystallising in white needles, m. p. 239° (decomp.),  $[\alpha]_D + 49.65^\circ$ . On reduction with hydriodic acid and phosphorus the diketone is converted into a yellow oil, from which crystals, having m. p. 130—132° and consisting of an *anhydride* of 1:9-dihydroxy-1:3-diphenyl-7-methyloctahydroindene (formula I) are occasionally deposited. Under the influence of sodium hydroxide, it condenses with benzaldehyde in alcoholic solution, yielding a *substance*, m. p. 156—157°, together with the compound,



the compound,

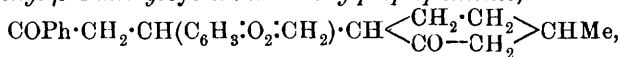


The latter compound forms white needles, m. p. 200—201.5°,  $[\alpha]_D^{18} - 47.45^\circ$ , and, on distillation, decomposes at 130—180° with the formation of acetophenone.

The stereoisomeric diketone of m. p. 135—137° has  $[\alpha]_D^{20} + 83.99^\circ$ , forms a *monoxime*, m. p. 204—205° (decomp.),  $[\alpha]_D^{15.5} - 86.80^\circ$ , and is converted by boiling with alcoholic hydroxylamine hydrochloride into 2:4-diphenyl-7-methyl-5:6:7:8-tetrahydroquinoline, m. p. 111—113°,  $[\alpha]_D + 48.55^\circ$ . All rotations given above refer to chloroform solutions.

F. B.

**Two Stereoisomeric Semicyclic 1:5-Diketones from 3-Methylcyclohexanone and Phenyl Methylenedioxystryl Ketone.** CURT STRIEGLER (*J. pr. Chem.*, 1912, [ii], 86, 257—269).—The condensation of *d*-3-methylcyclohexanone with phenyl *mp*-methylenedioxystryl ketone by means of sodium hydroxide, diethylamine, or piperidine in alcoholic solution gives rise to two stereoisomeric  $\beta$ -*mp*-methylenedioxyphenyl- $\beta$ -4-methylcyclohexan-2-onylpropiophenones,

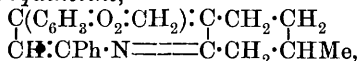


which are separated by fractional crystallisation from a mixture of ethyl acetate and alcohol. The less soluble modification has m. p. 152—154°,  $[\alpha]_D^{17} - 19.59^\circ$  in chloroform solution. Its alcoholic solution (solubility 1:520 at 17.5°) gives a yellow coloration with ferric chloride; the *disemicarbazone*,  $C_{25}H_{30}O_4N_6$ , has m. p. 223—224° (decomp.), and  $[\alpha]_D + 37.65^\circ$  in chloroform; the *monoxime* forms needles, m. p. 216—217°,  $[\alpha]_D - 26.08^\circ$  in glacial acetic acid solution. It is oxidised by chromium trioxide in glacial acetic acid solution to  $\beta$ -methyladipic and benzoic acids.

The more readily soluble diketone has m. p. 137—139°,  $[\alpha]_D^{17} + 69.17^\circ$

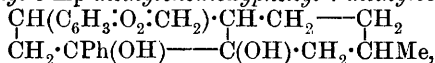
in chloroform solution, solubility in alcohol 1 : 376 at 17.5°, and forms a *disemicarbazone*, m. p. 172—173°,  $[\alpha]_D^{17} - 30.56^\circ$  in chloroform solution, a *monoxime*, m. p. 183—184°,  $[\alpha]_D - 16.08^\circ$  in acetone, and a *dioxime*,  $C_{25}H_{26}O_4N_2$ , crystallising in needles, m. p. 197—199°,  $[\alpha]_D - 104.90^\circ$  in acetone solution.

On treatment with hydrogen chloride in benzene solution the isomeric monoximes yield the same 2-phenyl-4-*mp*-methylenedioxyphenyl-7-methyl-5:6:7:8-tetrahydroquinoline,



which crystallises in leaflets, m. p. 125—126°,  $[\alpha]_D + 44.66^\circ$  in chloroform, gives an olive-green coloration with sulphuric acid, and may also be obtained by heating the stereoisomeric diketones (1 mol.) with hydroxylamine hydrochloride (3 mols.) in alcoholic solution; the *picrate*,  $C_{29}H_{24}O_9N_4$ , has m. p. 180—181° (decomp.),  $[\alpha]_D - 30.14^\circ$  in chloroform.

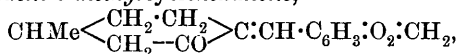
On reduction with hydriodic acid and phosphorus, or when dissolved in alcohol and the solution treated simultaneously with carbon dioxide and sodium amalgam, the diketones yield two stereoisomeric 1:9-dihydroxy-1-phenyl-3-*mp*-methylenedioxyphenyl-7-methyloctahydroindenes,



of which the one modification, obtained from the diketone of m. p. 152—154°, crystallises in white needles, m. p. 66—68°, and has  $[\alpha]_D - 3.82^\circ$  in chloroform, whilst the stereoisomeride, prepared from the more readily fusible diketone, crystallises in lustrous prisms, m. p. 83—84°, and has  $[\alpha]_D - 25.35^\circ$  in chloroform; both isomerides give a violet-red coloration with sulphuric acid.

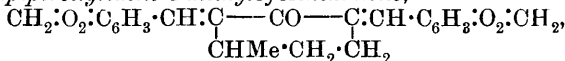
The diketones distil with partial decomposition at about 75°/12 mm., but under ordinary pressure are resolved at 165—175° into methylcyclohexanone and phenyl *mp*-methylenedioxyphenyl ketone. When heated either alone or in high boiling solvents, they undergo no racemisation.

#### 6-Piperonylidene-3-methylcyclohexanone,



prepared by the condensation of *d*-3-methylcyclohexanone and piperonaldehyde by means of alcoholic sodium ethoxide at a low temperature, crystallises in pale yellow needles, m. p. 85°,  $[\alpha]_D - 227.48^\circ$  in alcoholic solution.

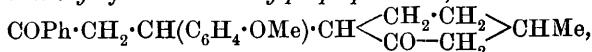
#### 2:6-Dipiperonylidene-3-methylcyclohexanone,



prepared from excess of piperonaldehyde in a similar manner, is orange-yellow, and has  $[\alpha]_D - 31.62^\circ$  in alcohol. F. B.

Semicyclic 1:5-Diketones Prepared by the Addition of 3 Methylcyclohexanone to Phenyl *p*-Methoxystyryl Ketone and Distyryl Ketone. GEORGE S. CRUIKSHANKS (*J. pr. Chem.*, 1912, [ii], 86, 269—272).—Under the influence of sodium hydroxide,

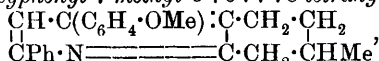
*d*-3-methylcyclohexanone condenses with phenyl *p*-methoxystyryl ketone in alcoholic solution, yielding two stereoisomeric  $\beta$ -*p*-methoxyphenyl- $\beta$ -4-methylcyclohexan-2-onylpropiophenones,



which are separated by fractional crystallisation from a mixture of ethyl acetate and light petroleum.

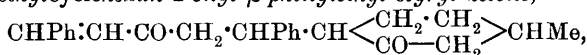
The more readily soluble isomeride has m. p. 128—130°,  $[\alpha]_D + 19.2^\circ$  in chloroform, and is oxidised by chromium trioxide in glacial acetic acid solution to  $\beta$ -methyladipic and benzoic acids, whilst the less soluble modification has m. p. 157—159°,  $[\alpha]_D + 71.21^\circ$  in chloroform, and gives a reddish-yellow coloration with sulphuric acid.

[With ALEXANDER SCHWYZER.]—When heated with hydroxylamine hydrochloride in alcoholic solution both isomerides are converted into 2-phenyl-4-*p*-methoxyphenyl-7-methyl-5:6:7:8-tetrahydroquinoline,



which forms an amorphous, yellow powder,  $[\alpha]_D + 46.35^\circ$  in chloroform, and yields a *picrate*,  $\text{C}_{29}\text{H}_{26}\text{O}_8\text{N}_4$ , m. p. 170°,  $[\alpha]_D - 45.55^\circ$  in chloroform, a yellow *platinichloride*, and a dark yellow *dichromate*.

$\beta$ -4-Methylcyclohexan-2-onyl- $\beta$ -phenylethyl styryl ketone,

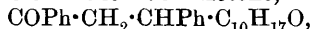


prepared by the condensation of distyryl ketone and 3-methylcyclohexanone by means of diethylamine, has m. p. 149—150°.

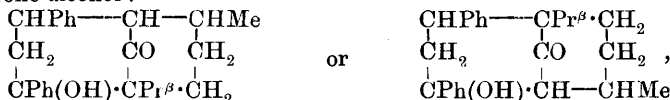
F. B.

**Bicyclic Ketone-Alcohol Prepared by the Addition of Menthone to Phenyl Styryl Ketone.** HANS STOBEE and ARTHUR ROSENBERG (*J. pr. Chem.*, 1912, [ii], 86, 226—232).—The condensation product from menthone and phenyl styryl ketone differs from the compounds (1:5-diketones) obtained by the combination of *cyclopentanone* and 3-methylcyclohexanone with  $\alpha\beta$ -unsaturated ketones (compare preceding abstracts) in behaving as a monoketone; thus it forms only a monoxime and a monosemicarbazone, does not condense with aromatic aldehydes, and cannot be converted by the action of hydroxylamine hydrochloride into a tetrahydroquinoline derivative.

The authors imagine that the 1:5-diketone,



first produced, undergoes internal condensation, with the formation of a ketone alcohol:

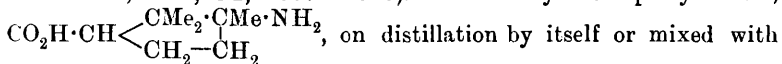


but all attempts to obtain evidence of the presence of a hydroxyl group by methylation, acylation, or by the action of phenylcarbimide proved unsuccessful.

4-Hydroxy-2:4-diphenyl-6(or 8)-methyl-1(or 5)-isopropylbicyclononan-9-one is prepared by the addition of sodium ethoxide to a solution of phenyl styryl ketone in menthone. It crystallises from

alcohol in needles, m. p. 128—129°,  $[\alpha]_D + 57.59^\circ$  in chloroform, distils almost unchanged under diminished pressure, and gives a light green coloration with sulphuric acid; the *oxime* has m. p. 184—185°,  $[\alpha]_D + 31.89^\circ$  in chloroform; the *semicarbazone*, m. p. 154—156° with previous sintering,  $[\alpha]_D + 20.13^\circ$  in chloroform. F. B.

**Molecular Rearrangements in the Camphor Series. X. Campholytic Acid and Related Compounds. Walden's Rearrangement.** WILLIAM A. NOYES and RALPH S. POTTER (*J. Amer. Chem. Soc.*, 1912, 34, 1067—1080).—Aminodihydrocampholytic acid,

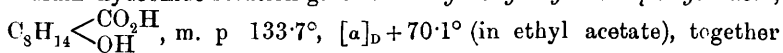


lime yields the *anhydride*,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CO} \\ \text{NH} \end{array}$ ,  $[\alpha]_D^{30} 72.8^\circ$  (in light petroleum);

the anhydride can also be obtained by warming the acid with acetic anhydride, but it is then accompanied by *acetylaminodihydrocampholytic acid*,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CO}_2\text{H} \\ \text{NHAc} \end{array}$ , m. p. 218°. By the action of nitrous acid

the anhydride is converted into the *nitroso*-derivative,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CO} \\ \text{N}\cdot\text{NO} \end{array}$ ,

needles, m. p. 188—189° (rapid heating), which on heating with sodium hydroxide solution gives *trans-hydroxydihydrocampholytic acid*,



with smaller quantities of campholytic acid,  $\text{C}_8\text{H}_{13}\cdot\text{CO}_2\text{H}$ , campholyto-

lactone,  $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CO} \\ \text{O} \end{array}$ , and *isolaurelene*,  $\text{CH}_2 \begin{array}{c} \text{CH}=\text{CMe} \\ \text{CH}_2\cdot\text{CMe}_2 \end{array}$ . The same

four products can be obtained by the direct decomposition of aminodihydrocampholytic acid with nitrous acid. Distillation of the *trans*-hydroxydihydrocampholytic acid or heating with water causes partial decomposition into campholytic acid, *isolaurelene*, and campholytolactone; to obtain *trans*-hydroxydihydrocampholytolactone it is necessary to heat the acid with acetic anhydride, when the product has m. p. 115—117°,  $[\alpha]_D^{27} + 121.9^\circ$  (in alcohol). Campholytolactone (Tiemann and Kerschbaum, Abstr., 1901, i, 5), although of almost the same m. p. (118—119°), has  $[\alpha]_D + 8.5^\circ$  (in alcohol), and gives *cis*-hydroxydihydrocampholytic acid, m. p. 118.5°,  $[\alpha]_D + 50.8^\circ$  (in alcohol), on treatment with sodium hydroxide solution, whereas the above lactone is reconverted into the *trans*-acid. As both the *cis*- and *trans*-acids are hydrolysed by dilute sulphuric acid to *iso*-

campholytic acid (otherwise  $\beta$ -campholytic acid),  $\text{CO}_2\text{H}\cdot\text{C} \begin{array}{c} \text{CMe}\cdot\text{CMe}_2 \\ \text{CH}_2-\text{CH}_2 \end{array}$ ,

and as the resistance to oxidation indicates a tertiary hydroxyl in each, the two acids are probably stereoisomerides; this view is supported by the relative conductivities of the acids (*trans*-acid,  $k 8.1 \times 10^{-6}$ ; *cis*-acid,  $k 35.8 \times 10^{-6}$ ). If this view of their structure is correct, a Walden inversion must occur in the decomposition of aminodihydrocampholytic acid by nitrous acid.

*l*-Campholytic acid could not be obtained of higher optical activity

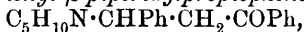
than  $[\alpha]_D^{20} - 74.3^\circ$  (in light petroleum); it has a slightly greater conductivity ( $k\ 9.8 \times 10^{-6}$ ) than *isocampholytic acid* ( $k\ 8.0 \times 10^{-6}$ ).

*d*-Iododihydrocampholytic acid can be prepared by the action of hydrogen iodide on a solution of *l*-campholytic acid in light petroleum, or on *cis*- and *trans*-hydroxydihydrocampholytic acids in carbon disulphide. The products in the three cases were apparently identical, treatment with sodium hydrogen carbonate yielding campholytic acid, *trans*-hydroxydihydrocampholytic acid, and campholytolactone, whilst reduction with zinc dust and dilute sulphuric acid gave dihydrocampholytic acid, an oily liquid,  $D_4^{20}\ 0.9915$ ,  $[\alpha]_D^{25} + 34.6^\circ$ ; *amide*, plates, m. p.  $86.5^\circ$ ,  $[\alpha]_D^{21} + 20.7^\circ$  (in light petroleum). Here, again, therefore, a rearrangement similar to that of Walden must have occurred.

The theoretical portion of the paper includes suggestions as to the mechanism of the Walden inversion. D. F. T.

**Attempts to Combine *d*-Fenchone or Camphor with Phenyl Styryl Ketone and Other  $\alpha\beta$ -Unsaturated Ketones.** ROBERT GEORGI and ALEXANDER SCHWYZER (*J. pr. Chem.*, 1912, [ii], 86, 273—276).—A record of unsuccessful attempts to condense *d*-fenchone and camphor with phenyl styryl ketone, benzylideneacetylacetone, and phenyl *p*-methoxystyryl ketone. An alcoholic solution of *d*-fenchone and phenyl styryl ketone, on treatment with aqueous sodium hydroxide, yields the  $\alpha$ -modification of dibenzylidenetriacetophenone (Kostanecki and Tambor, *Abstr.*, 1896, i, 557); the latter compound was also obtained by the action of piperidine, diethylamine, or sodium hydroxide on a mixture of camphor and phenyl styryl ketone in alcoholic or benzene solution.

Attempts to condense fenchone with phenyl styryl ketone by means of piperidine gave  $\beta$ -phenyl- $\beta$ -piperidylpropiophenone,



which forms a *hydrochloride*, m. p.  $123-124^\circ$ , a *picrate*, m. p.  $86-88^\circ$ , and is resolved by heating either alone or with water into piperidine and phenyl styryl ketone.

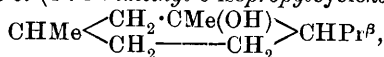
The interaction of fenchone, benzylideneacetylacetone, and piperidine yielded benzylidenediacetylacetone (Knoevenagel, *Abstr.*, 1895, i, 50).

F. B.

**Action of Sulphuric Acid on Borneol.** P. G. GOLUBEFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1061—1067).—The action of sulphuric acid on borneol yields *borneol ether*,  $(C_{10}H_{17})_2O$ , which is a pale yellow syrup, b. p.  $312-314^\circ$ ,  $[\alpha]_D - 88.56^\circ$ ,  $D_4^{18}\ 0.960$ ,  $n_D^{24}\ 1.494$ , volatilising at  $110^\circ$ . The ether is unchanged by 2% sulphuric acid solution at  $170^\circ$ , and is converted into camphor,  $[\alpha]_D + 29.27^\circ$ , by concentrated nitric acid, and into camphene hydrochloride, m. p.  $147^\circ$ , by hydrochloric acid. It is isomeric with the solid ether obtained by Bouchardat and Lafont (*Abstr.*, 1894, i, 612).

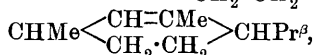
Besides the ether, the action of sulphuric acid on borneol gives camphene, m. p.  $48-49^\circ$ , b. p.  $157-160^\circ$ , which is very similar to the natural camphene from the ethereal oil of the Siberian fir (*Abstr.*, 1909, i, 943), but is optically inactive. T. H. P.

**Action of Methyl Iodide and Magnesium on Menthone.** IVAN VANIN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1068—1075).—3-Methylmenthan-3-ol (1 : 3-dimethyl-6-isopropylcyclohexan-1-ol),



prepared by the action of magnesium and methyl iodide on menthone, is a liquid, b. p. 102—103°/16—17 mm.,  $D_0^{20}$  0.9143,  $D_0^{20}$  0.8980, and has the normal molecular weight in boiling benzene. The corresponding chloro-derivative,  $\text{C}_{11}\text{H}_{21}\text{Cl}$ , b. p. about 101—103°/13 mm., could not be obtained pure.

When heated with potassium hydrogen sulphate, the alcohol is converted into the hydrocarbon,  $\text{CHMe} \begin{array}{c} \text{CH}_2 \cdot \text{CMe} \\ \text{CH}_2 \text{---} \text{CH}_2 \end{array} \text{CHPr}^\beta$  or



which is a colourless liquid, b. p. 185—187°/764.4 mm.,  $D_0^{20}$  0.8432,  $D_0^{20}$  0.8244, and has the normal molecular weight in boiling benzene. The hydrocarbon combines with 1 mol. of bromine, but the product loses 1 mol. of hydrogen bromide, giving the compound,  $\text{C}_{11}\text{H}_{19}\text{Br}$ , as a dense oil.

T. H. P.

**The Ethereal Oils of the Wood of the Spruce.** PETER KLASON and B. SEGERFELT (*Arkiv. Kem. Min. Geol.*, 1912, 4, No. 20, 1—3).—In the manufacture of spirit by the sulphite-cellulose process, it has been noticed that a reddish-brown oil, possessing a peculiar odour, collects in the middle of the fractionating tower. When this oil is distilled in a current of steam, a white substance possessing an odour similar to that of camphor collects in the condenser. It has a composition corresponding with the formula  $\text{C}_{10}\text{H}_{17}\cdot\text{OH}$ , and has m. p. 207°. It begins to sublime at 190° and is optically inactive. The properties point to it being borneol, but whether it is a mixture of borneol and isoborneol awaits further investigation. No definite conclusions can yet be drawn as to the condition in which the borneol existed in the original spruce wood, since it would probably be affected by the fermentation process. It was possibly present as bornyl acetate, which was saponified during the boiling with sulphite.

T. S. P.

**The Formation of Resin by the Action of Alkali Hydroxides on Aliphatic Aldehydes.** I. THOR EKECRANTZ (*Arkiv. Kem. Min. Geol.*, 1912, 4, No. 27, 1—34).—The present paper deals chiefly with the investigation of the products formed by the action of weak (3%) sodium hydroxide on acetaldehyde at low temperatures, and of the resin formed by the action of concentrated alcoholic sodium hydroxide (10%) on acetaldehyde. The method of preparation of the resin was similar to that adopted by Ciamician (*Abstr.*, 1881, 247), care being taken to keep the temperature down and so prevent the formation of compounds of very high molecular weight. The action of the weak sodium hydroxide was studied in order to obtain, if possible, compounds intermediate in composition between the aldehyde and the resin.

By precipitation with ether from acetone solution the resin was

separated into two chief components, which are isomerides having the formulæ  $C_{24}H_{36}O_6$ , and denoted as  $\alpha$ - and  $\beta$ -aldehyde-resin. They are probably formed by the condensation of 12 molecules of acetaldehyde with loss of  $6H_2O$ . The  $\alpha$ -compound is completely soluble in benzene, whilst the  $\beta$ -compound leaves a residue. They do not contain aldehydic, ketonic, hydroxylic or carboxylic groups, nor do they possess the characteristics of esters. By treatment with chlorine and bromine the following compounds were obtained: ( $\alpha$ )  $C_{24}H_{36}O_6Cl_4$ , white substance, m. p.  $160^\circ$  (decomp.);  $C_{24}H_{36}O_6Br_4$ , yellow precipitate, which decomposes at  $270^\circ$  without melting. ( $\beta$ )  $C_{24}H_{36}O_6Cl_4$ , light yellow precipitate, m. p.  $220$ — $230^\circ$ ;  $C_{24}H_{36}O_6Br_4$ , yellowish-grey precipitate, which decomposes on heating without undergoing fusion. The  $\beta$ -bromo-compound differs from the others in that it is insoluble in the ordinary solvents.

By treatment of the resin with sulphuric or hydrochloric acids, humus-like substances are readily obtained, which fact points to a constitution similar to that of certain of the carbohydrates.

By oxidation of the  $\beta$ -compound with 30% hydrogen peroxide in glacial acetic acid solution, a white, amorphous acid was obtained, having the composition  $C_{18}H_{24}O_8$ , and m. p.  $185^\circ$ . The corresponding  $\alpha$ -acid could not be obtained pure.

The products obtained by the action of 3% sodium hydroxide on acetaldehyde appear to be intermediate in composition between crotonaldehyde and aldehyde-resin, and are being further investigated, as also are the products of dry distillation of the resin with calcium oxide and with infusorial earth.

T. S. P.

[Structure of Polymerised Vinyl Bromide and Caoutchouc.]

NICOLAI N. LJUBAVIN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 906—907).—In Ostromisslensky's paper on this subject (this vol., i, 280), no mention is made of the work of Lwoff published in the *J. Russ. Phys. Chem. Soc.* in 1878 and 1880.

T. H. P.

The So-called "Insoluble" Constituent of Caoutchouc and its Influence on the Quality. CLAYTON BEADLE and HENRY P. STEVENS (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 61—65).—Observations have been made in reference to the influence of different factors (rolling, smoking, etc.) on the separation of the protein constituents of caoutchouc when plantation rubber is treated with "benzine." So far as the composition of the insoluble constituent is concerned, there appears to be essential difference between the products obtained from "fine para" and from plantation caoutchouc.

Elasticity tests with vulcanised products indicate that the protein constituent has an important influence on the properties of the caoutchouc, and it appears to behave much in the same way as antimony sulphide, that is, as a sulphur carrier. Since artificial rubber does not contain the protein constituent, there will necessarily be a difference in quality as compared with the natural substance.

H. M. D.

**Synthesis of Alkylglucosides by the Action of Emulsin.**  $\beta$ -Butylglucoside,  $\beta$ -isoButylglucoside,  $\beta$ -Allylglucoside. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1912, 155, 437—439; *J. Pharm. Chim.*, 1912, [vii], 6, 193—199).—The glucosides were prepared by the general method described already (this vol., i, 672).

$\beta$ -Butylglucoside crystallises in colourless, odourless, very hygroscopic needles, has  $[\alpha]_D - 35.4^\circ$  in water, is bitter to the taste, very soluble in water or alcohol, and moderately so in ethyl acetate.  $\beta$ -iso-Butylglucoside, m. p. 99—100°, resembles its isomeride, but is not hygroscopic; it has  $[\alpha]_D - 34.96^\circ$  in water.  $\beta$ -Allylglucoside, m. p. 97°, crystallises in colourless, hygroscopic needles, is less bitter than the foregoing, and has  $[\alpha]_D - 40.34^\circ$  in water.

All three glucosides were hydrolysed rapidly by emulsin in water. They all reduced alkaline copper solutions slightly, probably owing to the presence of a small amount of dextrose. T. A. H.

**New Synthesis of an Alkylglucoside by means of Emulsin.**  $\beta$ -Benzylglucoside. ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1912, 155, 523—524\*. Compare this vol., i, 592, 672).—Fischer (compare Abstr., 1894, i, 3) obtained, by the action of hydrogen chloride on a mixture of dextrose and benzyl alcohol, a white, amorphous product, which he concluded was a mixture of  $\alpha$ - and  $\beta$ -benzylglucosides.  $\beta$ -Benzylglucoside has now been prepared in a crystalline form by the synthesising action of emulsin. A mixture of benzyl alcohol, containing 5% of water (50 c.c.), dextrose (2 grams), and emulsin (0.2 gram), was left, with frequent shaking, for fifty days at 18—24°. The liquid was then filtered and extracted with water. The aqueous extract, after removal by ether of the last traces of benzyl alcohol, was evaporated to dryness under reduced pressure. The dry residue was dissolved in ethyl acetate, and, after remaining twenty-four hours, the solution was decanted and evaporated to a small bulk, from which, on cooling,  $\beta$ -benzylglucoside crystallised in needles, m. p. 106°;  $[\alpha]_D - 49.78^\circ$ . It has a bitter taste, is very soluble in water and alcohol, but does not reduce Fehling's solution. In aqueous solution it is almost completely hydrolysed in two days by means of emulsin. W. G.

**Picrotoxin.** I. JOHANNES SIELISCH (*Annalen*, 1912, 391, 1—22).—Meyer and Bruger have stated that picrotoxin is a complex of two compounds (picrotoxinin and picrotin) in definite but, apparently, not molecular proportions. The foundation of this statement is the estimation of the picrotoxinin by aqueous bromine. The author has examined thoroughly the accuracy of this method, and finds that the amount of picrotoxinin found can be varied at will by as much as 23% by altering the amount of bromine used or the duration of its action.

When a mixture of molecular quantities of picrotoxinin and picrotin is fractionally crystallised from water, the respective fractions have different rotatory powers; however, if the fractions are kept in contact with the mother liquor for two days, they all have approximately the

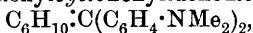
\* and *J. Pharm. Chim.*, 1912, [vii], 6, 298—301.

same rotatory power, which is identical with that of picrotoxin. Similar results are obtained when picrotoxin itself is fractionally crystallised.

The molecular weight of picrotoxin, determined in glacial acetic acid by the cryoscopic method, increases rapidly with the concentration of the solute, and approaches the value 602 required by the formula  $C_{30}H_{34}O_{13}$ .

The author is of opinion, therefore, that picrotoxin is an easily decomposable compound of picrotin and picrotoxinin in molecular proportions. C. S.

**Leuco-bases and Colouring Matters Derived from Diphenyl-ethylene; Oxidation of the Tetramethylcyclohexylidene Base by Lead Peroxide.** PAUL LEMOULT (*Compt. rend.*, 1912, 155, 355—358).—A reply to Schmidlin and von Escher (this vol., i, 437). Tetramethyldiaminodiphenylcyclohexylenemethane,



on oxidation with lead peroxide gives a pure blue colour which dyes tannin-mordanted cotton a deep blue. In aqueous solution the oxidation product gradually loses its colour, giving rise to a compound,  $C_6H_5:C(C_6H_4 \cdot NMe_2)_2$ , which crystallises from alcohol in needles, m. p. 169°. It is colourless or pale green, soluble in mineral acids without coloration, but dissolves in acetic acid to a blue solution. On oxidation with lead peroxide in acetic acid solution, it gives an intense blue colour, which gradually disappears on keeping the aqueous solution, and by precipitation with ammonia another leuco-base is obtained, m. p. 228°, which differs considerably from the leuco-base of malachite-green in its m. p., in the colours it produces, and in the absorption bands it gives with chloranil in alcoholic solution. W. G.

**The Chlorophyll Group. XVII. The Spectral Properties of the Two Chlorophyllans.** LÉON MARCHLEWSKI (*Biochem. Zeitsch.*, 1912, 43, 234—239. Compare this vol., i, 285).—The spectral measurements of *allochlorophyllan* agree well with those of Tsvett, with the exception that the latter found, in addition, a band  $\lambda$  628—622, and also with those of Willstätter (for “phæophytin component b,” which the author holds to be *allochlorophyllan*) with the exception of one band (Marchlewski,  $\lambda$  496·5—477·5; Willstätter  $\lambda$  515—491). The spectrum of *neochlorophyllan* showed also good agreement with the observations of Tsvett and Willstätter, with the exception that the former described a band  $\lambda$  637—632, which is absent from the pure preparation. S. B. S.

**The Nature of the Compound of Iodine and Tannin.** MARCEL BECQUET (*Chem. Zentr.*, 1912, i, 1635; from *Bull. Sci. Pharm.*, 1912, 18, 645—649).—Tannin and iodine are not chemically combined; the tannin serves as a substratum for hydrogen iodide. The preparation may be replaced by freshly prepared solutions of hydriodic acid of known strength. C. H. D.

**Methyltannin.** JOSEF HERZIG (*Monatsh.*, 1912, 33, 843—852. Compare Herzig and Renner, *Abstr.*, 1909, i, 713).—When 4 grams of methyltannin (tannin methyl ether) are heated with 10 c.c. of a 7.4% solution of potassium hydroxide in alcohol, the residue obtained on evaporation, after dissolving in water, gives an ether extract containing the ethyl ester of trimethylgallic acid, m. p. 52—55°. The aqueous solution, after extraction with ether, contains a mixture of tri- and di-methylgallic acids, which can be isolated by acidifying and again extracting with ether; the aqueous solution still contained a substance of reducing properties. The above ethyl ester can also be obtained (m. p. 53—55°) by a similar treatment of the corresponding methyl ester with a small amount of potassium hydroxide in ethyl alcoholic solution. If methyltannin is treated in solution in methyl alcohol with an insufficient amount of barium hydroxide, the product is the methyl ester of trimethylgallic acid.

That the results obtained above do not depend on the presence of methyl trimethylgallate as an impurity in the methyltannin is shown by the latter, after repeated recrystallisation from large quantities of alcohol, having an unaltered methoxyl content, and still exhibiting the same behaviour with alcoholic potassium hydroxide. Also, sublimation of methyltannin in an atmosphere of carbon dioxide gave as the only definite products, trimethylgallic acid (m. p. 166—168°) and a trace of a substance, m. p. 135—145°.

The inconsistency in  $[\alpha]_D$  for different specimens of methyltannin (Herzig and Renner, *loc. cit.*) appears to be due to the application of warm acetic acid in their preparation. Boiling with acetic acid raises the optical activity of methyltannin very considerably; the change is in all probability connected with the hydrolytic effect of the acetic acid, which causes complete hydrolysis in a sealed tube at 130—140°. Specimens of methyltannin in the preparation of which the use of acetic acid was avoided gave  $[\alpha]_D^{18} + 9.5^\circ$  to  $+ 10.7^\circ$ .

D. F. T.

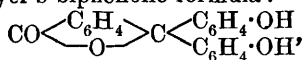
**The Compounds of Dimethylpyrone with Aluminium Bromide and with Trichloroacetic Acid.** WLADIMIR PLOTNIKOFF (*Chem. Zentr.*, 1912, i, 1839; from Reprint, 1911).—A compound,  $AlBr_3 \cdot C_7H_8O_2$ , is obtained in cold ethylene bromide solution, and has m. p. 120—123°. The freezing-point curve of aluminium bromide and dimethylpyrone indicates the existence of this compound, and of another,  $AlBr_3 \cdot 2C_7H_8O_2$ .

A similar freezing-point curve, with two maxima and three eutectic points, indicates the existence of two compounds with trichloroacetic acid,  $C_7H_8O_2 \cdot CCl_3 \cdot CO_2H$  and  $C_7H_8O_2 \cdot 2CCl_3 \cdot CO_2H$ . A third compound,  $2C_7H_8O_2 \cdot CCl_3 \cdot CO_2H$ , may also exist.

C. H. D.

**Constitution of the Phthaleins and Their Derivatives.** BERNARDO ODDO and ETTORE VASSALLO (*Gazzetta*, 1912, 42, ii, 204—236).—It has been found (Oddo, *Abstr.*, 1911, ii, 826) that treatment with magnesium ethyl iodide does not reveal the presence of active hydrogen in the phenolphthalein molecule. This result

throws doubt on Baeyer's biphenolic formula :



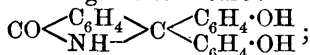
since such a compound should yield 2 mols. of ethane, corresponding with the two phenolic hydrogen atoms. Repetition of the above experiment with larger quantities shows that the lactonic group also remains indifferent, whereas in other similar compounds, such as coumarin and santonin, the oxygen of the carbonyl group undergoes replacement by two alkyl groups.

On the other hand, the *monopotassium* salt of phenolphthalein, which has been obtained crystalline in reddish-violet, rhomboidal plates, reacts with magnesium ethyl iodide, giving 1 mol. of hydrocarbon in accord with the dihydroxylic formula  $\text{C}_{20}\text{H}_{13}\text{O}_2(\text{OH}) \cdot \text{OK}$ ; but here, too, the presence of a lactonic group is not indicated.

Anhydrous ammonia, aniline, dimethylaniline, or pyridine gives no precipitate with an ethereal phenolphthalein solution, and the latter remains colourless. Also, in pyridine solution, phenolphthalein does not react with magnesium ethyl iodide.

Cryoscopic and ebullioscopic measurements give the following results. In freezing phenol, phenolphthalein has the normal molecular weight, even with considerable concentrations. In aniline, however, the molecular weight is only about one-third of the normal value for low concentrations, and only when the concentration exceeds 12% are normal values obtained; Ampola and Rimatori (Abstr., 1897, ii, 306) found that phenols showed normal behaviour in this solvent. In freezing veratrole or dimethylaniline, values agreeing with the simple molecular formula are obtained. In boiling methyl alcohol or acetone, the molecular weight has double the normal value when the concentration is low, and gradually diminishes as this is increased. With pyridine, however, normal ebullioscopic behaviour is shown even at low concentrations.

Unlike phenolphthalein, resorcinolphthalein is found to contain two active hydrogen atoms when treated with magnesium ethyl iodide, this result agreeing with the biphenolic formula; when treated with excess of the reagent, resorcinolphthalein gives, however, no indication of the presence of a lactonic group. Iminophenolphthalein, on the other hand, shows only one active hydrogen atom, although it is usually regarded as possessing the structure :



its diacetyl and triacetyl derivatives (see below) contain no such hydrogen atoms.

In boiling pyridine, fluorescein shows behaviour different from that of phenolphthalein, molecular weights lower than the theoretical values being obtained at low concentrations. Fluorescein differs from phenolphthalein in combining readily with pyridine in various proportions to form crystalline compounds.

The authors give a brief summary of the results of previous investigations on phenolphthalein and its salts and other derivatives, and discuss these in relation to those given above. The difference

between phenolphthalein and other hydroxylic compounds, such as fluorescein, is to be sought in the different functional disposition of the oxygen atoms usually regarded as hydroxylic. In fluorescein, the two hydroxyl groups are separated by an anhydridic oxygen atom, and their great distance apart and the stability of the triple hexagonal nucleus to which they are attached allows of their existence. With phenolphthalein, however, the hydroxyl groups are in close juxtaposition, and at the same time the benzene nuclei to which they are attached are free; it seems probable, therefore, that the molecule immediately tends to acquire a more stable arrangement, the two oxygen atoms assuming ethereal functions and binding the two benzene nuclei (annexed formula). The monoimino-compound would possess a similar structure.

For the potassium salt, however, must be assumed either the lacto-phenolic formula,  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C} \langle \text{C}_6\text{H}_4 \cdot \text{OK} \rangle$ , or the carboxy-quinonoid formula,  $\text{CO}_2\text{K} \cdot \text{C}_6\text{H}_4 \cdot \text{C} \langle \text{C}_6\text{H}_4 \cdot \text{OH} \rangle$ , the latter being the more probable.

The results at present obtained with phenolphthalein are also explainable by the formula:  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C} \langle \text{OPh} \rangle$ .

With pyridine, fluorescein forms yellow, crystalline compounds: (1)  $\text{C}_{20}\text{H}_{12}\text{O}_5(\text{C}_5\text{H}_5\text{N})_2$  and (2)  $\text{C}_{20}\text{H}_{12}\text{O}_5(\text{C}_5\text{H}_5\text{N})_3$ , m. p.  $95^\circ$ , which is unstable and is readily transformed into (1).

*Triacetylphenolphthaleinimide*,  $\text{CO} \langle \text{C}_6\text{H}_4 \rangle \text{C} \langle \text{C}_6\text{H}_4 \cdot \text{OAc} \rangle$ , forms triclinic [MADDALENA] crystals, m. p.  $238^\circ$ . T. H. P.

[Preparation of 14-Chlorocoeramidonine and Allied Compounds.] FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 246337. Compare Abstr., 1906, i, 687; 1907, i, 1067).—14-Chlorocoeramidonine, a brownish-yellow powder, is prepared from 4-chlorophenyl- $\alpha$ -aminoanthraquinone by the action of condensing agents; after treatment with sodium hyposulphite it yields a red vat, from which cotton is dyed in clear golden-yellow shades.

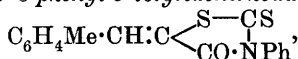
12:14-Dichlorocoeramidonine and benzocoeramidonine have similar properties, and are prepared from 2:4-dichlorophenyl- $\alpha$ -aminoanthraquinone and  $\alpha$ -naphthyl- $\alpha$ -aminoanthraquinone respectively.

14:14'-Coeramidonyl ketone is obtained by the condensation of di- $\alpha$ -anthraquinonyl-*pp*-diaminobenzophenone, whilst di- $\alpha$ -anthraquinonyl-*o*-tolidine furnishes 14:14'-bis-12:12'-methylcoeramidonyl.

F. M. G. M.

Substituted Rhodanins and Some of their Aldehyde Condensation Products. XII. HANS NÄGELE (*Monatsh.*, 1912, 33, 941—965. Compare Abstr., 1910, i, 764).—An extension of the work of Andreasch and Zipser (Abstr., 1903, i, 855).

Phenylrhodanin and *m*-tolualdehyde when heated with a little acetic acid condense to 3-phenyl-5-tolylidenerhodanin,



yellow crystals, m. p. 200°.

3-Phenyl-5-cuminyldenerhodanin, obtained in an analogous manner from cuminaldehyde, forms dark yellow crystals, m. p. 204°.

3-isoButylrhodanin, obtained by the action of ethyl chloroacetate on potassium isobutyldithiocarbamate, is an unpleasant smelling oil, b. p. 160°/11—12 mm.

5-Benzylidene-3-isobutylrhodanin, from the previous substance with benzaldehyde, forms yellow leaflets, m. p. 117°.

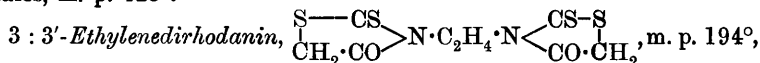
5-o-Hydroxybenzylidene-3-isobutylrhodanin, obtained analogously with salicylaldehyde, forms deep yellow needles, m. p. 184°. The isomeric 5-p-hydroxybenzylidene-3-isobutylrhodanin is a yellow, crystalline powder, m. p. 153°.

5-p-Methoxybenzylidene-3-isobutylrhodanin, from anisaldehyde, forms yellow crystals, m. p. 115°.

5-p-Dimethylaminobenzylidene-3-isobutylrhodanin, from dimethylaminobenzaldehyde, is a red, crystalline powder, m. p. 156°.

5-Piperonylidene-3-isobutylrhodanin, from piperonal, forms yellow crystals, m. p. 122°.

Potassium isobutyldithiocarbamate can be converted into isobutyl thiocarbimide (compare Kaluza, this vol., i, 440), which reacts with ammonia, forming isobutylthiocarbimide; cyanogen acts on an alcoholic solution of this substance, forming a solution of an intermediate product,  $\text{CS} \begin{array}{l} \text{N}(\text{C}_4\text{H}_9)\cdot\text{C}\cdot\text{NH} \\ \text{NH} \text{---} \text{C}\cdot\text{NH} \end{array}$ , which is easily hydrolysed by hydrochloric acid to isobutylthioparabanic acid; this is desulphurised by silver nitrate solution to isobutylparabanic acid,  $\text{C}_4\text{H}_9\cdot\text{N} \begin{array}{l} \text{CO}\cdot\text{CO} \\ \text{CO}\cdot\text{NH} \end{array}$ , scales, m. p. 125°.



is prepared from ethylenediamine through the dithiocarbamate in the same way as the corresponding isobutyl compound above; its formula was confirmed by analysis and molecular-weight determination in benzene. It condenses with aldehydes in the same way as the simpler rhodanins, but with rather more difficulty.

5 : 5'-Dibenzylidene-3 : 3'-ethylenedirhodanin forms deep yellow crystals, m. p. 265°.

5 : 5'-Di-p-hydroxybenzylidene-3 : 3'-ethylenedirhodanin chars without melting.

5 : 5'-Di-m-nitrobenzylidene-3 : 3'-ethylenedirhodanin forms pale yellow crystals, m. p. 258° (decomp.).

5 : 5'-Di-p-dimethylaminobenzylidene-3 : 3'-ethylenedirhodanin is a red substance, m. p. 212°.

5 : 5'-Di-p-methoxybenzylidene-3 : 3'-ethylenedirhodanin is a dark yellow, crystalline powder, m. p. 262° (decomp.).

5 : 5'-*Di-p-hydroxy-m-methoxybenzylidene-3 : 3'-ethylenedirhodanin*, formed from vanillin, is a yellow, crystalline powder, m. p. 270° (decomp.).

5 : 5'-*Dicinnamylidene-3 : 3'-ethylenedirhodanin* is a deep yellow powder, decomposing at 210°, m. p. 235°.

Ethylenediamine reacts with ethylthiocarbimide, forming diethylethylenethiocarbamide,  $(\text{NEt} \cdot \text{CS} \cdot \text{NH})_2 \text{C}_2\text{H}_4$ , colourless prisms and needles, m. p. 132°, which is converted by cyanogen into a brown, crystalline imino-compound, 
$$\begin{array}{c} \text{C}(\text{:NH}) \cdot \text{C}(\text{:NH}) \\ | \qquad \qquad | \\ \text{NEt} \text{-----} \text{CS} \text{> N} \cdot \text{C}_2\text{H}_4 \cdot \text{N} < \text{CS} \text{-----} \text{N} \cdot \text{C}_2\text{H}_4 \cdot \text{N} \\ | \qquad \qquad | \\ \text{C}(\text{:NH}) \cdot \text{C}(\text{:NH}) \end{array}$$

this on evaporation with hydrochloric acid yields *diethylethylenedithiodiparabanic acid*, pale yellow crystals, which decompose without melting; silver nitrate desulphurises the last substance in alcoholic solution to *diethylethylenediparabanic acid*, colourless crystals, m. p. 168°.

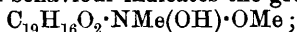
*Diallylethylenedithiodiparabanic acid*, yellow scales, m. p. 175°, is obtained in the same manner as the diethyl compound above, starting with allylthiocarbimide, and is convertible into *diallylethylenediparabanic acid*, colourless leaflets, m. p. 182°. This and all the above parabanic acids on treatment in aqueous solution with calcium chloride and ammonia deposit calcium oxalate.

*Diethylethylenedithiodihydantoin*, colourless needles, m. p. 184°, of which the molecular structure is uncertain, is obtained when diethylethylenedithiocarbamide is heated in aqueous solution with chloroacetic acid.

D. F. T.

**Alkaloids of Pareira Root.** FRANZ FALTIS (*Monatsh.*, 1912, 33, 873—897).—Commercial *Bebirinium sulphuricum* has been examined as to its constituents (compare Scholtz, Abstr., 1911, i, 913; 1907, i, 79, etc.); three have been isolated:  $\beta$ -bebeerine, *isobebeerine*, and *bebeerine-B*, full details of the method being given.

$\beta$ -Bebeerine  $\text{C}_{21}\text{H}_{28}\text{O}_4\text{N}$ , the chief constituent (termed  $\beta$ - in order to distinguish it from the very optically active chief constituent obtained by Scholtz), has m. p. 142—150°,  $[\alpha]_D^{25}$  (in alcohol) + 28.6°, (in pyridine) - 24.7°; the base and its salts are amorphous; the *iodide* decomposes at 245°. Its chemical behaviour indicates the groups



the *acetyl* derivative, m. p. 120—142°, can be further converted into a *triacetyl* compound, m. p. 140—165°, one acetyl group entering the nucleus. Benzoylation also yields a red *tribenzoyl* derivative, m. p. 144—147°. Methylation by nitrosomethylcarbamide gives a methyl derivative, needles, m. p. 81—83°; the action of methyl sulphate aided by heat causes methylation at the nitrogen atom, the quaternary *iodide*,  $\text{C}_{19}\text{H}_{16}\text{O}_2(\text{NMe}_2\text{I})(\text{OH}) \cdot \text{OMe}$ , obtained from the reaction product being soluble in alkali; treatment with methyl sulphate at 0° (compare Pschorr, Abstr., 1911, i, 908) methylates only the hydroxyl group, the *hydriodide* of the product,  $\text{C}_{19}\text{H}_{16}\text{O}_2\text{NMe}(\text{OMe})_2$ , having m. p. 244° (decomp.), and containing two molecules of water of crystallisation.

In an experiment in which  $\beta$ -bebeerine was boiled with benzene, some unknown impurity in the latter caused a conversion into an insoluble optically inactive product; endeavours to repeat the necessary conditions failed. The inactive compound is a *tertiary base*,

yielding a *methiodide*, decomposing at  $245^{\circ}$ ; under the influence of hydrogen iodide the base is converted into a quaternary *iodide*, m. p.  $250^{\circ}$  (decomp.), the base of which contains the elements of two molecules of bebeerine, together with those of a molecule of water. It is uncertain whether the coupling of the molecules occurred before or after the treatment with hydrogen iodide.

The alkaloid *B* is a yellow powder, m. p.  $220^{\circ}$  (decomp.),  $[\alpha]_D + 56.7^{\circ}$  (in pyridine). Fusion with potassium hydroxide causes the formation of protocatechuic acid, and investigation of the groups indicates a formula  $C_{20}H_{15}O_2(NMe)(OH)_2 \cdot OMe$ .

*iso*Bebeerine,  $C_{19}H_{15}O(NMe)(OH)_2 \cdot OMe$ , forms rhombic needles, m. p.  $290^{\circ}$  (decomp.); it is optically inactive.

It is suggested that the bebeerine ( $\alpha$ -bebeerine) obtained by Scholtz (*loc. cit.*) was really of the same composition as the  $\beta$ -bebeerine above, and actually a stereoisomeride.

D. F. T.

**The Constituents of Buphane disticha.** FRANK TUTIN (*Arch. expt. Path. Pharm.*, 1912, 69, 314).—Lewin (this vol., i, 577) has recently described the isolation of an alkaloid from *Buphane disticha*, for which he proposes the name "hæmanthine." The author points out that he has previously published an investigation on the same material (*Trans.*, 1911, 99, 1240), and shown that it contains at least four alkaloids. Probably, hæmanthine is a mixture of at least two alkaloids, buphanine being the main constituent.

H. W.

**Hydrogenated Derivatives of apoHarminine.** VICTOR HASENFRATZ (*Compt. rend.*, 1912, 155, 284—286. Compare this vol., i, 577).—Fischer (*Abstr.*, 1889, 730) prepared dihydroapoharminine by reduction of apoharminine with phosphorus and hydriodic acid. The author has repeated the process and obtained, in addition, *tetrahydroapoharminine*,  $C_8H_{12}N_2 \cdot H_2O$ , which crystallises from water in long, colourless, flattened needles, m. p.  $96^{\circ}$ . It is readily soluble in hot water, sparingly so in cold, and gives a *picrate*, very soluble in cold water.

Dihydroapoharminine gives a *methiodide*, which is not decomposed by boiling aqueous potassium hydroxide. The existence of methylapoharminine and nitrosodihydroapoharminine shows the presence of an :NH group in apoharminine and its dihydro-derivative. Since, however, the methiodide of the latter, unlike that of the former, is not decomposed by potassium hydroxide, the methyl iodide in the latter must be attached to a tertiary amino-group; thus dihydroapoharminine is both a secondary and a tertiary base, and this also applies to apoharminine, harminine and harmaline, the alkaloids of *Peganum harmala*.

W. G.

**Ethylmorphine and Ethylmorphine Hydrochloride (Dionine).** GEORGE L. SCHAEFER (*Amer. J. Pharm.*, 1912, 84, 389—391).—The figures published for the m. p.'s and solubilities of ethylmorphine and ethylmorphine hydrochloride are very discordant. The author has prepared pure ethylmorphine and finds that it has no distinct m. p., but begins to soften at about  $88^{\circ}$ , becomes transparent at  $90$ — $91^{\circ}$ , and slowly liquefies at  $110$ — $115^{\circ}$ . Its solubility is 1 : 480 in water, 1 : 75 in ether, and 1 : 1.5 in alcohol at  $25^{\circ}$ . The hydrochloride, also, has no

definite m. p., but softens at  $110^{\circ}$ , becomes translucent at about  $120^{\circ}$ , and liquefies, with decomposition, at a higher temperature. Solubility determinations yielded the following results:

15°	1 : 11.5 in water	1 : 26 in alcohol
25	1 : 8        "	1 : 20       "
40	1 : 4        "	1 : 8.25     "
50	1 : 2.5     "	1 : 5        "

The following test is proposed for ascertaining the purity of ethylmorphine hydrochloride: 2 c.c. of a solution of the specimen in water (1:40) at  $25^{\circ}$  are treated with 3 drops of ammonia (10%). If the salt is pure, the solution remains clear, and soon deposits distinct needle-shaped crystals of ethylmorphine. If the salt is not pure, and amorphous by-products are present, the solution becomes milky, and the separation of crystals may be retarded for hours, according to the amount of amorphous material contained in the preparation.

Salts of ethylmorphine may easily be distinguished from those of methylmorphine by dissolving 0.05 gram of the specimen in water (5 c.c.) and adding 5 drops of ammonia (10%). If allowed to remain for about two hours, ethylmorphine will separate, whilst a solution of methylmorphine remains clear, without separating crystals.

H. W.

**Preparation of Compounds from Alkylarylbarbituric Acids and Cinchona Alkaloids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 247188).—When the cinchona alkaloids are treated at the ordinary temperature with equimolecular proportions of alkylarylbarbituric acids in alcoholic or aqueous-alcoholic solution they furnish crystalline compounds of therapeutic value. The compounds from phenylethylbarbituric acid with quinine and with hydroquinine ( $C_{20}H_{26}O_2N_2 \cdot 2H_2O$ ) have m. p.'s  $182$ — $183^{\circ}$  and  $165^{\circ}$  respectively.

F. M. G. M.

**Solanidine from *Solanum tuberosum*** II. AMEDEO COLOMBANO (*Gazzetta*, 1912, 42, ii, 101—116. Compare Abstr., 1908, i, 99).—The author has prepared solanidine from *Solanum tuberosum* in three different ways, the three products having the same crystalline characters and melting point,  $214$ — $215^{\circ}$ . Analysis leads to the formula  $C_{25}H_{39}ON$ , which, however, requires confirmation.

Solanidine from *Solanum tuberosum* differs from solanidine from *S. sodomaeum*, not only as regards m. p., but also in its behaviour towards bromine. The latter does not decolorise aqueous or chloroform solutions of bromine, whilst the former combines with bromine, giving a moderately stable compound, m. p.  $103$ — $108^{\circ}$  (decomp.), which is rich in bromine, but has not yet been analysed.

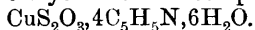
Solanidine from *S. tuberosum* yields a camphorsulphonate (from Reyckler's camphorsulphonic acid: Abstr., 1899, i, 445), forming tufts of crystals, m. p.  $170$ — $180^{\circ}$ , and a bromocamphorsulphonate, m. p.  $160$ — $180^{\circ}$ . These salts have not yet been analysed.

T. H. P.

**Strychnine and Brucine.** RICCARDO CIUSA and G. SCAGLIARINI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 84—87. Compare Abstr., 1911, i, 155, 1016).—The action of bromine on isostrychnine gives a compound

which crystallises from alcohol in colourless prisms of the composition  $\text{CO}_2\text{Et}\cdot\text{C}_{20}\text{H}_{22}\text{NBr}_3\cdot\text{NH}_4\text{HBr}$ , 1 mol. of bromine being added to the molecule and a further atom introduced in place of a hydroxyl group of the *isostrychnine*. Crystallisation from pyridine in place of alcohol yields the *pyridine* salt,  $\text{CO}_2\text{H}\cdot\text{C}_{20}\text{H}_{21}\text{NBr}_3\cdot\text{NH}_4\text{C}_5\text{H}_5\text{N}$ , which has a curarine action greater than that of *isostrychnine*, whilst the strychnine action has completely disappeared T. H. P.

**Compounds of Cupric Thiosulphate with Various Amines.** G. ROSSI (*Gazzetta*, 1912, 42, ii, 185—188).—The final product of the interaction of a cupric salt with sodium thiosulphate consists of cuprous thiosulphate, which, according to the conditions, crystallises either alone or combined with sodium thiosulphate. That cupric thiosulphate is formed as an intermediate product of the reaction is shown by the fact that the simultaneous presence of pyridine results in the separation of blue crystals of the compound



Similarly, with aniline,  $\text{CuS}_2\text{O}_3\cdot\text{NH}_2\text{Ph}$ , and with hexamethylene-tetramine,  $\text{CuS}_2\text{O}_3\cdot\text{C}_6\text{H}_{12}\text{N}_4\cdot 4\text{H}_2\text{O}$ , are formed. T. H. P.

**Preparation of Glycocyamidine.** ERNST SCHMIDT (*Zeitsch. Allg. Oesterr. Apothekervereins*, 1912, reprint 3 pp.).—Whilst creatine is readily converted into creatinine by repeated evaporation with concentrated hydrochloric acid, its homologue, glycocyamine, only yields small quantities of glycocyamidine when heated with the same reagent. When, however, glycocyamine is warmed on the water-bath during twenty-four hours with concentrated sulphuric acid, a good yield of glycocyamidine hydrochloride, darkening at  $200^\circ$ , m. p.  $208\text{--}210^\circ$  (decomp.), is obtained. H. W.

**Purines. VII. 2-Oxy-6:8:9-trimethylpurine, 2-Oxy-6:9-dimethylpurine, and 2-Oxy-8:9-dimethylpurine.** CARL O. JOHNS (*J. Biol. Chem.*, 1912, 12, 91—96).—None of the many isomerides of the monoxymethyl purines has yet been described, and if they occur in the cleavage of nuclein they might easily be overlooked, since they would probably be readily soluble in water.

*2-Oxy-6:8:9-trimethylpurine* is rather soluble in water, in spite of the fact that two of the three methyl groups are attached to carbon atoms. It was prepared by heating *5-acetyl-amino-6-methyl-amino-4-methyl-2-pyrimidone* (decomp.  $290\text{--}300^\circ$ ) at  $225\text{--}230^\circ$  with acetic anhydride. It contains  $2\text{H}_2\text{O}$  and decomposes at  $275^\circ$ ; the *picrate* decomposes at  $253^\circ$ .

*2-Oxy-6:9-dimethylpurine*, prepared by the action of 85% formic acid on *5-amino-6-methyl-amino-4-methyl-2-pyrimidone*, does not melt at  $320^\circ$ ; the *picrate* decomposes at  $224^\circ$ . When *5-amino-6-methyl-amino-2-pyrimidone* is heated with acetic anhydride at  $150\text{--}160^\circ$ , a 90% yield of *2-oxy-8:9-dimethylpurine* is obtained. This does not melt at  $320^\circ$  and is readily soluble in cold water; its *picrate* decomposes at  $233^\circ$ . W. D. H.

**Desmotropism in the  $\psi$ -Thiohydantoins.** TREAT B. JOHNSON and JOSEPH A. AMBLER (*Amer. Chem. J.*, 1912, 48, 197—205).—An

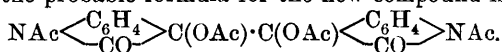
attempt to throw light on the possible tautomerism of the  $\psi$ -thiohydantoin by an investigation of the properties of a salt of  $\psi$ -thiohydantoinacetic acid with an active base.

$\psi$ -Thiohydantoinacetic acid,  $\text{CO}_2\text{H}\cdot\text{CH}\cdot\text{C}\begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ | \\ \text{C}(\text{:NH})\cdot\text{S} \end{smallmatrix}$  (Tambach,

Abstr., 1895, i, 13; Andreasch, Abstr., 1896, i, 89), obtained by heating together fumaric acid and thiocarbamide suspended in a little water, has m. p.  $245\text{--}250^\circ$ ; although it contains an asymmetric carbon atom it has not been resolved into active constituents. The *hydrochloride*, forms prisms, m. p.  $210\text{--}212^\circ$  (decomp.); *barium* salt crystallises with one molecule of water of crystallisation; *cinchonine* and *strychnine* salts, extremely soluble in water. The acid is hydrolysed by hydrochloric acid to dioxythiazoleacetic acid.

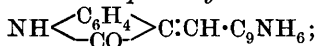
The *brucine* salt, m. p.  $177^\circ$ , could not be resolved by recrystallisation from water; the aqueous solution shows mutarotation, initial  $[\alpha]_D^{20} - 12\cdot65^\circ$ , changing slowly for several days or rapidly on boiling to  $[\alpha]_D^{20} - 25\cdot0^\circ$  to  $-25\cdot2^\circ$ . This alteration is attributed to a desmotropic change in the molecule of the acid. D. F. T.

**Reactions of the Isatins.** MORITZ KOHN and ARTUR KLEIN (*Monatsh.*, 1912, 33, 929—940).—When isatin is cautiously warmed with acetic anhydride and zinc dust until the mixture becomes decolorised, a colourless substance, monoclinic crystals, m. p.  $223^\circ$ , is obtained. Analysis and molecular-weight determinations indicate a formula  $\text{C}_{16}\text{H}_8\text{O}_4\text{N}_2\text{Ac}_4$ , and the substance is probably *tetra-acetylisatide*, possibly previously isolated by Heller (Abstr., 1904, i, 416). The existence of such a derivative favours the old pinacone structure for isatide, and the probable formula for the new compound is

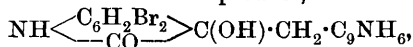


In an analogous manner, 5-bromoisatin reacts with zinc dust and acetic anhydride, producing 5:5'-*dibromotetra-acetylisatide*, monoclinic prisms, m. p.  $238\text{--}242^\circ$  (decomp.).

Isatin and 2-methylquinoline when heated together at  $160\text{--}170^\circ$  undergo condensation to form 3-*quinaldylideneisatin*,



it forms orange-red needles, m. p.  $234^\circ$ . 5-Bromoisatin forms an analogous 5-bromo-3-*quinaldylideneisatin*, orange-red needles, which decompose at  $265\text{--}267^\circ$ . Unlike the previous two cases, a mixture of 5:7-dibromoisatin and 2-methylquinoline in suspension in boiling amyl alcohol forms an aldol condensation product,



a colourless substance, tablets, decomposing at  $205^\circ$  approx.

1-Methylisatin reacts with phosphorus pentachloride on warming, with the formation of 2-*dichloro-1-methylisatin*, needles, m. p.  $142\text{--}145^\circ$ ; on treatment with barium hydroxide solution this gives 1-methylisatic acid as the *barium* salt, yellow needles; *silver* salt, deep yellow needles. D. F. T.

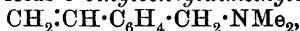
[Preparation of Benzoyl- $\alpha$ -isatinanilide.] FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 246715).—*Benzoyl- $\alpha$ -isatinanilide*, yellow crystals, m. p. 258—259°, is prepared by boiling  $\alpha$ -isatinanilide (10 parts) with benzoyl chloride (50 parts) until the mixture assumes a yellowish-brown colour, the product (which separates on cooling) is washed with benzoyl chloride, and crystallised from xylene; it forms a colourless, sparingly soluble (in water) compound with sodium hydrogen sulphite, and with fuming sulphuric acid furnishes soluble sulphonated derivatives, which dye wool in yellow shades. F. M. G. M.

A Red Compound of Cuprous Iodide with Quinoline Methiodide. MORITZ KOHN (*Monatsh.*, 1912, 33, 919—922).—An aqueous solution of quinoline methiodide colours cuprous iodide red, due to the formation of a substance which can be prepared more conveniently by the interaction of an aqueous solution of the methiodide and cuprous iodide dissolved in aqueous potassium iodide. The product is a red powder (microscopic needles); it can also be prepared by dissolving cuprous iodide in warm quinoline and treating with methyl iodide at room temperature.

The compound, which can be washed with water without appreciable decomposition, is shown by analysis to have the composition  $\text{CuI}, \text{C}_9\text{H}_7\text{N}, \text{CH}_3\text{I}$ . D. F. T.

Doubly-linked Carbon Atoms and the Carbon-Nitrogen Linking. X. Degradation of Quinoline and of *iso*Quinoline by Reduction. HERMANN EMDE (*Annalen*, 1912, 391, 88—109. Compare Abstr., 1911, i, 718).—1 : 1-Dimethyltetrahydroquinolinium iodide, which is obtained conveniently by mixing tetrahydroquinoline, methyl iodide, methyl alcohol, and sodium methoxide, is stable in aqueous solution towards sodium amalgam. The corresponding chloride, however, is readily attacked in concentrated aqueous solution on the water-bath, yielding *o*-propyldimethylaniline,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_4\text{Pr}$ , b. p. 228—229°/733 mm. This base forms a *picrate*, m. p. 99°; *platinichloride*, m. p. 152°, and *methiodide*, m. p. 179°; the *aurichloride*, yellow leaflets, and *platinichloride*, orange-red needles, of the last have m. p. 179° and 223° (decomp.) respectively.

In a similar manner, 2 : 2-dimethyltetrahydroisoquinolinium chloride in concentrated aqueous solution is decomposed by sodium amalgam on the water-bath, and yields *o*-vinylbenzyl dimethylamine,



b. p. 216—218°/754 mm. The substance, which has not been obtained quite pure by this method, forms a *picrate*, m. p. above 100°, yellow needles; *aurichloride*, m. p. 135°, golden leaflets, and *methiodide*, m. p. 199°, colourless needles (*picrate*, m. p. 154°; *aurichloride*, m. p. 120—140°; *platinichloride*, decomp. 235°). *o*-Vinylbenzyl dimethylamine in a purer condition is obtained by the distillation of a concentrated aqueous solution of 2 : 2-dimethyltetrahydroisoquinolinium hydroxide; the *picrate*, *aurichloride*, and *platinichloride* have m. p. 105°, 165°, and 184° respectively. The methiodide has m. p. 199°, and the *picrate*,

aurichloride, and platinichloride derived therefrom have m. p.  $165^{\circ}$  and  $171-172^{\circ}$ , and decomp.  $235^{\circ}$  respectively.

It seems, therefore, that in the tetrahydroisoquinoline series, Hofmann's method and the author's method yield the same initial fission product. Whilst, however, the further treatment of this product by Hofmann's method does not give satisfactory results, the elimination of the nitrogen from it is readily accomplished by the author's process.

*o*-Vinylbenzyl dimethylamine is converted into its methochloride, an aqueous solution of which is then reduced on the water-bath by 5% sodium amalgam. Trimethylamine is obtained together with *o*-methylstyrene,  $\text{CH}_2\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Me}$ , b. p.  $168^{\circ}/746$  mm., which readily polymerises to a substance resembling caoutchouc. *o*-Methylstyrene has also been prepared from *o*-xylene as follows: *o*-Xylene is converted successively into *o*-xylyl bromide, *o*-tolylacetonitrile, and  $\beta$ -*o*-tolylethylamine,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_2$ , by the usual methods. The base has b. p.  $227^{\circ}$ , and forms a *carbamate*,

$\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\cdot\text{NH}_3\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\text{Me}$ ,  
m. p.  $111^{\circ}$ , *hydrochloride*,  $\text{C}_9\text{H}_{13}\text{N}\cdot\text{HCl}\cdot 3\text{H}_2\text{O}$ , m. p.  $78^{\circ}$  ( $227^{\circ}$  when anhydrous), *platinichloride*, decomp. about  $253^{\circ}$ , *picrate*, m. p.  $177^{\circ}$ , and *aurichloride*, which has different m. p.'s according to the amount of water of crystallisation it contains, but decomposes at about  $195^{\circ}$ . A methyl-alcoholic solution of the carbamate reacts with methyl iodide and sodium methoxide to form *trimethyl- $\beta$ -*o*-tolylethylammonium iodide*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}_3\text{I}$ , m. p.  $250^{\circ}$ . The corresponding *picrate*, m. p.  $152.5^{\circ}$ , long, orange-yellow needles, *aurichloride*, m. p.  $156^{\circ}$ , golden-yellow needles, and *platinichloride*, decomp.  $244^{\circ}$ , orange needles, are described. By distillation with 33% potassium hydroxide, the iodide is decomposed, and yields trimethylamine and *o*-methylstyrene.

C. S.

**Asymmetric Selenites. II. Additive Products of Piperidine with Selenious and Sulphurous Acids.** LUIGI MARINO and A. TONINELLI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 98—103. Compare this vol., i, 127).—In boiling methyl alcohol the compound  $\text{C}_5\text{H}_{11}\text{N}\cdot\text{SeO}_2$  appears to be dissociated to some extent, whilst the analogous sulphur derivative,  $\text{C}_5\text{H}_{11}\text{N}\cdot\text{SO}_2$  (compare Michaelis, *Abstr.*, 1895, i, 430), exhibits the normal molecular weight. The specific conductivities of the selenium and sulphur compounds in methyl-alcoholic solutions at  $25^{\circ}$  are 0.006972 and 0.006303 respectively.

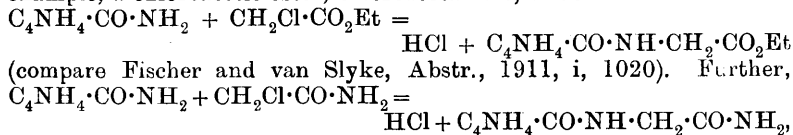
These compounds being good electrolytes, measurements were made with their methyl-alcoholic and aqueous-alcoholic solutions by Bredig and Fraenkel's method (*Abstr.*, 1905, ii, 692) to ascertain if they are acidic in character. The results indicate no interchange of position of the iminic hydrogen to give an acid analogous to aminosulphinic acid.

T. H. P.

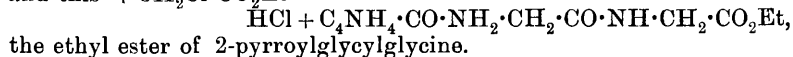
**Syntheses in the Pyrrole Group. VII. Derivatives of Pyrrole-2- and -3-carboxylic Acids.** BERNARDO ODDO and AUGUSTO MOSCHINI (*Gazzetta*, 1912, 42, ii, 244—256. Compare this vol., i, 721).—In the

preparation of pyrrole-2-carboxylic acid by means of magnesium pyrrol iodide (Abstr., 1909, i, 672), a yield of 85% of the acid, calculated on the pyrrole used, is obtainable.

The syntheses of polypeptides may be effected economically and efficiently by treating the amide of pyrrole-2-carboxylic acid with, for example, a chloroacetic ester, chloroacetamide, etc.:



and this  $+ \text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Et} =$



In a similar manner, the application of chlorides of carbamic acids,  $\text{Cl}\cdot\text{CO}\cdot\text{NH}_2$ , and of esters of chloro-formic acid, leads to pyrrole-2-amino-acids of the simplest type,  $\text{C}_4\text{NH}_4\cdot\text{CO}\cdot\text{NH}\cdot[\text{CO}\cdot\text{NH}]_n\cdot\text{CO}_2\text{H}$ .

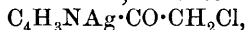
Pyrrolyl chloride may be obtained by the action of thionyl chloride on pyrrole-2-carboxylic acid (compare Fischer and van Slyke, *loc. cit.*).

*n*-Propyl pyrrole-2-carboxylate,  $\text{C}_4\text{NH}_4\cdot\text{CO}_2\text{Pr}$ , prepared from magnesium pyrrol bromide and propyl chloroformate, it is a dense, colourless liquid, b. p. 164—167°/50 mm. The isobutyl ester,  $\text{C}_9\text{H}_{13}\text{O}_2\text{N}$ , b. p. 119—122°/70 mm., and the isoamyl ester,  $\text{C}_{10}\text{H}_{15}\text{O}_2\text{N}$ , b. p. 186—190°/100 mm., are dense, faintly yellow liquids.

The amide of pyrrole-2-carboxylic acid may be obtained, more economically than by Fischer and van Slyke's method (*loc. cit.*), by the action of aqueous ammonia on an ester (methyl) of the acid in a sealed tube (at 155—160°).

By passing a current of carbon dioxide over magnesium pyrrol chloride, heating the mass at 250—270°, and treating with acid, pyrrole-3-carboxylic acid is obtained, the group  $\text{CO}_2\text{MgX}$  migrating from the 2- to the 3-position under the influence of heat. T. H. P.

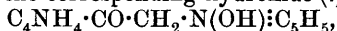
**Syntheses in the Pyrrole Group. VIII. Halogen- and Amino-derivatives of Methylpyrrolyl.** BERNARDO ODDO and AUGUSTO MOSCHINI (*Gazzetta*, 1912, 42, ii, 257—266. Compare preceding abstract).—2-Pyrrolyl chloromethyl ketone,  $\text{C}_4\text{H}_4\text{N}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , prepared by the action of chloroacetyl chloride on magnesium pyrrol bromide, forms white needles, m. p. 115°, and exhibits normal cryoscopic behaviour in acetic acid; its silver derivative,



was prepared. Oxidation of the ketone with permanganate gives 2-pyrrolylgyoxylic acid (compare Oddo, Abstr., 1910, i, 426). Under the influence of water or dilute alkali solution, the ketone is converted into 2-pyrrolyl hydroxymethyl ketone, which readily undergoes resinification.

The action of pyridine on 2-pyrrolyl chloromethyl ketone yields the pyridonium compound,  $\begin{array}{c} \text{CH}\cdot\text{CH} \\ | \quad \diagup \\ \text{CH}\cdot\text{NH} \end{array} \text{C}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NCl} \begin{array}{c} \diagdown \\ \text{CH}\cdot\text{CH} \\ | \quad \diagdown \\ \text{CH}\cdot\text{CH} \end{array} \text{CH}$  which forms needles, m. p. 135°, has a distinct alkaline reaction, gives ionic chlorine in aqueous solution, and yields crystalline precipitates

with platinic and auric chlorides. When treated with potassium hydroxide, it yields the corresponding hydroxide (I),



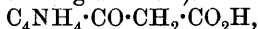
m. p.  $153^\circ$  (decomp.).

*2-Pyrryl aminomethyl ketone*,  $\text{C}_4\text{NH}_4 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NH}_2$ , forms dark yellow, nacreous leaflets, reduces ammoniacal silver and alkaline copper solutions, and is soluble in dilute hydrochloric acid, from which it is reprecipitated by ammonia.

*2-Pyrryl bromomethyl ketone*,  $\text{C}_6\text{H}_6\text{ONBr}$ , forms white needles, m. p.  $96^\circ$ .

*2-Pyrryl iodomethyl ketone*,  $\text{C}_6\text{H}_6\text{ONI}$ , forms faintly yellow needles, m. p.  $81^\circ$ . T. H. P.

**Syntheses in the Pyrrole Group. IX. Pyrroylacetic Acid.** BERNARDO ODDO and AUGUSTO MOSCHINI (*Gazzetta*, 1912, 42, ii, 267—269. Compare preceding abstract).—*2-Pyrroylacetic acid*,

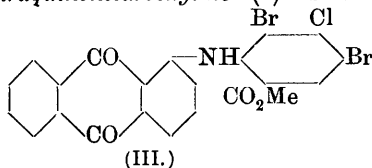
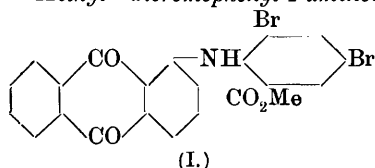


obtained as ester by the action of the chloride of monoethyl malonate on magnesium pyrryl bromide, forms slender, white needles, m. p.  $95^\circ$  (decomp.). The *ethyl* ester,  $\text{C}_9\text{H}_{11}\text{O}_3\text{N}$ , forms a felted mass of long, canary-yellow fibres, m. p.  $71^\circ$ , has the normal molecular weight in freezing benzene, and decomposes into  $\text{C}_4\text{NH}_4 \cdot \text{CO} \cdot \text{Me} + \text{CO}_2 + \text{Et} \cdot \text{OH}$  when heated with dilute alkali; its alcoholic solution gives a green coloration with ferric chloride. T. H. P.

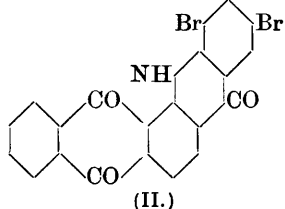
**Preparation of Condensation Products in the Anthracene Series.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 246966. Compare Abstr., 1911, i, 855).—When the esters of arylaminoanthraquinone-carboxylic or diaryldiaminoanthraquinonedicarboxylic acids are reduced, they furnish acridone derivatives, which dye cotton.

*1:5-Anthraquinonediacridone*, a violet powder, is prepared by reducing dimethyl 1:5-dianilinoanthraquinone-*o*-dicarboxylate with zinc and 30% ammonium hydroxide.

*Methyl dibromophenyl-1-aminoanthraquinonecarboxylate* (I) is ob-



tained by condensing 1-chloroanthraquinone with methyl 3:5-dibromoanthranilate; on reduction with sodium hyposulphite it furnishes *dibromoanthracridone* (II), which is isolated in the form of red flakes by subsequent oxidation (aerial or otherwise).



*Methyl chlorodibromophenyl-1-aminoanthraquinonecarboxylate* (III) is obtained in a similar manner from 1-chloroanthraquinone and methyl 4-chloro-3:5-dibromoanthranilate; on reduction it yields *chlorodibromoanthracridone*.

F. M. G. M.

Action of Heat on *d*-Lupanine,  $C_{16}H_{24}ON_2$ . S. Di PALMA (*Chem. Zentr.*, 1912, i, 1839; from *Giorn. Pharm. Chim.*, 1912, 61, 152—166).—Lupanine melts to an orange liquid, which darkens, evolving vapours with an odour of pyridine. The residue contains a *base*,  $C_{15}H_{22}N_2$ , which forms a *platinichloride*, m. p. 117—119° after dehydration, an *aurichloride*, m. p. 160—165° (decomp.), and a *hydrochloride*, m. p. 165° (decomp.). C. H. D.

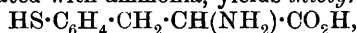
**Hydantoins. XII. Synthesis of Thietyrosine.** TREAT B. JOHNSON and CHARLES A. BRAUTLEOHT (*J. Biol. Chem.*, 1912, 12, 175—196. Compare this vol., i, 585).—2-Thio-1-phenyl-4-*p*-nitrobenzylidenehydantoin,  $NO_2 \cdot C_6H_4 \cdot CH : C \begin{smallmatrix} \text{CO-NPh} \\ \text{NH-CS} \end{smallmatrix}$ , prepared by condensation of nitrobenzaldehyde with thiophenylhydantoin, separates from glacial acetic acid in yellow prisms, m. p. 278—279°. When heated with ethyl bromide and sodium ethoxide in alcoholic solution, it yields 2-ethylthiol-1-phenyl-4-*p*-nitrobenzylidenehydantoin, yellow needles, m. p. 212—213°, which, when digested with hydrochloric acid, gives a quantitative yield of 1-phenyl-4-*p*-nitrobenzylidenehydantoin, needles, m. p. 300°. Reduction, by hydriodic acid and phosphorus, transforms this into 1-phenyl-4-*p*-aminobenzylhydantoin, prisms, m. p. 143°, the *hydriodide*, m. p. 275° (decomp.), *hydrochloride*, m. p. 260—262° (decomp.), *sulphate*, decomposing at 190—250° according to rate of heating, and *nitrate*, similarly decomposing at 190—240°, of which were also examined.

4-*p*-Aminobenzylhydantoin *hydrochloride* is obtained in good yield by the reduction of 4-*p*-nitrobenzylidenehydantoin by means of tin and hydrochloric acid, or by digestion of the corresponding *hydriodide* (formed in needles decomposing at 220° by reduction of *p*-nitrobenzylhydantoin with hydriodic acid and phosphorus) with an aqueous suspension of silver chloride. It forms prisms, m. p. 255—257° (decomp.), and, when treated with alkali, yields the corresponding 4-*p*-aminobenzylhydantoin, prisms, m. p. 145°. When diazotised and heated, the latter substance is transformed into tyrosinehydantoin, m. p. 258°.

4-*p*-Nitrobenzylhydantoin, pale yellow prisms, m. p. 238—240° (decomp.), obtained by nitration of benzylhydantoin at 0° by nitric acid (D 1.52), is transformed by tin and hydrochloric acid into the above-mentioned hydrochloride of 4-*p*-aminobenzylhydantoin.

When a solution of potassium xanthate is added to a diazotised solution of 4-aminobenzylhydantoin hydrochloride, 4-*p*-diazobenzylhydantoin *ethylxanthate* separates as an unstable voluminous, yellow precipitate, which, when allowed to remain at the ordinary temperature, or when heated at 90°, is converted into 4-benzylhydantoin *p*-ethylxanthate,  $EtO \cdot SCS \cdot C_6H_4 \cdot CH_2 \cdot CH \begin{smallmatrix} \text{CO-NH} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$ , m. p. about 170° (decomp.). Saponification with alkali or digestion with water transforms this into *thietyrosinehydantoin*, m. p. 248—249°, from which, after prolonged treatment with barium hydroxide, the *sulphate* of *thietyrosine disulphide* is obtained. The latter, when heated with

water, deposits *thiotyrosine disulphide*,  $[\text{CO}_2\text{H}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4]_2\text{S}_2$ , m. p.  $278^\circ$  (decomp.), which can also be obtained directly by diazotising the hydrochloride of 4-*p*-aminobenzylhydantoin, addition of the requisite quantity of potassium xanthate, separation of the yellow diazonium compound, and treatment of the latter with boiling barium hydroxide solution. The disulphide is characterised by its very sparing solubility in organic media, except glacial acetic acid. It does not give Adamkiewicz's reaction, Millon's test, or the biuret reaction. When heated with concentrated sulphuric acid, it yields a purple colour, which disappears when the solution is diluted with water. This test serves to detect the presence of traces of thiotyrosine in tyrosine. Its *sulphate* and *hydrochloride*, decomposing at  $278^\circ$ , were analysed. The *dibenzoyl* derivative decomposes at about  $200^\circ$  (decomp.). Potassium cyanate transformed the hydrochloride of thiotyrosine disulphide into the corresponding *hydantoin*,  $\text{C}_{20}\text{H}_{18}\text{O}_4\text{N}_4\text{S}_2$ , which decomposes at about  $278^\circ$ . *Thiotyrosine hydrochloride*, m. p.  $249^\circ$  (decomp.), is obtained by reduction of the disulphide with tin and hydrochloric acid, and, when heated with ammonia, yields *thiotyrosine*,



m. p. about  $250^\circ$ , according to mode of heating. The latter does not give Millon's test for tyrosine, and reacts with sulphuric acid in the same manner as the disulphide. A characteristic benzoyl derivative could not be prepared from it. It is very readily oxidised to the disulphide.

Thiotyrosine disulphide was also prepared from 1-phenyl-4-*p*-aminobenzylhydantoin by diazotisation in hydrochloric acid solution, followed by addition of potassium xanthate, separation of the diazonium compound so formed, and treatment of the latter with water and barium hydroxide. Reduction of the disulphide thus prepared leads to the isolation of thiotyrosine hydrochloride. H. W.

**Hydantoins. XIII. A New Method for the Synthesis of Phenylalanine.** TREAT B. JOHNSON and WILLIAM B. O'BRIEN (*J. Biol. Chem.*, 1912, 12, 205—213).—2-Thio-4-benzylidenehydantoin (Johnson and Nicolet, this vol., i, 53) when reduced by tin and hydrochloric acid gives an almost quantitative yield of phenylalanine.

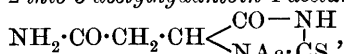
2-Thio-4-benzylidenehydantoin, when treated with aqueous chloroacetic acid, is desulphurised, with the formation of 4-benzylidenehydantoin.

When phenylalanine and potassium thiocyanate are heated during thirty minutes in a mixture of acetic acid and acetic anhydride, a quantitative yield of 2-thio-3-acetyl-4-benzylhydantoin, m. p.  $257^\circ$ , is obtained; this, when hydrolysed by hydrochloric acid, yields 2-thio-4-benzylhydantoin, m. p.  $185^\circ$ . Desulphurisation by means of aqueous chloroacetic acid converts this compound into the hydantoin of phenylalanine, m. p.  $190^\circ$ .

2-Thio-3-benzoylhydantoin was condensed with anisaldehyde in the presence of sodium acetate and acetic acid to 2-thio-4-anisylidenehydantoin, m. p.  $257^\circ$  (decomp.), and with piperonal to 2-thio-4-piperonylidenehydantoin, decomposing above  $285^\circ$ . H. W.

**Hydantoins. XIV. The Action of Potassium Thiocyanate on Asparagine.** TREAT B. JOHNSON and HERBERT H. GUEST (*Amer. Chem. J.*, 1912, 48, 103—111. Compare preceding abstracts).—Aspartic acid like glutamic acid (Johnson and Guest, this vol., i, 316) when treated with potassium thiocyanate in acetic anhydride solution yields practically no thiohydantoin derivative, the amido-nitrogen of the acid being eliminated as ammonia.

Asparagine, on the other hand, reacts normally with the above reagents, producing 2-thio-3-acetylhydantoin-4-acetamide,



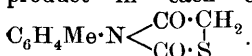
prismatic crystals, m. p. 222—223° (decomp.); a small amount of 2-thiohydantoin-4-acetamide, m. p. 246° (decomp.), is obtained at the same time. By hydrolysis of the first compound there is formed 2-thiohydantoin-4-acetic acid, hexagonal plates, m. p. 222° (decomp.); this substance can be desulphurised by digesting with an aqueous solution of chloroacetic acid, when the product is hydantoin-4-acetic acid,  $\text{CO}_2\text{H} \cdot \text{CH}_2 \cdot \text{CH} \begin{array}{l} \text{CO} \cdot \text{NH} \\ \text{NH} \cdot \text{CO} \end{array}$ , m. p. 214—215° (compare Dakin, Abstr., 1910, i, 590; Lippich, Abstr., 1908, 861; etc.). D. F. T.

**Hydantoins. XV. The Desulphurisation of 2-Thiohydantoins.** TREAT B. JOHNSON, GEORGE MORTON PFAU, and WILLARD WELLINGTON HODGE (*J. Amer. Chem. Soc.*, 1912, 34, 1041—1048).—A further continuation of the investigation on the desulphurisation of 2-thiohydantoins by chloroacetic acid (compare preceding abstract; also Wheeler and Liddle, Abstr., 1908, i, 692; and Johnson and Nicolet, this vol., i, 52); it is found that the action of chloroacetic acid on disubstituted thiocarbamides is of a different nature, producing thiazole derivatives.

2-Thio-1-*p*-tolylhydantoin,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{N} \begin{array}{l} \text{CO} \cdot \text{CH}_2 \\ \text{CS} \cdot \text{NH} \end{array}$ , is obtained by warming a solution of *p*-tolyl thiocarbimide with glycine and an equimolecular quantity of potassium hydroxide; it forms yellow crystals, m. p. 228° (compare Marckwald, Neumark, and Stelzner, Abstr., 1892, 149), and on heating with an aqueous solution of chloroacetic acid is converted into 1-*p*-tolylhydantoin, m. p. 206°; the action of benzaldehyde on this substance in the presence of sodium acetate and acetic acid gives 1-*p*-tolyl-4-benzylidenehydantoin,  $\text{C}_6\text{H}_4\text{Me} \cdot \text{N} \begin{array}{l} \text{CO} \cdot \text{C} \cdot \text{CHPh} \\ \text{CO} \cdot \text{NH} \end{array}$ , plates, m. p. 259°, which can also be obtained by the action of chloroacetic acid on 2-thio-1-*p*-tolyl-4-benzylidenehydantoin, plates, m. p. 188°, obtained in an analogous manner from the thio-*p*-tolylhydantoin.

2-Thio-1-benzylhydantoin, obtained from benzyl thiocarbimide and glycine, has m. p. 128°.

When *s*-phenyl-*p*-tolylthiocarbimide, *p*-tolylthiocarbimide, or *s*-*p*-tolylpiperidylthiocarbimide are digested with chloroacetic acid solution, the product in each case is 2:4-diketo-3-*p*-tolyltetrahydrothiazole,



For the smooth interaction of *o*-tolylthiocarbimide and glycine to

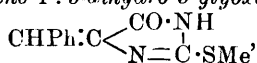
form 2-thio-1-*o*-tolylhydantoin, yellow plates, m. p. 149—150° (compare Marchwald, Neumark, and Stelzner, *loc. cit.*), the presence of two molecular proportions of potassium hydroxide is necessary; the product can be desulphurised by chloroacetic acid to 1-*o*-tolylhydantoin, prismatic crystals, m. p. 148°; this is almost quantitatively converted by benzaldehyde into 1-*o*-tolyl-4-benzylidenehydantoin, prismatic crystals, m. p. 193—194°, which is also obtained when 2-thio-1-*o*-tolyl-4-benzylidenehydantoin (prisms, 165°), the product of the action of thio-*o*-tolylhydantoin and benzaldehyde, is desulphurised.

Contrary to a previous statement (Brautlecht, Abstr., 1911, i, 922), 2-thio-1-phenylhydantoin is easily converted by digestion with a concentrated aqueous solution of chloroacetic acid into 1-phenylhydantoin.

D. F. T.

**Hydantoins. XVI. The Alkylation of 2-Thio-4-benzylidenehydantoin.** TREAT B. JOHNSON and BEN H. NICOLET (*J. Amer. Chem. Soc.*, 1912, 34, 1048—1054. Compare Johnson and Nicolet, this vol., i, 585).—The alkylation of the aldehyde condensation products of hydantoin and 2-thiohydantoin is of especial interest on account of the similarity in the structure of these substances and of uracil and thiouracil.

Methylation of 2-thio-4-benzylidenehydantoin (Wheeler, Nicolet, and Johnson, Abstr., 1911, i, 1031), with excess of methyl iodide in the presence of one molecular proportion of potassium hydroxide yields 2-methylthiol-4-benzylidene-1:5-dihydro-5-glyoxalone,



creamy needles, m. p. 202°, which can be hydrolysed by concentrated hydrochloric acid to 4-benzylidenehydantoin. Methylation of the original substance with two molecular proportions of sodium ethoxide and excess of methyl iodide produces 2-methylthiol-4-benzylidene-1-methyl-1:5-dihydro-5-glyoxalone, yellow prisms, m. p. 105°, which on hydrolysis gives 4-benzylidene-1-methylhydantoin, flat, colourless prisms, m. p. 221°.

Alkylation of 2-thio-4-benzylidenehydantoin with ethyl iodide gives 2-ethylthiol-4-benzylidene-1:5-dihydro-5-glyoxalone, pale yellow needles, m. p. 165—166°, which can be methylated to 2-ethylthiol-4-benzylidene-1-methyl-1:5-dihydro-5-glyoxalone, yellow, prismatic crystals, m. p. 94—95°. If the original alkylation with ethyl iodide be performed in the presence of sodium ethoxide, the product is 2-ethylthiol-4-benzylidene-1-ethyl-1:5-dihydro-5-glyoxalone, an oil which on hydrolysis yields 4-benzylidene-1-ethylhydantoin, colourless prisms, m. p. 160°; this can also be obtained by the action of ethyl bromide and alkali on 4-benzylidenehydantoin, and by further treatment with methyl iodide and sodium ethoxide is converted into 4-benzylidene-3-methyl-1-ethylhydantoin, yellow flakes, m. p. 94°; also by alkylation with ethyl bromide it gives 4-benzylidene-1:3-diethylhydantoin, m. p. 91—92°.

D. F. T.

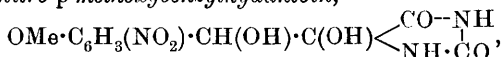
**Hydantoins. XVII. Synthesis of the Hydantoin of 3-Aminotyrosine.** TREAT B. JOHNSON and ROBERT BENGIS (*J. Amer. Chem. Soc.*, 1912, 34, 1054—1061).—4-Anisylhydantoin,

$\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH} \begin{smallmatrix} \text{CO} - \text{NH} \\ | \\ \text{NH} - \text{CO} \end{smallmatrix}$ , m. p. 175—176°, together with a certain amount of *anisylhydan-toic acid*,

$\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}(\text{CO}_2\text{H}) \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$ , m. p. 156°, is obtained by the reduction of 4-anisylidenehydantoin (Wheeler and Hoffman, Abstr., 1911, i, 498) in aqueous suspension with sodium amalgam; on treatment with a mixture of concentrated and fuming nitric acid, it yields 4-*m*-nitro-*p*-methoxybenzylhydantoin, prisms, m. p. 186—188°, with half a molecule of water of crystallisation (compare Johnson and Brautlecht, Abstr., 1911, i, 813); this can be quantitatively reduced by ferrous sulphate and ammonia solution to 4-*m*-amino-*p*-methoxybenzylhydantoin, a crystalline solid, m. p. 175—177°, *hydrochloride*, needles, m. p. 271—272° (decomp.); the constitution of this base is proved by its identity with that of the base mentioned below.

*m*-Nitro-*p*-methoxybenzaldehyde, m. p. 83°, obtained by nitration of anisaldehyde, condenses with hydantoin when heated with sodium acetate and acetic acid, producing 4-*m*-nitro-*p*-methoxybenzylidenehydantoin, flat prisms (from acetic acid), containing one molecule of acetic acid of crystallisation, m. p. 276—277° (decomp.); this is reduced by phosphorus and hydriodic acid to 4-*m*-amino-*p*-hydroxybenzylhydantoin (the hydantoin of aminotyrosine), *hydrochloride*, prismatic crystals, m. p. 254° (decomp.), containing one molecule of water of crystallisation; reduction by ferrous sulphate and ammonia, on the other hand, affects only the nitro-group, producing 4-*m*-amino-*p*-methoxybenzylidenehydantoin, *hydrochloride*, needles, m. p. 285—286° (decomp.); this base can be further reduced by tin and hydrochloric acid to the above 4-*m*-amino-*p*-methoxybenzylhydantoin, *hydrochloride*, m. p. 271—272°.

The action of ordinary concentrated nitric acid on 4-anisylidenehydantoin causes oxidation to a glycol derivative, 4-*hydroxy*-4-*α*-*hydroxy m*-nitro-*p*-methoxybenzylhydantoin,



yellow needles, m. p. 206—207°.

D. F. T.

**Hydantoins. XVIII. Synthesis of 3-Bromotyrosine.**  
TREAT B. JOHNSON and ROBERT BENGIS (*J. Amer. Chem. Soc.*, 1912, 34, 1061—1066).—*m*-Bromoanisaldehyde (pale yellow prisms, m. p. 52—53°, from the action of bromine on anisaldehyde) condenses with hydantoin under the usual treatment, producing 4-*m*-bromo-*p*-methoxybenzylidenehydantoin, yellow needles, m. p. 267—268°, which can be reduced in alcoholic solution by tin and hydrogen chloride to 4-*m*-bromo-*p*-methoxybenzylhydantoin, triclinic crystals, m. p. 210—211°. This last substance can also be obtained from 4-*m*-amino-*p*-methoxybenzylhydantoin (Johnson and Bengis, preceding abstract) by diazotisation and subsequent treatment with a solution of cuprous bromide. On heating with barium hydroxide solution under pressure, the hydantoin ring is disrupted with formation of *α*-amino-*β*-*m*-bromo-*p*-methoxyphenylpropionic acid  $\text{OMe} \cdot \text{C}_6\text{H}_3\text{Br} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{CO}_2\text{H}$ , rect-

angular plates, m. p. 235—236° (decomp.); this acid is easily demethylated by boiling with hydrobromic acid, with the production of 3-bromotyrosine,  $\text{OH}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}\cdot\text{H}_2\text{O}$ , tetrahedral crystals of sweet taste, m. p. 247—248° (decomp.), *hydrobromide*, m. p. 190—191° (decomp.); *picrate* and *platinichloride* are extremely soluble in water.

*m*-Bromo-*p*-hydroxybenzaldehyde condenses with hydantoin, giving a poor yield of 4-*m*-bromo-*p*-hydroxybenzylidenehydantoin, yellow needles, decomposing at 295°; this is reduced by hydriodic acid to 4-*p*-hydroxybenzylhydantoin (tyrosinehydantoin).

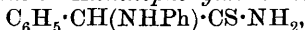
4-*m*-Amino-*p*-hydroxybenzylhydantoin (Johnson and Bengis, *loc. cit.*), when diazotised and treated with cuprous bromide solution, gives 4-*m*-bromo-*p*-hydroxybenzylhydantoin (3-bromotyrosinehydantoin),

$\text{OH}\cdot\text{C}_6\text{H}_3\text{Br}\cdot\text{CH}_2\cdot\text{CH}\begin{smallmatrix} \text{CO}\text{---}\text{NH} \\ \text{NH}\cdot\text{CO} \end{smallmatrix}$ , prisms, m. p. 284—285° (decomp.).

D. F. T.

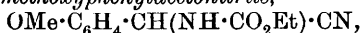
**Hydantoins. XIX. Synthesis of 5-Thiohydantoins.** TREAT B. JOHNSON and LEWIS H. CHERNOFF (*J. Amer. Chem. Soc.*, 1912, **34**, 1208—1213).—Although carbethoxyglycinamide does not undergo condensation to hydantoin (Fischer and Otto, *Abstr.*, 1893, i, 608), it is found that the thioamide condenses smoothly, whereas in the cases of the isomeric ethyl hydantoates it is the thio-ester which is indifferent (compare Harries and Weiss, *Abstr.*, 1893, i, 738). The phenylated thioamides are also found to condense, resembling the substituted carbethoxyglycinamides of Lehmann (*Abstr.*, 1901, i, 275) and of Clark and Francis (*Trans.*, 1911, **99**, 319).

5-Thiohydantoin,  $\text{NH}\begin{smallmatrix} \text{CS}\text{---}\text{CH}_2 \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$ , obtained by dissolving carbethoxy-aminoacet-thioamide (this vol., p. 305) in 5—10% sodium hydroxide containing one molecular proportion of alkali and acidifying, crystallises from hot water in colourless, lanceolate crystals, which decompose above 220°. Unlike 2-thiohydantoin, it undergoes oxidation in aqueous or alkaline solution, the latter changing colour from pink to deep red. Concentrated hydrochloric acid converts it into hydrogen sulphide and hydantoin, and it yields with benzaldehyde a brownish-yellow, insoluble product. *Anilinophenylacetothioamide*,



prepared by the addition of hydrogen sulphide to anilinophenylacetonitrile (Knoevenagel, *Abstr.*, 1904, i, 989), crystallises from spirit in long, slender prisms, m. p. 130°; similarly, *carbethoxyaminophenylacetothioamide*,  $\text{C}_6\text{H}_5\cdot\text{CH}(\text{NH}\cdot\text{CO}_2\text{Et})\cdot\text{CS}\cdot\text{NH}_2$ , from urethanophenylacetonitrile (Lehmann, *loc. cit.*), crystallises in colourless needles, m. p. 127°, which dissolve in 10% sodium hydroxide, yielding the

stable 5-thio-4-phenylhydantoin,  $\text{NH}\begin{smallmatrix} \text{CS}\text{---}\text{CHPh} \\ \text{CO}\cdot\text{NH} \end{smallmatrix}$ , as a yellow powder, decomposing at about 259°. Condensation of urethane with *p*-methoxymandelonitrile in presence of zinc chloride furnishes *carbethoxyamino-p-methoxyphenylacetonitrile*,



m. p.  $117^{\circ}$ , which may be converted into the *thioamide*, m. p.  $146^{\circ}$ , and this into 5-thio-4-p-methoxyphenyl/hydantoin,



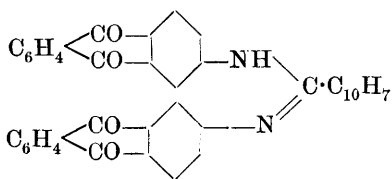
this separates as a yellow solid decomposing at about  $263^{\circ}$ .

J. C. W.

**1:5-Naphthylenediamine.** FRANZ KUNCKELL and HANNS SCHNEIDER (*Chem. Zeit.*, 1912, 36, 1021).—1:5-Naphthylenediamine, dissolved in benzene, was treated with acetic anhydride, whereby the corresponding *diacetyl* compound, m. p. about  $360^{\circ}$ , was obtained in poor yield. The authors have made the unpleasant discovery that this compound causes violent irritation of the skin. Since 1:5-naphthylene-diamine has been investigated by a number of chemists and no such unpleasant action has been noted, it would appear that the latter is a specific property of the acetyl derivative.

H. W.

**Preparation of Condensation Products in the Anthraquinone Series.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 246477).—



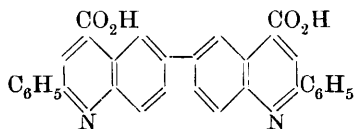
The compound (annexed formula) is obtained when a fusion of 2-aminoanthraquinone (10 parts), naphthalene (50 parts), and copper (0.5 part) is carefully treated at  $100\text{--}120^{\circ}$  with carbon tetrachloride, the temperature raised to  $140\text{--}150^{\circ}$ , and maintained until evolution of hydrogen

chloride ceases; it crystallises from chlorobenzene, and has m. p.  $298\text{--}302^{\circ}$  (about).

The analogous compound obtained by replacing the naphthalene with diphenyl dissolves in acetic acid; these products furnish on sulphonation readily soluble *sulphonic acids*, which dye wool in yellow shades.

F. M. G. M.

**Preparation of 2-Phenyl- and Substituted 2-Phenyl-6:6'-di-quinolyl-4:4'-dicarboxylic Acids, their Homologues and Derivatives.** CHEMISCHE FABRIK AUF ACTIEN VORM. E. SCHERING (D.R.-P. 246078).—2-Phenylquinoline-4-carboxylic acid, prepared from aniline, benzaldehyde, and pyruvic acid, has previously been described; it is now found that analogous reactions take place when the aniline is replaced by benzidine, tolidine, or dianisidine, and the benzaldehyde by substituted benzaldehydes, yielding substituted phenyldiquinolylcarboxylic acids.



6:6' - Diquinolyl - 2:2' - diphenyl - 4:4' - dicarboxylic acid (annexed formula), m. p.  $225^{\circ}$ , is prepared by boiling together an alcoholic solution of benzidine (65 parts), pyruvic acid (61 parts), and benzaldehyde (75

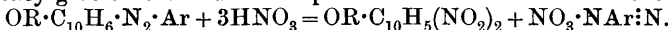
parts) during several hours, when the product separates in yellowish-brown crystals.

6 : 6'-*Diquinolyl-2 : 2'-dihydroxydiphenyl-4 : 4'-dicarboxylic acid*, m. p. 248°, is obtained when the benzaldehyde in the foregoing reaction is replaced by salicylaldehyde, whilst 6 : 6'-*diquinolyl-2 : 2'-diphenyl-8 : 8'-dimethyl-4 : 4'-dicarboxylic acid*, a yellow powder, results from the employment of *o*-toluidine; it is insoluble in the ordinary organic solvents and does not melt below 300°.

8 : 8'-*Dimethoxy-6 : 6'-diquinolyl-2 : 2'-diphenyl-4 : 4'-dicarboxylic acid*, m. p. 290° (about), is prepared in an analogous manner from *o*-dianisidine. F. M. G. M.

**Compounds of Certain Hydrated Metallic Salts with Caffeine.** FILIPPO CALZOLARI (*Gazzetta*, 1912, 42, ii, 15—21).—The addition of caffeine to concentrated solutions of salts yields the following compounds, which are stable to the action of air and light, and are decomposed by water, alcohol or chloroform in the cold with separation of caffeine:  $\text{MgI}_2 \cdot 8\text{H}_2\text{O} \cdot 2\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ ;  $\text{MnI}_2 \cdot 8\text{H}_2\text{O} \cdot 2\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ ;  $\text{CoI}_2 \cdot 8\text{H}_2\text{O} \cdot 2\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ ;  $\text{NiI}_2 \cdot 8\text{H}_2\text{O} \cdot 2\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ ;  $\text{Mg}(\text{ClO}_4)_2 \cdot 8\text{H}_2\text{O} \cdot 2\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ ;  $\text{Mn}(\text{ClO}_4)_2 \cdot 8\text{H}_2\text{O} \cdot 2\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ ;  $\text{Co}(\text{ClO}_4)_2 \cdot 8\text{H}_2\text{O} \cdot 2\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ ;  $\text{Ni}(\text{ClO}_4)_2 \cdot 8\text{H}_2\text{O} \cdot 2\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ ;  $\text{Mg}(\text{SCN})_2 \cdot 6\text{H}_2\text{O} \cdot 2\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ ;  $\text{Mn}(\text{SCN})_2 \cdot 8\text{H}_2\text{O} \cdot 2\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ ;  $\text{Fe}(\text{SCN})_2 \cdot 8\text{H}_2\text{O} \cdot 2\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ ;  $\text{Co}(\text{SCN})_2 \cdot 8\text{H}_2\text{O} \cdot 2\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ ;  $\text{Ni}(\text{SCN})_2 \cdot 8\text{H}_2\text{O} \cdot 2\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ ;  $\text{Ni}(\text{NO}_3)_2 \cdot 8\text{H}_2\text{O} \cdot 2\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4$ , (compare Barbieri and Calzolari, *Abstr.*, 1911, i, 184, 266, 268; Barbieri and Lanzoni, *Abstr.*, 1911, i, 268). T. H. P.

**Etherification of *o*-Hydroxyazo-compounds.** I. G. CHARRIER and G. FERRERI (*Atti R. Accad. Sci. Torino*, 1912, 47, 811—840; *Gazzetta*, 1912, 42, ii, 117—144).—It has been previously shown (*Abstr.*, 1910, i, 287; 1911, i, 1045) that *o*-aminoazo- and *o*-hydroxyazo-compounds tend to react as true azo-compounds, for instance,  $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{N} : \text{NPh}$  and  $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{N} : \text{NPh}$ , and not as the tautomeric forms,  $\text{NH} : \text{C}_{10}\text{H}_6 \cdot \text{N} \cdot \text{NHPh}$  and  $\text{O} : \text{C}_{10}\text{H}_6 \cdot \text{N} \cdot \text{NHPh}$ , containing a quinonoid instead of an aromatic nucleus. Also, in their reactions with alkyl sulphates, the *o*-hydroxyazo-compounds are now found to behave as true azo-compounds, and a series of methyl and ethyl ethers of the general formula  $\text{OR} \cdot \text{C}_{10}\text{H}_6 \cdot \text{N} : \text{NAr}$  have been prepared. These ethers are decomposed by nascent hydrogen according to the equation:  $\text{OR} \cdot \text{C}_{10}\text{H}_6 \cdot \text{N}_2 \cdot \text{Ar} + 2\text{H}_2 = \text{NH}_2\text{Ar} + \text{OR} \cdot \text{C}_{10}\text{H}_6 \cdot \text{NH}_2$ , whilst with nitric acid they give ethers of dinitronaphthols and diazonium nitrates:



The ethers crystallise well and are readily hydrolysed by dilute mineral acids, but show great stability towards alkalis. They exhibit marked basic properties, forming salts with mineral acids and unstable double salts with mercuric, platinic, and stannic chlorides, etc.

1-*Benzeneazo-2-naphthyl methyl ether*,  $\text{OMe} \cdot \text{C}_{10}\text{H}_6 \cdot \text{N} : \text{NPh}$ , prepared by the interaction of 1-benzeneazo-2-naphthol and methyl sulphate in sodium hydroxide solution (30%), forms garnet-red plates m. p. 62°, and

dissolves in dilute mineral acids, giving intense red colorations, and in concentrated sulphuric acid, forming a ruby-red solution; its *hydrochloride*,  $C_{17}H_{14}ON_2 \cdot HCl$ , forms red crystals with metallic lustre. 1-Amino-2-naphthyl methyl ether,  $NH_2 \cdot C_{10}H_6 \cdot OMe$ , obtained together with aniline by the action of nascent hydrogen on the methoxyazo-compound, forms silky, white needles, m. p.  $53^\circ$ . 1-Acetylamino-2-naphthyl methyl ether forms white prisms, m. p.  $178^\circ$ . 1:6-Dinitro-2-naphthyl methyl ether,  $OMe \cdot C_{10}H_5(NO_2)_2$ , crystallises in pale yellow needles, m. p.  $157-158^\circ$ .

1-o-Toluenazo-2-naphthyl methyl ether,  $OMe \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4Me$ , forms red leaflets, m. p.  $58^\circ$ , and gives a ruby-red solution in concentrated sulphuric acid and red solutions in dilute mineral acids. The *hydrochloride*,  $C_{18}H_{16}ON_2 \cdot HCl$ , forms cantharides-green needles.

1-p-Toluenazo-2-naphthyl methyl ether crystallises in garnet-red plates, m. p.  $68^\circ$ , and yields red solutions in concentrated sulphuric and dilute mineral acids. The *hydrochloride* forms minute, green needles with metallic lustre.

1-o-Methoxybenzeneazo-2-naphthyl methyl ether,  
 $OMe \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4 \cdot OMe$ ,

prepared from either 1-o-hydroxybenzeneazo-2-naphthol or 1-o-anisylazo-2-naphthol by the action of methyl sulphate and sodium hydroxide, forms mammillary masses of bright red leaflets with a golden lustre, m. p.  $93-94^\circ$ , and gives a red solution in concentrated sulphuric acid. The *hydrochloride*,  $C_{18}H_{16}O_2N_2 \cdot HCl$ , separates in emerald-green needles.

1-p-Hydroxybenzeneazo-2-naphthol,  $OH \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4 \cdot OH$ , prepared by the action of *p*-hydroxybenzenediazonium chloride on  $\beta$ -naphthol in alkaline solution, forms cantharides-green needles or leaflets, m. p.  $194^\circ$ . 1-p-Acetoxybenzeneazo-2-naphthol,

$OH \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4 \cdot OAc$ ,

crystallises in shining orange-red needles, m. p.  $115^\circ$ , and the corresponding benzoyl derivative,  $C_{23}H_{16}O_3N_2$ , in red needles, m. p.  $164^\circ$ .

1-p-Methoxybenzeneazo-2-naphthyl methyl ether,  
 $OMe \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4 \cdot OMe$ ,

obtained by the interaction of methyl sulphate and 1-p-hydroxybenzeneazo-2-naphthol in 30% sodium hydroxide solution, forms prismatic needles, m. p.  $107^\circ$ , and dissolves in sulphuric acid with red coloration. Its *hydrochloride*,  $C_{18}H_{16}O_2N_2 \cdot HCl$ , separates in emerald-green needles showing metallic lustre.

The action of methyl sulphate on 1-p-hydroxybenzeneazo-2-naphthol in 15% sodium hydroxide solution yields: (1) 1-p-methoxybenzeneazo-2-naphthol,  $OH \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4 \cdot OMe$ , m. p.  $137^\circ$ , and (2) 1-p-hydroxybenzeneazo-2-naphthyl methyl ether,  $OMe \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4 \cdot OH$ , which crystallises in reddish-brown leaflets, m. p.  $225^\circ$  (decomp.), and dissolves in sulphuric acid with a red coloration, and in dilute solutions of alkali hydroxides or carbonates, or ammonia, giving yellow or orange liquids according to the concentration; its *hydrochloride*,

$C_{17}H_{14}O_2N_2 \cdot HCl$ ,

forms emerald-green needles with metallic lustre.

1-o-Methoxybenzeneazo-2-naphthyl ethyl ether,  
 $OEt \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4 \cdot OMe$ ,

forms bright red leaflets, m. p.  $75^{\circ}$ , its *hydrochloride*,  $C_{19}H_{18}O_2N_2 \cdot HCl$ , giving red crystals.

1-p-Methoxybenzeneazo-2-naphthyl ethyl ether crystallises in red, prismatic plates, m. p.  $52-53^{\circ}$ , and its *hydrochloride* in greenish-brown needles.

1-o-Ethoxybenzeneazo-2-naphthyl methyl ether,  
 $OMe \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4 \cdot OEt$ ,  
 forms long, flat, red needles or golden-yellow plates, m. p.  $136^{\circ}$ ; its *hydrochloride* separates in metallic, green needles.

1-o-Ethoxybenzeneazo-2-naphthyl ethyl ether,  
 $OEt \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4 \cdot OEt$ ,  
 crystallises in pale red needles, m. p.  $102^{\circ}$ , and its *hydrochloride* as a reddish-brown powder with a green, metallic lustre.

1-p-Ethoxybenzeneazo-2-naphthyl methyl ether,  
 $OMe \cdot C_{10}H_6 \cdot N:N \cdot C_6H_4 \cdot OEt$ ,  
 forms flat, orange needles, m. p.  $113^{\circ}$ , and its *hydrochloride*, green crystals with a golden, metallic lustre.

1-p-Ethoxybenzeneazo-2-naphthyl ethyl ether forms orange-yellow needles, m. p.  $81^{\circ}$ .

1- $\alpha$ -Naphthaleneazo-2-naphthyl methyl ether,  $OMe \cdot C_{10}H_6 \cdot N:N \cdot C_{10}H_7$ , separates in reddish-brown leaflets, m. p.  $67^{\circ}$ , and its *hydrochloride* in cantharides-green crystals.

1- $\alpha$ -Naphthaleneazo-2-naphthyl ethyl ether forms flat, dark garnet-red needles, m. p.  $105-106^{\circ}$ , and its *hydrochloride*, a green, crystalline mass with a metallic lustre.

1- $\beta$ -Naphthaleneazo-2-naphthyl methyl ether crystallises in garnet-red prisms, m. p.  $94-95^{\circ}$ , and its *hydrochloride* in slender, metallic green needles.  
 T. H. P.

**Preparation of Chloro-1-diazo-2-oxy- and of Chloro-2-diazo-1-oxy-naphthalenesulphonic Acids.** KALLE & Co. (D.R.-P. 246573 and 246574).—The chlorination of *o*-diazo-oxynaphthalene-sulphonic acids has not previously proved satisfactory; it is now found to proceed smoothly at higher temperatures and in the presence of sulphuric acid containing sulphur trioxide.

1-Diazo-2-oxynaphthalene-4-sulphonic acid (125 parts), dissolved in concentrated sulphuric acid (285 parts), is treated at a temperature not exceeding  $20^{\circ}$  with 100 parts of sulphuric acid containing 70% anhydride, and subsequently maintained at  $50^{\circ}$  during the passage of a stream of chlorine; the *chloro-1-diazo-2-oxy-4-naphthalenesulphonic acid* is isolated as a yellow, crystalline powder.

The chlorination of 2-diazo-1-oxynaphthalene-5-sulphonic acid is carried out in a similar manner, but at lower temperatures ( $10-15^{\circ}$  and  $40-45^{\circ}$  respectively).

The second patent states that a more satisfactory method consists in lowering the temperature in both cases to about  $10^{\circ}$ , but forcing an excess of chlorine in under a pressure of 7–8 atmospheres in the first case and 5–6 atmospheres in the second, and keeping the mixtures continually agitated during about twelve hours at the ordinary temperature. *Chloro-2-diazo-1-oxynaphthalene-5-sulphonic acid* forms pale greenish-grey crystals.  
 F. M. G. M.

**Amylases. IV. A Further Investigation of the Properties of Pancreatic Amylase.** HENRY CLAPP SHERMAN and M. D. SCHLESINGER (*J. Amer. Chem. Soc.*, 1912, 34, 1104—1111. Compare Abstr., 1911, i, 827).—Preparations of pancreatic amylase made during the summer months proved to be less active than those obtained during colder weather; a method of preparation is now described with special precautions as to temperature.

Recalculation of the composition of the amylase on the assumption that the apparent ash is mainly phosphoric acid gives a composition C 51.9, H 6.6, N 15.3, S 1.0, P 0.8, O (and undetermined) 24.4, which is rather similar to that of casein; the heat of combustion (5568 calories per gram) is, however, rather lower than that of casein (5629). The aqueous solution of the amylase (which coagulates completely at 70°) shows great activity towards starch, and a portion of one preparation hydrolysed 1,000,000 times its weight of starch (the concentration of the amylase in this solution was 1:100,000,000) to the erythrodextrin stage in thirty hours, and to products exhibiting no reaction with iodine in forty-eight to ninety-six hours. The sugars formed were maltose and dextrose. The enzyme, which also shows proteoclastic power, deteriorates rapidly when dissolved in pure water, but retains its activity for a much longer period in aqueous solution containing sodium chloride and sodium phosphate, or when dissolved in 50% alcohol or acetone. D. F. T.

**The Proteolytic Action of Taka-diastrase.** OLGA SZÁNTÓ (*Biochem. Zeitsch.*, 1912, 43, 31—43).—Acids inhibit the action of taka-diastrase in very low concentration. The inorganic acids inhibit Taka-diastrase much less than they do trypsin. On the other hand, Taka-diastrase is far more sensitive towards organic acids. In addition to the inhibiting action, acids also destroy the ferment. Hydrochloric acid acts the most strongly; its destructive power on trypsin is much less than that on Taka-diastrase. In spite of their strong inhibitory action, organic acids only have a weak destructive action on the ferment. Alkalis also inhibit the action, but much less than acids. They do not possess a destructive power. Salts, with the exception of sodium lactate, have but little effect on the proteolytic action of Taka-diastrase. The inhibitory action of sodium lactate on this ferment is about three times as great as it is on trypsin. Dextrose, lactose, and starch have no action, whereas lævulose has a slight inhibitory action. S. B. S.

**The Relation of Certain Nucleic Acids to Enzymes which Split Glucosides.** HELENE TSCHERNORUTZKY (*Zeitsch. physiol. Chem.* 1912, 80, 298—306).—The glucoside structure of nucleic acids (Steudel) led to the enquiry whether emulsin and myrosin will split nucleic acids. The answer is in the affirmative, but consideration of the quantitative yield of purine substances and phosphoric acid liberated, finally led to the conclusion that the cleavage in question was due, not to the enzymes mentioned, but to nucleases mixed with them. W. D. H.

**Enzyme Action. XVI. Enzymes of the Emulsin Type. I.** Prunase, the Correlate of Prunasin. HENRY E. ARMSTRONG, EDWARD F. ARMSTRONG, and EDWARD HORTON (*Proc. Roy. Soc.*, 1912, *B*, 85, 359—362. Compare this vol., i, 594).—The conclusion was previously drawn that the action of almond emulsin on amygdalin is effected through the agency of two distinct enzymes: amygdalase, by which the amygdalin is converted into dextrose and Fischer's glucoside (*d*-mandelonitrile), and  $\beta$ -glucose, by which the latter glucoside is further resolved into dextrose and phenylhydroxyacetonitrile. This conclusion is verified by the discovery in the leaf of the cherry laurel (*Prunus laurocerasus*) of a  $\beta$ -glucose which is without action on amygdalin, yet readily decomposes Fischer's glucoside.

The name *prunasin* is given to Fischer's glucoside, on account of its general occurrence in the various species of *Prunus*, and the enzyme is termed *prunase*.

Prunasin is found to occur in the leaf of these plants, whereas amygdalin has only been found in the fruit kernel; the two enzymes are found to occur in a corresponding manner.

A discussion on the selective action of enzymes is given. W. J. Y.

**Enzyme Action. XVII. Enzymes of the Emulsin Type. II. The Distribution of  $\beta$ -Enzymes in Plants.** HENRY E. ARMSTRONG, EDWARD F. ARMSTRONG, and EDWARD HORTON (*Proc. Roy. Soc.*, 1912, *B*, 85, 363—369. Compare preceding abstract).—Several plants were tested with regard to their hydrolytic activity towards the glucosides linamarin, amygdalin, prunasin, and salicin in order to determine the distribution of the enzymes linase, amygdalase, prunase, and salicase.

The material was washed, cut up in a mincing machine, dried, and ground to a fine powder, and employed as such in the experiments. The extent of hydrolysis of the first three glucosides was determined by the quantity of hydrogen cyanide set free, and of the salicin by the dextrose liberated. The results, given in a table, show that amygdalase is sparsely distributed, and is almost confined to those seeds of plants in which amygdalin is present. Prunase is widely distributed, and the experiments point to the probability that a distinct enzyme, salicase, does exist, which is only capable of acting on salicin. On the other hand, prunase appears to act on salicin but less actively than on prunasin. It is possible that prunase, which is controlled by dextrose, becomes attached to the dextrose section of the molecule, and for this reason is able to attack so large a proportion of the  $\beta$ -glucosides.

In most cases, it is noticed that the quantity of hydrogen cyanide obtained varies with the season at which the plants were gathered.

The enzymes occurring together with many of the glucosides may owe their specific character to the fact that they act, not through the dextrose group of the molecule, but with the radicle associated with it, and with which they are compatible. W. J. Y.

**Enzyme Action. XVIII. Enzymes of the Emulsin Type. III. Linase and Other Enzymes in Linacææ.** HENRY E. ARMSTRONG and J. VARGAS EYRE (*Proc. Roy. Soc.*, 1912, *B*, 85, 370—378. Compare preceding abstract).—The name *linase* is given

to the enzyme occurring in a large number of species of *Linaceae*, which hydrolyses the glucoside linamarin (phaseolunatin). A study of the enzymes present in the leaf and seed of sixty species of the *Linaceae* has been made with the same glucosides and in a similar manner to that given in the preceeding abstract. The enzymic activity towards these glucosides is correlated with the presence of a cyanophoric glucoside; thus the yellow-flowered species, which are free from cyanophoric glucosides, exhibit little activity towards the four glucosides employed, whereas the blue-, white-, or red-flowered varieties all yield hydrogen cyanide. The amount of both enzymes and glucosides in the plants vary with the period of growth. In all but one case the prunasin was hydrolysed to a very much less extent than the linamarin. The activity towards linamarin is attributed to the enzyme linase alone, and as this enzyme is accompanied by prunase in the *linaceae* and also in *Phaseolus lunatus*, it is possible that the former enzyme is without action on prunasin.

From the values obtained with salicin it is questionable whether linase has any action on this substance.

W. J. Y.

**Exciting Action of Alkalis, Especially Ammonia, on Peroxydases.** JULES WOLFF (*Compt. rend.*, 1912, 155, 484—486. Compare Abstr., 1909, i, 862).—Barley sprouts, 0.1 metre high, contain an active peroxydase unassociated with catalase, tyrosinase, or laccase. This peroxydase is rendered much less active on addition of ammonia, but in contact with this reagent, it regains its activity and at the end of fourteen hours attains a maximum activity twice as great as the original, which it retains for some hours and then gradually loses. An analogous series of changes takes place in the presence of sodium hydroxide, but much more rapidly, this reagent destroying the enzyme more quickly than ammonia. Sulphuric and phosphoric acids, even when very dilute, reduce the activity. The foregoing results were obtained with guaiacol as a test of oxidising capacity. With pyrogallol or quinol, on the contrary, ammonia appears to increase the activity of the enzyme immediately, and there is no variation in activity on keeping.

T. A. H.

**The Influence of Toluene on Zymases and Phosphatase.** HANS VON EULER and DAVID JOHANSSON (*Zeitsch. physiol. Chem.*, 1912, 80, 175—181).—Living yeast which under normal conditions in solutions containing phosphates produces no ester formation, produces in the presence of toluene a rapid formation of large amounts of a phosphate-carbohydrate combination.

W. D. H.

**A New Glucolytic Ferment of Yeast.** VICTOR BIRCKNER (*J. Amer. Chem. Soc.*, 1912, 34, 1213—1229).—Whilst failing to prepare maltase from the yeast of Californian "steam beer," which is brewed at a higher temperature and with more extensive aeration than common lager beers, a ferment has been discovered which is very active at 70° towards dextrose, polyphenols, and lactates. It manifests itself in the case of dextrose by a rapid darkening of the mixture, a strongly acid reaction, a gradual formation of a carbonaceous solid

deposit, and the development of a caramel-like odour, but it causes no formation of gas or of alcohol. It accelerates the oxidation of quinol, and traces of manganese sulphate intensify this activity.

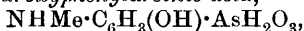
This yeast glucase may be extracted from yeast powder, which is best obtained by treating the cells with ethyl alcohol. The aqueous extract of this powder is prepared at 70°, and is very stable under sterile conditions, whilst boiling does not destroy its activity. Repeated precipitation with alcohol results in a brittle mass, which still contains many gum-like substances, and is not so strong a ferment. Many of the properties of the glucase have been studied; it gives a strong pyrrole reaction (see Neuberg, *Abstr.*, 1905, ii, 127), but it does not act as a peroxylase towards dextrose, neither does it contain tyrosinase. Among the transformation products of dextrose, pentose and formaldehyde were ascertained, but the acids have not been identified.

Since it is an oxidative ferment, which at the same time acts on dextrose, it is classed with zymase, with which, however, it is not identical, apart from the oxydases and hydrolytic ferments, among the "Gärungsenzyme" of Euler. J. C. W.

**The So-called Terpentiphosphorous Acid.** ERNST SIEBURG (*Biochem. Zeitsch.*, 1912, 43, 280—314).—The author shows that the waxy substance obtained by dissolving phosphorus in *l*-pinene in the presence of air is a monobasic acid. The substance was obtained by expressing from the waxy-mass the excess of pinene, and dissolving it in sodium hydroxide solution, from which it was precipitated by excess of hydrochloric acid. It was then dissolved in chloroform, the chloroform solution was repeatedly washed with water, and then dried over sodium sulphate. On evaporating off the chloroform, the substance used for investigation was obtained. Its analyses agree with the formula  $C_{10}H_{17}O_3P$ , and the sodium, lithium, lead, and barium salts were obtained and analysed. It appears to be a derivative of hypophosphorous acid. On gentle oxidation (by bromine water, etc.), it is converted into a phosphorous acid derivative of terpene. It is practically non-toxic, as demonstrated by numerous experiments on fowls, rabbits, and dogs, and is oxidised in the organism, being excreted in the urine in the form of an acid,  $C_{10}H_{17}PO(OH)_2$ , a terpinolphosphoric acid. No glycuronate was found. S. B. S.

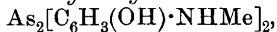
**Methylated Diaminodihydroxyarsenobenzenes.** ALFRED BERTHEIM (*Ber.*, 1912, 45, 2130—2136).—The following substances have been prepared for the purpose of tracing the change of the biological properties of salvarsan by the successive introduction of methyl groups into the amino-groups. Since the direct methylation of salvarsan is a complicated process, its methyl derivatives have been obtained as follows.

**3-Methylamino-4-hydroxyphenylarsinic acid,**

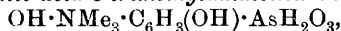


m. p. 263—263·5° (decomp.), is prepared from 3-amino-4-hydroxyphenylarsinic acid and methyl sulphate (0·5 mol.) in alkaline solution at the ordinary temperature. The crystals contain  $\frac{1}{2}H_2O$ . By reduc-

tion with alkaline sodium hyposulphite at about  $50^{\circ}$ , the acid yields 3 : 3'-dimethylamino-4 : 4'-dihydroxyarsenobenzene,



the dihydrochloride of which is a yellow, microcrystalline powder, resembling salvarsan in many respects, but differing from it by developing a brownish-orange coloration and no precipitate with an hydrochloric acid solution of *p*-dimethylaminobenzaldehyde. 3-Dimethylamino-4-hydroxyphenylarsinic acid,  $\text{NMe}_2\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{AsH}_2\text{O}_3$ , m. p.  $119-121^{\circ}$  (decomp.), obtained from 3-amino-4-hydroxyphenylarsinic acid and methyl sulphate (1 mol.) in alkaline solution at the ordinary temperature, is reduced by alkaline sodium hyposulphite to 3 : 3'-bisdimethylamino-4 : 4'-dihydroxyarsenobenzene,  $\text{As}_2[\text{C}_6\text{H}_3(\text{OH})\cdot\text{NMe}_2]_2$ , the dihydrochloride of which is a yellowish-white powder. By repeated treatment with *N*-sodium hydroxide and methyl iodide at the ordinary temperature, 3-amino-4-hydroxyphenylarsinic acid in the presence of methyl alcohol is converted into a mixture which yields 4-hydroxyphenylarsinic acid-3-trimethylammonium hydroxide,



and its iodide by treatment with acetic acid. The former, which is obtained pure in glistening prisms by crystallising the mixture from water, has m. p.  $262-264^{\circ}$  (decomp.), loses  $\text{H}_2\text{O}$  at  $110-114^{\circ}$  with the formation of an inner anhydride, and is reduced by alkaline sodium hyposulphite to salts of 4 : 4'-dihydroxyarsenobenzene-3 : 3'-bistrimethylammonium hydroxide,  $\text{As}_2[\text{C}_6\text{H}_3(\text{OH})\cdot\text{NMe}_3\text{X}]_2$ .

[With FRIDA LEUPOLD.]—All three methylated diaminodihydroxyarsenobenzenes are decidedly more toxic than salvarsan itself, the dimethyl and tetramethyl compounds being ten times, and the hexamethyl compound three to five times, as poisonous.

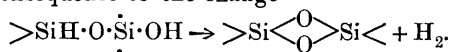
The introduction of the methyl groups causes an extraordinary deterioration in the curative effect of the substance. The ammonium compound has no effect at all. The dimethyl compound, in a quantity equal to half the lethal dose, renders the animal free from trypanosoma only for a few days, whilst the tetramethyl compound kills a sick animal when given in a quantity equal to half the lethal dose for a healthy animal, and has no effect on the trypanosoma when given in one-third of the lethal dose. C. S.

**New Class of Organo-Silicon Compounds which Evolve Hydrogen.** GEOFFREY MARTIN (*Ber.*, 1912, 45, 2097—2106).—By the action of Grignard reagents on silicon tetrachloride under definite conditions, complex organic silicon compounds are obtained, which are insoluble in ether, in other organic solvents, and in dilute mineral acids, and evolve the same amount of hydrogen by heating at  $400-500^{\circ}$  or by solution in dilute alkali hydroxides. When kept for some time or when boiled with acids, the substances are converted into others which no longer evolve hydrogen by solution in alkalis, but still evolve hydrogen when heated, the amount of hydrogen produced being the same as that obtained by the solution of the original substance in alkali.

The peculiar behaviour of these substances is explained by assuming that the original compounds contain one or more of the groups

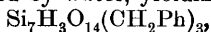


By solution in potassium hydroxide, each of these groups changes into  $\text{OK}\cdot\dot{\text{Si}}\cdot\text{O}\cdot\dot{\text{Si}}\cdot\text{OK}$ , with the evolution of one molecule of hydrogen; the quantity of hydrogen evolved, therefore, is a measure of the number of directly linked silicon atoms in the substance. When the substance is kept or boiled with acids, the group changes to  $>\text{SiH}\cdot\text{O}\cdot\dot{\text{Si}}\cdot\text{OH}$ . The new compound, therefore, no longer evolves hydrogen by treatment with potassium hydroxide, because it does not contain directly linked silicon atoms; by heating, however, one molecule of hydrogen is evolved in consequence of the change



Silicon tetrachloride (1 mol.) in dry ether is treated with magnesium (2 atoms) and ethyl bromide (1 mol.). The product is washed with ether and decomposed by water. After being washed with water, alcohol, and ether, the final *product* is obtained as a yellow powder, which is found to have the composition  $\text{Si}_4\text{H}_6\text{O}_7\text{Et}_2$ , and to contain 3 pairs of directly linked silicon atoms by means of the amount of hydrogen evolved by solution in potassium hydroxide. By acidifying the alkaline solution, a white *substance*,  $\text{Si}_4\text{H}_2\text{O}_8\text{Et}_2$ , is obtained.

In a similar manner, magnesium  $\alpha$ -naphthyl bromide (1 mol.), silicon tetrachloride (7 mols.), and magnesium (1 atom) yield a *substance*,  $\text{Si}_6\text{H}_5\text{O}_{12}\cdot\text{C}_{10}\text{H}_7$ , containing two Si-Si groups; bromobenzene (1 mol.), magnesium (2 atoms), and silicon tetrachloride (1 mol.) yield a *substance*,  $\text{Si}_4\text{H}_3\text{O}_8\text{Ph}$ , containing one Si-Si group (the ethereal extract contains a substance which is decomposed by water, forming a *substance*,  $\text{Si}_7\text{H}_5\text{O}_{11}\text{Ph}_3$ , containing four Si-Si groups); magnesium benzyl chloride and silicon tetrachloride yield a *substance* which is unstable, evolves hydrogen by treatment with hot water, and changes in three weeks to a *substance*,  $\text{Si}_5\text{H}_3\text{O}_{16}(\text{CH}_2\text{Ph})_3$ , which is not easily soluble in potassium hydroxide (the ethereal extract contains a substance which is decomposed by water, yielding a *substance*,



and a second *substance*,  $\text{Si}_3\text{H}_3\text{O}_6\cdot\text{CH}_2\text{Ph}$ ).

The constitutions of the preceding compounds and also the changes they undergo by keeping or by treatment with acids or alkalis are represented by provisional formulæ.

C. S.

## Organic Chemistry.

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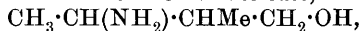
**Action of Aqueous Solutions of Acids on Olefines.** ARTHUR MICHAEL and ROGER F. BRUNEL (*Amer. Chem. J.*, 1912, 48, 267—279. Compare Abstr., 1909, i, 197).—It has been stated by Scheschukoff (Abstr., 1886, 680) that when *isobutylene* is passed into aqueous hydriodic acid, saturated at 0°, *tert.*-butyl iodide is produced until the acid has attained the concentration represented by  $2\text{HI} + 11\text{H}_2\text{O}$  ( $D = 1.7$ ), and at this point the reaction ceases, the *isobutylene* being no longer absorbed. It has now been found that these observations are not correct. The absorption of the hydrocarbon does not cease when the acid has  $D = 1.7$  although it decreases considerably. The rate of formation of *tert.*-butyl iodide is, however, no longer a criterion for the rate of absorption of the gas, as part of the hydrocarbon dissolves with production of the soluble tertiary carbinol.

Similar experiments have been made with trimethylethylene and hydrobromic acid, which have shown that 9.66*N*-acid yields chiefly the bromide, whilst a solution more dilute than 5.54*N* gives carbinol only; intermediate concentrations yield mixtures of the two compounds. The mechanism of the reaction is discussed, and it is shown that it is probable that the hydrocarbon reacts with both the water and the acid simultaneously. At a concentration equivalent to  $\text{HBr} + 8\text{H}_2\text{O}$ , the amylene reacts with amounts of water and acid in the same ratio. It is suggested that this may be explained by assuming the formation of a "polymolecule," such as  $\text{C}_5\text{H}_{10} \cdot \text{HBr} \cdot \text{H}_2\text{O}$ , and theoretical evidence is adduced for expecting that the decomposition of  $x$  "polymolecules" would proceed with the production of  $x/2$  mols. of haloid and carbinol respectively, whilst a system containing a larger or smaller proportion of the hydrogen bromide should give a corresponding increase or decrease in the amount of haloid produced.

The combination of water with olefines resembles the hydrolysis of methyl acetate and sucrose, and it was therefore considered of interest to ascertain whether the catalytic effects of acids stand in the same relation to each other in the first case as in the latter reactions. The velocity of solution of trimethylethylene and *isobutylene* in dilute solutions of acids was therefore determined. It was found that the order in which hydriodic, hydrobromic, and hydrochloric acids in dilute solutions exert a catalytic influence in inducing the addition of water to the amylene is the same as that of the facility of addition of the acids themselves to unsaturated hydrocarbons, and also as that of the reactivity of these acids in converting carbinols into haloids. E. G.

**Preparation of Isoprene and Erythrene.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 247144 and 247271. Compare Abstr., 1888, 1292, and this vol., i, 742).—I. The conversion of  $\beta$ -methylpyrrolidine into isoprene as recorded by Euler has led to the following method of preparing both isoprene and erythrene. Keto-

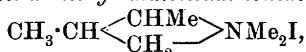
methylbutanol,  $\text{CH}_3\cdot\text{CO}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{OH}$ , was converted into its *oxime* b. p.  $144^\circ/20$  mm., and this reduced to the *base*,



a viscous oil, b. p.  $96^\circ/18.5$  mm., which was condensed by the action of halogen acids to 2:3-*dimethyltrimethylenimine*,

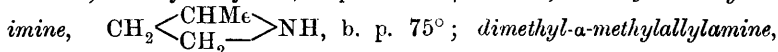


an oil, b. p.  $88^\circ$ . This compound on exhaustive methylation furnished 2:3-*dimethyltrimethylendimethylammonium iodide*,

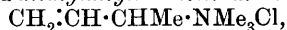


m. p.  $191^\circ$ , which was converted by silver oxide into the quaternary *base*, and on distillation furnished *dimethyl- $\alpha\beta$ -dimethylallylamine*,  $\text{CH}_2\cdot\text{CMe}\cdot\text{CHMe}\cdot\text{NMe}_2$ , a colourless oil, b. p.  $105\text{--}106^\circ$ , with an odour of piperidine, which after conversion into the quaternary *ammonium iodide* (leaflets, m. p.  $138\text{--}140^\circ$ ) can be readily converted by alkali or alkaline-earth hydroxides into isoprene and trimethylamine.

The preparation of erythrene by a similar series of reactions from ketobutanol,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , furnished the following intermediate compounds: the *oxime*,  $\text{CH}_2\cdot\text{C}(\text{NOH})\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , b. p.  $125\text{--}130^\circ/20$  mm.; the hydroxy-*base*, b. p.  $82\text{--}85^\circ/19$  mm.; 2-*methyltrimethylenimine*,



$\text{CH}_2\cdot\text{CH}\cdot\text{CHMe}\cdot\text{NMe}_2$ , a colourless oil, b. p.  $90\text{--}93^\circ$ , with an odour of coniine, and *trimethyl- $\alpha$ -methylallylammonium chloride*,



a crystalline, colourless, hygroscopic mass.

II. When the quaternary ammonium haloids of the hydroxy-bases,  $\text{CH}_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$  and  $\text{CH}_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}\cdot\text{CH}_3\cdot\text{CH}_2\cdot\text{OH}$ , are heated with halogen acids, the hydroxyl groups are replaced by a halogen atom, and the halogenated bases thus obtained are readily converted by alkali or alkaline-earth hydroxides into isoprene or erythrene respectively; the compounds  $\text{Br}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CHMe}\cdot\text{NMe}_3\text{Cl}$  and  $\text{Br}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{NMe}_3\text{Cl}$  are syrups. F. M. G. M.

Course of the Intramolecular Transformations of Alkyl Bromides. II. ARTHUR MICHAEL and FRITZ ZEIDLER (*Annalen*, 1912, 393, 81—111. Compare Abstr., 1911, i, 250).—The authors have undertaken experiments in order to ascertain whether the presence of impurities may not be the cause of the discordant results obtained by different observers during investigations of the transformation of *isobutyl* bromide into the tertiary isomeride (*loc. cit.*). It has been found that the majority of the methods of preparing alkyl bromides do not yield pure products.

The *isobutyl* alcohol employed, details of the purification of which are given, had b. p.  $107.7\text{--}107.8^\circ/761.4$  mm. for one sample and  $107.2\text{--}107.3^\circ/750.5$  mm. for another.

*isoButyl* bromide prepared by Norris's method (Abstr., 1907, i, 1034) contains *diisobutylene*, which cannot be removed by distillation. Such *isobutyl* bromide yields only 1.36% of *tert.*-butyl bromide by heating for three hours at  $141^\circ$  in the apparatus described by Michael

and Zeidler (this vol., i, 2). After removing the diisobutylene by 2% potassium permanganate, the thus purified isobutyl bromide has a more constant b. p., 91.3—91.7°/758.1 mm., and yields 30.73% and 45.68% of tertiary bromide after heating for three and ten hours respectively at 141°. When Norris's isobutyl bromide is freed from diisobutylene by treatment with bromine and subsequent fractionation, the purified isobutyl bromide has b. p. 91.6—92.1°/763.8 mm., and shows a still greater velocity of transformation, yielding 39.40% of tertiary bromide after three hours at 141°. By adding 1—2% of diisobutylene to this purified isobutyl bromide, its velocity of transformation is diminished enormously, only about 10% of tertiary bromide being formed after three hours at 141°.

isoButyl bromide, obtained from isobutyl alcohol, potassium bromide, and sulphuric acid, contains a considerable amount of diisobutylene, and yields only 1½% of the tertiary bromide by heating at 141° for three hours.

A purer product is obtained by saturating isobutyl alcohol with hydrogen bromide at 0° and subsequently heating at 100°. The isobutyl bromide, after fractionation, has b. p. within 0.1°, and yields 12—24% of the tertiary bromide at 141°; the transformation then ceases, but at 262° more than 75% of the tertiary bromide is produced. Several variations of the preceding method have been tested in order to obtain an isobutyl bromide which is easily transformed into the tertiary bromide. Finally, the following process is adopted. Hydrogen bromide, prepared from purified bromine, purified red phosphorus, and water, is washed by moist red phosphorus and by ferrous bromide solution, and is then absorbed in water. By distillation the solution gave an acid, b. p. 125—126°, which is free from hydrogen phosphide. This acid is used for the absorption of further quantities of hydrogen bromide, and by heating the saturated solution, very pure hydrogen bromide is obtained. Equal volumes of isobutyl alcohol and hydrobromic acid, b. p. 125—126°, are saturated with hydrogen bromide and heated in a sealed vessel at 75—80° for two hours. The resulting isobutyl bromide (95% yield) yields after purification and careful fractionation a sample, b. p. 91.85—92°/762.2 mm., which gives 73.28% of tertiary bromide after one hour at 141° and 71.89% after one hour at 262°. By mixing this pure isobutyl bromide with 2.66% of diisobutylene, 3.74% of *tert.*-butyl alcohol, and 2.31% of isobutyl alcohol, the amounts of *tert.*-butyl bromide obtained after one hour at 141° are 4.94%, 0%, and 7.06% respectively.

The limit of the transformation of isobutyl bromide into *tert.*-butyl bromide attained in these experiments is about 76%. The same limit is attained from the other side. Pure *tert.*-butyl bromide, b. p. 72.8—73.1°/762.85 mm. and 71.6—72.0 (two samples), prepared from purified *tert.*-butyl alcohol and hydrobromic acid, D 1.78, yields 23.88% and 23.18% respectively of isobutyl bromide after one hour at 262°, the amount and the velocity of the transformation being much smaller at lower temperatures. A sample of *tert.*-butyl bromide, prepared from isobutylene and concentrated hydrobromic acid by Roozeboom's method and having b. p. 72.5—72.6°/747.3 mm., and containing 100% of the tertiary bromide, yielded, curiously enough,

only 19.56% of *isobutyl* bromide after two hours at 262°; apparently, the transformation of the tertiary bromide is slower the purer it is.

*isobutyl* chloride is transformed by heating into the tertiary chloride very much more slowly than *isobutyl* bromide is changed to the tertiary bromide. A sample, prepared by saturating *isobutyl* alcohol with pure hydrogen chloride at 0° and then heating at 120° in a sealed vessel, had b. p. 68.8—69.2°/769.2 mm. after purification, and yielded 0% of the tertiary chloride after one hour at 184°, and only 7.94% after six hours at 306°.

The deductions drawn by Brunel from his experiments (Abstr., 1911, ii, 974) are adversely criticised. C. S.

**Pyrogenic Decomposition of Methyl Alcohol by means of the Electric Current.** WALTHER LÖB (*Zeitsch. Elektrochem.*, 1912, 18, 847—850).—The method of experiment has already been described (compare Abstr., 1901, ii, 371; 1902, i, 3). A nickel wire of 0.3 mm. diameter was electrically heated to about 700°, and its action on methyl alcohol investigated. In the first series of experiments a mixture of methyl alcohol and water was used, and it was found that the gaseous products were almost exclusively formaldehyde and hydrogen, according to the equation:  $\text{CH}_3\cdot\text{OH} = \text{CH}_2\text{O} + \text{H}_2$ . When mixtures of methyl alcohol and benzene were used, the same products were obtained, with traces only of diphenyl; owing to the absence of water, the formaldehyde partly condensed to paraformaldehyde. At rather higher temperatures, formaldehyde decomposes into carbon monoxide and hydrogen. In the presence of ammonia, the pyrogenic decomposition of methyl alcohol yields a considerable proportion of hexamethylenetetramine. G. S.

**Chemical Action of Methyl and Ethyl Alcohols.** HANS VON LIEBIG (*Arch. Pharm.*, 1912, 250, 403—413).—In medicinal and in plant chemistry, methyl and ethyl alcohols are the solvents which are most commonly used for extraction or crystallisation. Since the assumption is generally made that these alcohols have no chemical action on the substance extracted by, or crystallised from, them, the author calls attention to some instances in which the assumption is untenable, particularly in the resorcinolbenzein and fluorescein series (Abstr., 1907, i, 45; this vol., i, 378). The alcohols have both a hydrolysing and etherifying action. The constitutions of the products are discussed.

The conversion of phytylchlorophyllide into ethylchlorophyllide by ethyl alcohol may be due to the chemical action of the alcohol, not to the action of the enzyme chlorophyllase, as stated by Willstätter.

C. S.

**The History of Alcohol and its Name.** EDMUND O. VON LIPPMANN (*Zeitsch. angew. Chem.*, 1912, 25, 2061—2065).—Contrary to the usual statement, alcohol was unknown to the Arabian chemists. The process of distillation was also unknown in Asia. The discovery of alcohol probably took place in Italy. It is first mentioned in an Italian work of the ninth or tenth century. C. H. D.

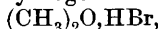
**Basic Properties of Oxygen. Two-Component Systems of the Halogen Hydrides with Organic Substances Containing Oxygen.** O. MAASS and DOUGLAS MCINTOSH (*J. Amer. Chem. Soc.*, 1912, 34, 1273—1290).—It is pointed out that the compounds formed by the combination of halogens and halogen hydrides with organic substances containing oxygen may be regarded as quite distinct from the so-called molecular compounds, such as salts containing water, alcohol, or ether of crystallisation.

In an earlier paper (Abstr., 1911, i, 256), an account has been given of two-component systems of ether with hydrogen bromide, chlorine, and bromine. The existence of two compounds of ether and hydrogen bromide is now confirmed, and it is shown that an excess of ether favours the formation of the monohydrobromide, and an excess of hydrogen bromide that of the dihydrobromide.

The systems chloroform-hydrogen bromide and chloroform-hydrogen chloride have been studied in comparison with the oxygen compounds. No compound is formed in either case, but the f. p. of each component is lowered by the addition of the other until the eutectic point is reached.

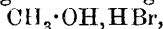
The systems toluene-hydrogen bromide and toluene-chlorine show the formation of *compounds*,  $C_7H_8 \cdot HBr$  and  $C_7H_8 \cdot Cl_2$ , but these are very unstable as compared with the oxonium complexes.

Methyl ether yields with hydrogen bromide the *compound*,



m. p.  $-13^\circ$ , with hydrogen iodide the *compound*,  $(CH_3)_2O \cdot HI$ , m. p.  $-22^\circ$ , and with hydrogen chloride the *compounds*,  $(CH_3)_2O \cdot HCl$ , m. p.  $-96^\circ$ , and  $(CH_3)_2O \cdot 3HCl$  or  $(CH_3)_2O \cdot 4HCl$ , m. p.  $-102^\circ$ .

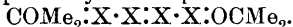
Methyl alcohol and hydrogen bromide give the *compound*,



m. p.  $-12^\circ$ , in the formation of which much heat is developed. With bromine, the existence of the *compound*,  $CH_3 \cdot OH \cdot Br$ , m. p.  $-66^\circ$ , is indicated.

Ethyl alcohol yields with hydrogen bromide and bromine the *compounds*,  $C_2H_5 \cdot OH \cdot HBr$ , m. p.  $-30^\circ$ , and  $C_2H_5 \cdot OH \cdot Br$ , m. p.  $-58^\circ$ . In order to explain the constitution of the latter substance, the formula must be doubled and the compound represented as  $C_2H_5 > O : Br \cdot Br : O < C_2H_5$ .

Acetone gives the *compounds*,  $COMe_2 \cdot HBr$ , m. p.  $-4^\circ$ ,  $COMe_2 \cdot Br_2$ , m. p.  $-8^\circ$ , and  $COMe_2 \cdot Cl_2$ , m. p.  $-54^\circ$ . The constitution of the halogen compounds is probably best represented by the formula



Ethyl acetate yields the *compounds*  $CH_3 \cdot CO_2Et \cdot HBr$ , m. p.  $-36^\circ$ ,  $2CH_3 \cdot CO_2Et \cdot 5HBr$ , m. p.  $-52^\circ$ ,  $CH_3 \cdot CO_2Et \cdot 4HBr$ , m. p.  $-57^\circ$ ,  $CH_3 \cdot CO_2Et \cdot 3Br$ , m. p.  $-35^\circ$ , and  $CH_3 \cdot CO_2Et \cdot 3Cl$ , m. p.  $-68^\circ$ .

All the halogen hydride complexes have m. p.'s much above those of either constituent. The compounds are formed with the development of an amount of heat equal to, or greater than, that liberated when a halogen acid is neutralised by potassium hydroxide. The compounds, either in the fused state or in a solution of either constituent, readily conduct the electric current.

The chlorine and bromine compounds are formed with the development of but little heat, and are non-conducting. Their constitutions are doubtful, but it is evident that they must differ radically from those of compounds ionised in solution. E. G.

**Ethyl Ether.** GEORG KASSNER (*Arch. Pharm.*, 1912, 250, 436—447).—Instances of the spontaneous explosion of ether by heating have been placed on record. A sample of ether, a portion of which exploded violently when it was being sealed in a Dumas bulb in the determination of its vapour density, has been carefully examined by the author. It contained traces of hydrogen peroxide and acetaldehyde, and a relatively large amount of vinyl alcohol. The author is of opinion that the explosion was caused by the presence of an organic peroxide (ethyl peroxide) which had been produced by autoxidation. C. S.

**Commercial Sodium Glycerophosphates.** VINCENZO PAOLINI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 350—352. Compare Abstr., 1911, i, 774).—The author has examined several commercial sodium glycerophosphates, and finds them to have the same composition as Poulenc's product. R. V. S.

**Bromination of Aliphatic Acids.** CLARENCE SMITH and WILLIAM LEWCOCK (*Ber.*, 1912, 45, 2358—2359).—The theory of the bromination of aliphatic acids advanced by Aschan (this vol., i, 599), involving successive enolisation of the acid (or acid chloride, in practice), addition of the halogen, and elimination of halogen hydride, is supported by the behaviour of isobutyryl chloride towards bromine. When heated together in equal molecular quantities at 100° for four hours, the isobutyryl chloride is converted almost entirely into  $\alpha$ -bromoisobutyryl bromide. In accordance with the theory,  $\alpha$ -bromoisobutyryl chloride is unaffected by bromine at 100°. C. S.

**Saponification of Triglycerides.** V. FORTINI (*Chem. Zeit.*, 1912, 36, 1117).—It has been held by some authors that in the saponification of fats, the triglycerides are immediately hydrolysed to the fatty acids and glycerol, whilst others have asserted that the hydrolysis takes place in steps, diglycerides and monoglycerides being formed (compare Lewkowitsch, *Proc.*, 1899, 15, 190; Marcusson, *Abstr.*, 1906, i, 924; Kremann, *Abstr.*, 1906, ii, 731; Stritar, *Abstr.*, 1908, ii, 677, 1021; Grün and Corelli, this vol., i, 409). The results now recorded support the second view.

The curves obtained by plotting (1) quantity of triglyceride hydrolysed against time, or (2) acetyl number against time, each consist of three parts corresponding with (a) formation of diglycerides, (b) formation of monoglycerides, (c) formation of free fatty acids. The experiments were made by saponifying triolein with alkali hydroxide in alcohol at 20°. T. A. H.

**Oil from the Seeds of *Jatropha mahafalensis*.** HENRI BIMAR (*Bull. Soc. chim.*, 1912, [iv], 11, 914—915).—The seeds contain 75% of their weight of kernels, and the latter yield on extracting with

carbon disulphide 60%, or under pressure 44·5%, of an amber-tinted slightly fluorescent oil,  $D^{15}_D$  0·9213,  $n^{20}_D$  1·4648, titre  $21^\circ$ , saponification number 194, acid number 17·6, iodine value 111·8, acetyl number 17, which dries in twenty-six hours at  $50^\circ$ . The mixed ethyl esters of the fatty acids gave the following fractions: (1) b. p.  $180\text{--}185^\circ/5$  mm., saponification number 186, iodine value 98; (2) b. p.  $188\text{--}190^\circ/5$  mm., saponification number 186, iodine value 105; (3) b. p.  $193\text{--}195^\circ/5$  mm., saponification number 184, iodine value 112, indicating that the fat contains linoleic acid and no acids of lower molecular weight than palmitic acid.

T. A. H.

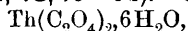
**Purification of Ammonium Hydrogen Salts of  $\alpha$ -Hydroxy-acids.** RICHARD ESCALES and HANS KOEPKE (D.R.-P. 247240).—The readiness with which lactic and glycollic acids lose water when heated has rendered their purification difficult; it is now found that the ammonium hydrogen salts can be distilled in a vacuum without decomposition. Ammonium hydrogen glycolate has b. p.  $160^\circ/10$  mm., and crystallises on cooling, whilst the corresponding lactate has b. p.  $140^\circ/10$  mm., and remains a viscous syrup. F. M. G. M.

**$\beta$ -Aldehydopropionic Acid.** CARL D. HARRIES (*Ber.*, 1912, 45, 2583—2585).—In a recent communication, Carrière (this vol., i, 410) gives values for the m. p. of various derivatives of  $\beta$ -aldehydopropionic acid, differing considerably for those previously obtained by the author (Abstr., 1909, i, 132, 133, 364; compare also Langheld, *loc. cit.*, i, 557). The latter has therefore repeated his earlier work and fully confirmed the results already given.  $\beta$ -Aldehydopropionic acid has b. p.  $143\text{--}145^\circ/16\text{--}20$  mm., and is transformed after two days into a solid bimolecular form, m. p.  $147^\circ$ , and not a termolecular form of m. p.  $167^\circ$  as stated by Carrière.

The *p*-nitrophenylhydrazone, after repeated crystallisation from water, has m. p.  $177^\circ$ .

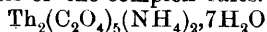
F. B.

**The Chemistry of Thorium.** OTTO HAUSER and FRITZ WIRTH (*Zeitsch. anorg. Chem.*, 1912, 78, 75—94).—Ordinary thorium oxalate,



is much less soluble in sulphuric acid than the oxalates of the tervalent earths (Abstr., 1908, ii, 778). The solubility in hydrochloric acid first increases and then falls rapidly, owing to the formation of the compound  $3\text{Th}(\text{C}_2\text{O}_4)_2 \cdot \text{ThCl}_4 \cdot 20\text{H}_2\text{O}$  (compare Wyruboff and Verneuil, Abstr., 1899, ii, 598). In contact with dilute acids the oxalate is gradually converted into the stable modification, which forms tetragonal crystals. Both modifications yield the dihydrate over sulphuric acid, the crystalline hexahydrate retaining its crystalline form during dehydration, but exhibiting optical anomalies. Another hydrate,  $4\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 3\text{H}_2\text{O}$ , is obtained on heating.

The solution of thorium oxalate in ammonium oxalate solution at  $25^\circ$  takes place in two stages:  $2\text{Th}^{+++} + 5\text{C}_2\text{O}_4^{--} = [\text{Th}_2(\text{C}_2\text{O}_4)_5]^{--}$  and  $\text{Th}^{+++} + 3\text{C}_2\text{O}_4^{--} = [\text{Th}(\text{C}_2\text{O}_4)_3]^{--}$ . The stable tetrahydrate is always formed by the hydrolysis of the complex salts. The salts



and  $\text{Th}(\text{C}_2\text{O}_4)_3(\text{NH}_4)_2 \cdot 3\text{H}_2\text{O}$  have been prepared. The former crystallises in thin laths, whilst the latter, the limits of stability of which have been determined, has only been obtained in an amorphous form. The complex salts are only stable in presence of a large excess of ammonium oxalate, and the precipitation by acids is a function both of the concentration of the oxalate and of the acid. It is rather remarkable that the solubility of ammonium oxalate in water is increased five times by the addition of thorium oxalate. C. H. D.

**The Walden Inversion.** GEORGE SENTER (*Ber.*, 1912, 45, 2318—2322).—With reference to a preliminary paper by Holmberg with the same title as above (compare this vol., i, 603), in which it is shown that when an aqueous solution of the sodium salt of *l*-monobromosuccinic acid is heated the  $\text{Br}'$  ion concentration increases at first more rapidly than the free acid, the author states that he made a similar observation with sodium bromoacetate solution one and a-half years ago, and some of the conclusions drawn from the detailed investigation have already been published (compare *Proc.*, 1911, 27, 153). The phenomenon is only observed in concentrated solution. The suggestion of Holmberg that it can be accounted for on the theory of the intermediate formation of lactones is criticised. The detailed results will be published later. G. S.

**Symmetric and Asymmetric Acid Dichlorides.** ERWIN OTT (*Annalen*, 1912, 392, 245—285).—The author approaches the problem of the constitution of acid dichlorides, such as succinyl chloride and phthalyl chloride (compare Scheiber, this vol., i, 559, 701), by means of criteria obtained by a comparative examination of maleinoid and fumaroid acid dichlorides. These criteria indicate that maleinoid chlorides have a lactonoid constitution, whilst fumaroid chlorides are acyclic and symmetric.

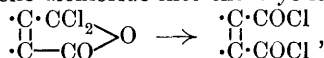
The criteria are the following. Fumaroid and maleinoid acid dichlorides exhibit extraordinarily great difference in their velocity of reaction in a homogenous system. All fumaroid dichlorides in *N*/50-solution in ether or benzene react momentarily with a primary base, such as aniline, to give the calculated amount of aniline hydrochloride. All maleinoid chlorides do not thus react under the same conditions; only after many days is the separation of the aniline hydrochloride complete. Thus chlorofumaryl chloride and dibromofumaryl chloride react instantly, whilst chloromaleyl chloride and dibromomaleyl bromide require sixteen days and fifty hours respectively. The same differences are observed in the rates of ester formation between the four acid dihaloids and methyl alcohol, the two symmetric compounds yielding 100% hydrogen chloride instantly, whilst the asymmetric dihaloids require many hours.

This difference in behaviour is not explicable by formulating maleinoid and fumaroid acid dihaloids as acyclic isomerides differing only in the spatial distribution of the  $\cdot\text{COX}$ -groups, because the examination of *s-o*-phthalyl chloride (see below) shows that the mere spatial approximation of two  $\cdot\text{COCl}$ -groups is insufficient to cause a diminution of the reaction velocity. Assuming what is now very generally

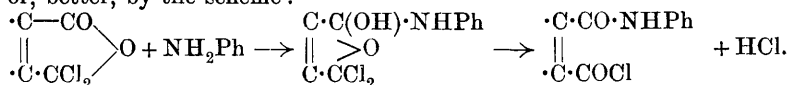
accepted, that acyl haloids owe their reactivity, not to direct substitution, but to addition, followed by elimination, the preceding differences are satisfactorily explained by formulating maleinoid dihaloids as

cyclic ketones,  $\begin{array}{c} \cdot\text{C}\cdot\text{CCl}_2 \\ || \\ \text{C}-\text{CO} \end{array} > \text{O}$ , because an acyl halogen atom is no longer

present. The reaction with aniline is then due, either to a transformation of the cyclic dichloride into the acyclic,



or, better, by the scheme :



Both explanations account for the production of the symmetric dianilide, but the latter is preferable, because, according to the former, the velocity of reaction of maleinoid dichlorides should be proportional to the stability of the  $\gamma$ -lactone ring, which is found not to be the case.

A second criterion is the colour of the aluminium chloride compounds. Chlorofumaryl chloride and aluminium chloride form a yellow mass, m. p. about  $50^\circ$ , from which chlorofumaryl chloride is regenerated by water at  $0^\circ$ . By warming, however, the mass becomes reddish-brown, and then has m. p. about  $100^\circ$  and yields chloromaleyl chloride by treatment with ice water. The reddish-brown substance is the aluminium chloride compound of chloromaleyl chloride, and its more intense colour is accounted for if chloromaleyl chloride has the cyclic ketonic structure, since the aluminium chloride compounds of cyclic ketones are intensely coloured. At  $180$ – $230^\circ$ , the aluminium chloride compound of chloromaleyl chloride decomposes into carbon monoxide, hydrogen chloride,  $\alpha\beta$ -dichloroacrylyl chloride, and carbonyl chloride; the formation of the last substance is taken as evidence of the constitution,  $\begin{array}{c} \text{CCl}\cdot\text{CCl}_2 \\ || \\ \text{CH}-\text{CO} \end{array} > \text{O}$ , of chloromaleyl chloride.

A third criterion is the comparison of the degree of unsaturation of the ethylenic linking in chloromaleyl chloride and chlorofumaryl chloride respectively. In sunlight, the latter adds on 80–85% of the theoretical amount of bromine within five hours, whilst the addition of bromine to chloromaleyl chloride is not appreciable after a week. This difference is attributed to the presence of the two carbonyl groups in conjugated positions in chlorofumaryl chloride, and to their absence in the cyclic ketonic chloromaleyl chloride.

A fourth criterion is found in the molecular volume. A difference of 4.4 units should exist in the molecular volumes of isomeric maleinoid and fumaroid acid dihaloids if the former have a cyclic structure. This difference actually occurs in chloromaleyl chloride and chlorofumaryl chloride, which have molecular volumes 137.63 and 142.3 respectively at the b. p.

Since  $\gamma$ -lactones are frequently dimorphous, the existence of chloromaleyl chloride in two forms, m. p.  $10.5$ – $11^\circ$  and  $2.5$ – $3^\circ$  respectively (the more fusible changes to the less fusible merely by keeping for several weeks), is also indicative of its ketonic structure.

The application of these criteria to succinyl and phthalyl chlorides gives the following results, which on the whole indicate that the two chlorides have the symmetric constitution. They both react rapidly with aniline or with methyl alcohol. The molecular volume, 180.35, of phthalyl chloride at its b. p. agrees with that calculated, 180.0, for the acyclic formula; the molecular volume of succinyl chloride, 133.7, is intermediate between those, 136.0 and 131.6, calculated for the symmetric and asymmetric formulæ respectively. A conversion of succinyl chloride by aluminium chloride, corresponding with that of chlorofumaryl into chloromaleyl chloride, does not occur, but *s*-phthalyl chloride, which is conveniently obtained by slowly heating phthalic anhydride with a small excess of phosphorus pentachloride for half a day at 150° and finally at 250° until the phosphoryl chloride has distilled away, is converted, by dry aluminium chloride on the water-bath and subsequent treatment of the product with water at 0°, into an *isomeride*, m. p. 88–89°, b. p. 275.2°(corr.)/719.8 mm., large prisms, which is regarded as *as*-phthalyl chloride,  $C_6H_4 \begin{smallmatrix} \diagup CCl_2 \\ \diagdown CO \end{smallmatrix} O$ , on account of its slow velocity of reaction with aniline or methyl alcohol. By distillation, by prolonged heating on the water-bath, or in the presence of hydrogen chloride, the asymmetric chloride is converted into the ordinary symmetric chloride. Dibromofumaric acid is obtained in 92–93% yield, free from dibromomaleic acid, by leading air containing bromine vapour into an aqueous solution of acetylenedicarboxylic acid in darkness until the theoretical quantity of bromine has been absorbed. A suspension of dibromofumaric acid in petroleum is converted by phosphorus pentachloride and subsequent treatment with ice into *dibromofumaryl chloride*,  $C_4O_2Cl_2Br_2$ , b. p. 92.5°/9.5 mm. *Dibromomaleyl chloride*, m. p. 39°, b. p. 128°/14.5 mm., colourless leaflets, cannot be conveniently prepared in a similar manner, but is obtained by heating dibromofumaryl chloride at about 150° for four days or with aluminium chloride at 100° for a few hours. Dibromofumaryl chloride and aluminium bromide on the water-bath give a good yield of *dibromomaleyl bromide*, m. p. 55–57°, yellow leaflets, after treating the product with ice water. C. S.

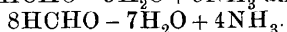
**Cholic Acid.** I. HEINRICH WIELAND and FRIEDRICH JOSEF WEIL (*Zeitsch. physiol. Chem.*, 1912, 80, 287–297).—On distillation of cholic acid in a vacuum (12 mm.) at 200–300°, a heavy, almost colourless oil distils over, and solidifies to a resin which consists mainly of triply unsaturated *cholatrienecarboxylic acid*,  $C_{24}H_{34}O_2$ . It crystallises in well formed plates, aggregated in large bunches; when heated it softens at 140°, m. p. 163–164°;  $[\alpha]_D^{20} = -19.7^\circ$ . The acid dissolves in sulphuric acid with a deep yellow coloration; after a time the solution exhibits a green fluorescence. Bromine is at first decolourised, then hydrogen bromide is set free, and the acid solution becomes a golden-yellow.

In aqueous-alcoholic solution of the alkali salt, the acid is partly hydrogenated by the action of palladium-hydride, forming *choladienecarboxylic acid*,  $C_{24}H_{36}O_2$ . This crystallises similarly to the parent acid, but has m. p. 178°.

Reduction by means of palladium black and hydrogen in acetic acid suspension leads to *cholanecarboxylic acid*,  $C_{24}H_{40}O_2$ . It crystallises in radially arranged pointed crystals, m. p.  $157.5^\circ$ ;  $[\alpha]_D^{20} + 20.3^\circ$ . This acid gives no coloration with sulphuric acid, and does not react with bromine.

E. F. A.

**Influence of Sunlight on the Synthesis of Alkaloid Bases by the Action of Alcoholic Ammonia on Aldehydes.** IV. GIUSEPPE INGHILLERI (*Zeitsch. physiol. Chem.*, 1912, 80, 64—72).—Sealed tubes containing formaldehyde, concentrated aqueous ammonia, and methyl alcohol were exposed to sunlight for seven months. Crystals of a base,  $C_6H_8ON_2$  were produced, which decomposed without melting at  $185^\circ$ , formed a microcrystalline platinichloride, decomp.  $220^\circ$ , and gave a number of alkaloid reactions. From the portion of the reaction mixture insoluble in ether, three platinichlorides, containing 47.3, 26, and 25.5% of platinum respectively, were isolated. The two latter represent bases formed by the changes corresponding with the equations:  $6HCHO - 5H_2O + 3NH_3$  and



E. F. A.

**Methylglyoxal.** JAKOB MEISENHEIMER (*Ber.*, 1912, 45, 2635—2641. Compare Harries and Türk, *Abstr.*, 1905, i, 413; Denis, *Abstr.*, 1907, i, 997).—Methylglyoxal is most readily prepared by hydrolysing its acetal (Wohl and Lange, *Abstr.*, 1908, i, 943) with *N*-sulphuric acid and extracting the residue, obtained by evaporation of its neutralised solution, with ether. After removal of the ether, the methylglyoxal is obtained as a yellow syrup, consisting of the termolecular form, from which the unimolecular variety is obtained by distilling it under diminished pressure and allowing the vapours to pass over anhydrous calcium chloride.

The unimolecular form is an intensely yellow, very mobile liquid, having a pungent odour. When heated under ordinary pressure, it begins to distil at  $72^\circ$ , forming a yellowish-green vapour; the greater part, however, is transformed into the termolecular form. At the ordinary temperature the transformation is complete in the course of eight to ten days.

When dissolved in water, the termolecular form passes into the unimolecular form (or its hydrate) in twenty-four hours.

F. B.

**The Action of Dilute Sodium Hydroxide on Glyceraldehyde and Dihydroxyacetone.** MAX OPPENHEIMER (*Biochem. Zeitsch.*, 1912, 45, 134—139).—In view of the assumed formation of glyceraldehyde and dihydroxyacetone as intermediary products in the degradation of dextrose to lactic acid, the relative rate of formation of this acid from these substances was investigated when they were submitted to the action of sodium hydroxide. From the results of experiments with *N*- and *N*/10-acid at room temperature and at  $37^\circ$ , the conclusion was drawn that lactic acid is formed most readily from dihydroxyacetone and least readily from the sugar.

S. B. S.

**Preparation of Pinacone from Acetone and Sodium.** BADISCHE ANILIN- and SODA-FABRIK (D.R.-P. 248252).—The reduction

of acetone by sodium has previously furnished unsatisfactory yields of pinacone (Abstr., 1894, ii, 217); this reaction is now found to proceed smoothly in the presence of a liquid (such as ether) which is indifferent to sodium.

F. M. G. M.

**Styracitol.** YASUHIKO ASAHINA (*Ber.*, 1912, 45, 2363—2369. Compare Abstr., 1908, ii, 58; 1909, i, 288).—By treating a solution of styracitol in aqueous sodium carbonate with bromine, and subsequently acidifying and treating successively with sodium hydrogen sulphite, sodium acetate, and phenylhydrazine, an *osazone*,  $C_{18}H_{20}O_3N_4$ , m. p. 185°, thin leaflets, is obtained, which is optically active, and is not identical with Fischer and Zach's anhydroglucosazone.

By treatment in aqueous ferrous sulphate with 3% hydrogen peroxide and subsequently in acetic acid with phenylhydrazine, styracitol yields several products, among which *d*-phenylglucosazone has been identified. This substance is also produced when aqueous styracitol is oxidised by Caro's reagent at 0°.

Styracitol forms a *tetra-acetate*, prismatic crystals, m. p. 66—67°, or clusters of needles, m. p. 58°, which has  $[\alpha]_D^{25} - 20.86^\circ$ . Styracitol reacts readily with thionyl chloride on the water-bath to form a *disulphite*,  $C_6H_8O_7S_2$ , prismatic crystals, which is unaffected by boiling acetic anhydride.

C. S.

**Preparation of Mineral Acid Esters of Carbohydrates, the Corresponding Hydroxy-acids, and Higher Alcohols.** CHEMISCHE WERKE VORM. HEINRICH BYK (D.R.-P. 247809).—*Calcium saccharophosphate* is obtained by treating a cooled suspension of sugar in calcium hydroxide with phosphoryl chloride, followed by the addition of chloroform:

$2C_{12}H_{22}O_{11} + 2POCl_3 + 5CaO = 3CaCl_2 + H_2O + 2C_{12}H_{21}O_{10} \cdot O \cdot PO_3Ca$ ; it is a colourless powder, readily soluble in water, and does not give a precipitate with soluble copper or lead salts.

*Calcium erythrosulphate* is prepared from erythritol, calcium hydroxide, and chlorosulphonic acid, and a *compound* from calcium *d*-gluconate with phosphoryl chloride is also mentioned in the original.

F. M. G. M.

**New Form of Soluble Starch.** AUGUSTE FERNBACH (*Compt. rend.*, 1912, 155, 617—618).—By slowly pouring weak aqueous solutions of starch, not exceeding 2% in strength, into a large excess of pure acetone, a flocculent precipitate is obtained, which on filtering, extracting with more acetone, and drying in a vacuum yields a starch which is completely soluble in cold water, its solution giving a very pure blue colour with iodine.

W. G.

**Crystallised Polysaccharides from Starch.** HANS PRINGSHEIM and ALFRED LANGHANS (*Ber.*, 1912, 45, 2533—2546).—An extension of the work of Schardinger (Abstr., 1911, i, 181). The generic term *amylose* is suggested for the polysaccharides of the formula  $(C_6H_{10}O_5)_n$ .

Dextrin- $\beta$ , which decomposes at 268°, is too sparingly soluble in water for accurate cryoscopy, but dextrin- $\alpha$  (tetra-amylose), decom-

posing at  $292^{\circ}$ , proves to have a molecular weight,  $(C_6H_{10}O_5)_4$ . Both forms are acetylated by acetic anhydride in the presence of zinc chloride, but scission of the molecules occurs at the same time; dextrin- $\alpha$  yields the *hexa-acetate* of a *diamylose*, needles (decomp.  $151.5-152.5^{\circ}$  (corr.),  $[\alpha]_D^{24} + 100.6^{\circ}$  in acetic acid), whilst dextrin- $\beta$  gives the *nona-acetate* of a *triamylose* (tablets, decomp.  $142^{\circ}$  (corr.),  $[\alpha]_D^{24} + 112.6^{\circ}$  in acetic acid). Hydrolysis of these acetates by cold alcoholic potassium hydroxide produces respectively *diamylose*,  $(C_6H_{10}O_5)_2$  (decomp. about  $300^{\circ}$ ,  $[\alpha]_D^{24} + 136.2^{\circ}$  in water), which crystallises from water in needles with  $2H_2O$ , and *triamylose*,  $(C_6H_{10}O_5)_3$ , needles, crystallising with  $4H_2O$ , decomposing near  $300^{\circ}$ ;  $[\alpha]_D^{24} + 151.8^{\circ}$  in water. Crystallographic details of the above amyloses are given. D. F. T.

**Fermentative Decomposition of the Hemicelluloses. I. A Trisaccharide as Intermediate Product of the Hydrolysis of Mannan.** HANS PRINGSHEIM (*Zeitsch. physiol. Chem.*, 1912, 80, 376—382).—By the action of a bacterial infusion on vegetable ivory nut turnings (Pringsheim, this vol., ii, 587), hydrolysis of the mannan takes place with the formation of mannose and a trisaccharide, probably a *trimannose*, identified by means of the *phenylosazone*, which crystallises in stellate aggregates of needles, decomp.  $196^{\circ}$  (corr.). It is completely fermented by most yeasts, but untouched by a yeast, No. 583, which is also without action on maltose, and may thus be separated from the monosaccharide. Emulsin hydrolyses it slowly, probably to a mixture of mono- and di-saccharide. E. F. A.

**Acetylations in Ether Solutions.** WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1912, 34, 1399—1409).—The reactions of acetyl chloride with organic bases are usually carried out by bringing the substances into direct contact, and the final products are generally the result of the decomposition of the original products by water or alkali. A study has now been made of the action of acetyl chloride on various bases in solution in dry ether. It has been found that in most cases a precipitate is produced, consisting of a mixture of the hydrochloride and acetyl chloride additive compound of the base, whilst the acetyl derivative remains dissolved in the ether. The results show that the acetyl chloride first unites with the base, thus:  $RNH_2 + CH_3 \cdot COCl \rightarrow R(CH_3 \cdot CO) \cdot NH, HCl$ . In the case of tertiary amines, an acetyl chloride additive product is invariably produced. With primary and secondary amines, it is sometimes the most abundant product, as in the case of benzylamine, but other substances are usually formed in accordance with the equations:  $2RNH_2 + CH_3 \cdot COCl \rightarrow RNH_2, HCl + R(CH_3 \cdot CO)NH$  and  $2R_2NH + CH_3 \cdot COCl \rightarrow R_2NH, HCl + R_2(CH_3 \cdot CO)N$ .

When dry ammonia is passed into an ethereal solution of acetyl chloride, ammonium chloride and acetamide are formed. By the reaction of acetamide with acetyl chloride, diacetamide and acetamide hydrochloride,  $2NH_2Ac, HCl$ , are produced. Benzamide, under similar conditions, yields acetylbenzamide and its *hydrochloride*,



which is rapidly hydrolysed by water.

Ethylamine yields its hydrochloride together with those of mono- and di-acetylethylamine. *Diacetylethylamine* has b. p.  $195-199^{\circ}$ ;

its *hydrochloride*, m. p.  $65^{\circ}$ , forms lustrous, hygroscopic needles. *iso*Amylamine gives its hydrochloride and that of its acetyl derivative. *Acetylisoamylamine* has b. p.  $220-224^{\circ}$ ; its *hydrochloride* forms hygroscopic needles. With aniline, the hydrochloride and acetanilide are produced. Acetanilide furnishes its hydrochloride and diacetyl-aniline. *p*-Toluidine gives its hydrochloride, aceto-*p*-toluidide, and diaceto-*p*-toluidide, the *hydrochloride* of which has m. p.  $120^{\circ}$ .  $\alpha$ - and  $\beta$ -Naphthylamine yield their hydrochlorides and the acetanaphthalides; aceto- $\alpha$ - and - $\beta$ -naphthalide *hydrochlorides* have m. p.  $137^{\circ}$  and  $152^{\circ}$  respectively. With benzylamine, the chief product of the reaction is acetylbenzylamine hydrochloride, m. p.  $134^{\circ}$ .

Diethylamine, diamylamine, methylaniline, ethylaniline, and piperidine yield their respective hydrochlorides, together with those of their acetyl derivatives. Acetomethylanilide *hydrochloride* has m. p.  $71^{\circ}$ .

Tripropylamine gives a mixture of its *hydrochloride*, m. p.  $90^{\circ}$ , with the acetyl chloride additive compound,  $N(C_3H_7)_3 \cdot CH_3 \cdot COCl$ . The additive compound of dimethylaniline has m. p.  $60-70^{\circ}$ . Diethylaniline, diethyl-*p*-toluidine, pyridine, quinoline, quinaldine, and acridine also yield additive compounds with acetyl chloride. The pyridine additive compound has m. p.  $71^{\circ}$ , and the acridine compound, m. p.  $236^{\circ}$ .

Quinine yields the additive compound,  $C_{20}H_{24}O_2N_2 \cdot 2CH_3 \cdot COCl$ . *m*-Nitroaniline gives a mixture of its hydrochloride with that of its acetyl derivative.

E. G.

**Action of Iodoform on Organic Bases.** WILLIAM M. DEHN and RAY B. CONNER (*J. Amer. Chem. Soc.*, 1912, **34**, 1409—1414).—In earlier papers (Abstr., 1911, i, 829, 914; this vol., i, 240, 242), it has been shown that when certain halogen derivatives of methane and ethane are added to solutions of organic bases in dry ether, molecular compounds are produced. It has now been found that iodoform reacts with organic bases in a similar manner to form compounds containing one mol. of iodoform with one, two, or three mols. of the base. The reactions are much accelerated by direct sunlight. The molecular compounds are readily decomposed by an excess of the base, by water, by heat, and by hot organic solvents. The following compounds are described.

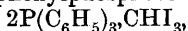
The diethylamine compound,  $NH(C_2H_5)_2 \cdot CHI_3$ , m. p.  $124^{\circ}$ , crystallising in white prisms: the triethylamine compound,  $NEt_3 \cdot CHI_3$ ; the dipropylamine compound,  $NH(C_3H_7)_2 \cdot CHI_3$ , m. p.  $144^{\circ}$ ; the diamylamine compound,  $NH(C_5H_{11})_2 \cdot CHI_3$ , m. p.  $221^{\circ}$ , forming prismatic needles. *iso*Propylamine, *isobutylamine*, *isoamylamine*, and allylamine yield heavy, brown oils.

The benzylamine compound,  $2CH_2Ph \cdot NH_2 \cdot CHI_3$ , m. p.  $158^{\circ}$ , forms long, yellow prismatic needles. With phenylhydrazine, a molecular compound is not obtained, but phenylhydrazine hydriodide, iodo-benzene, and traces of phenylcarbimide are produced. The piperidine compound,  $C_5H_{11}N \cdot CHI_3$ , m. p.  $107^{\circ}$ , forms white or pale yellow needles, and when distilled with steam yields piperidine hydriodide, iodoform, formic acid, and traces of di-iodoacetylene. The pyridine

*compound*,  $3C_5H_5N,CHI_3$ , m. p.  $183^\circ$ , crystallises in white needles, and is decomposed by water with formation of iodoform, iodic acid, and pyridine hydriodide. The  $\alpha$ -picoline *compound*,  $2C_5H_4MeN,CHI_3$ , is obtained as a red, gummy mass, and when heated with water yields iodine, iodoform, and picoline hydriodide. Lutidine gives a dark brown oil. Collidine yields a dark brown oil and long, transparent needles. The quinoline *compound*,  $2C_9H_7N,CHI_3$ , m. p.  $132^\circ$ , forms small, reddish-brown needles. The caffeine *compound*,



has m. p.  $154^\circ$ . The triphenylphosphine *compound*,



m. p.  $129^\circ$ , is an amorphous, yellow substance.

Various other bases yield dark-coloured precipitates, which have not yet been investigated; that furnished by morphine has m. p.  $248^\circ$ .  
E. G.

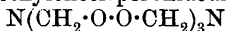
**Isolation of Betaine Hydrochloride from Molasses Residue.** FELIX EHRLICH (*Ber.*, 1912, 45, 2409—2413).—Stoltzenberg's method (this vol., i, 680) of isolating betaine hydrochloride from molasses residue differs only in unessential details from the author's patented process (1904, D.R.-P. 157173). Since betaine hydrochloride is easily purified, is not hydrated or hygroscopic, can be dried at  $110^\circ$ , and is extensively hydrolytically dissociated in aqueous solution, and can be used with the customary indicators, the author proposes that it shall be the standard substance in the preparation of solutions for acidimetry and alkalimetry.  
C. S.

**Isomeric Allylamines.** PRAFULLA CHANDRA RÂY and RASIK LAL DATTA (*J. and Proc. Asiatic Soc. Bengal*, 1912. Reprint 1 p.).—Hydrolysis of allylthiocarbimide by dilute sulphuric acid gives a poor yield of allylamine, b. p.  $57-58^\circ$  (Hofmann, *Ber.*, 1867, 1, 182; Rinne, *Abstr.*, 1874, 50). The substitution of 20% hydrochloric acid for sulphuric acid gives a better yield of an allylamine, b. p.  $55-58^\circ$  (Gabriel and Eschenbach, *Abstr.*, 1897, i, 395). On repeating the latter experiment, the authors find that the bulk of the amine has b. p.  $53-54^\circ$ , only a small portion passing over between  $57^\circ$  and  $58^\circ$ . It therefore appears that a third isomeric allylamine is formed during hydrolysis of the thiocarbimide by hydrochloric acid.  
H. W.

**The Action of Hydrogen Peroxide on Hexamethylene-tetramine.** CONWAY VON GIRSEWALD (*Ber.*, 1912, 45, 2571—2576).—In many reactions, hydrogen peroxide acts as a monobasic acid, dissociating into the ions  $H^+$  and  $O\cdot OH^+$ . In accordance with this behaviour, when hexamethylenetetramine is dissolved in excess of 30% hydrogen peroxide and the solution evaporated in a vacuum, thick, colourless crystals of a salt, *hexamethylenetetramine hydrogen peroxide*,  $(CH_2)_6N_4, H_2O_2$ , are obtained. It decomposes with explosion under the action of concentrated sulphuric acid, and liberates chlorine from concentrated hydrochloric acid. The solution shows the characteristic properties of the components.

When acids are present, the dissociation of the hydrogen peroxide is

prevented, and it reacts with hexamethylenetetramine forming a peroxide, namely, hexamethylenetriperoxidediamine,



(compare Baeyer and Villiger, *Abstr.*, 1900, i, 626). Citric acid is the most convenient acid to use in the preparation, the reagents being used in the proportion: 28 grams of hexamethylenetetramine, 42 grams of citric acid, and 140 grams of 30% hydrogen peroxide. The compound separates on warming the solution.

Hexamethylenetriperoxidediamine is a dangerously explosive substance, its explosive properties being much greater than those of mercury fulminate.

T. S. P.

**Preparation of *d*-Glucosamine.** CARL NEUBERG (*Biochem. Zeitsch.*, 1912, 43, 500—507).—This substance can be conveniently prepared by heating the calcium-free lobster-shells with concentrated hydrochloric acid in a water-bath. After evaporating and allowing the crystals to separate from the concentrated solution, alcohol should be added.

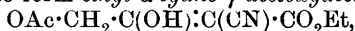
S. B. S.

**Conversion of Aminoethyl Alcohol (Colamine) into Choline.** GEORG TRIER (*Zeitsch. physiol. Chem.*, 1912, 80, 409—411).—Aminoethyl alcohol has been found in lecithin preparations from a number of sources. The name colamine is suggested for it. When methylated with methyl iodide and methyl-alcoholic potassium hydroxide it is converted into choline. Intermediate products, such as monomethyl- and dimethyl-aminoethyl alcohol are not formed.

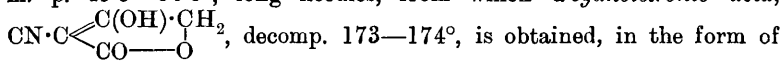
It is considered that choline is formed in the plant as a degradation product of methylated lecithin.

E. F. A.

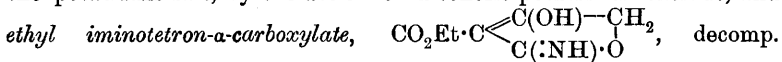
**Iminotetronic Acid.** RICHARD ANSCHÜTZ (*Ber.*, 1912, 45, 2374—2378).—Ethyl sodiocyanoacetate and acetylglucosyl chloride react in benzene to form *ethyl α-cyano-γ-acetoxyacetoacetate*,



m. p. 49·5—50·5°, long needles, from which *α-cyanotetronic acid*,



the potassium salt, by the action of alcoholic potassium ethoxide, and



243·5°, by boiling with alcohol. The latter, which yields the potassium salt of the former by boiling with alcoholic potassium ethoxide, is shown to be identical with Benary's ester-amide of tetramic acid (*Abstr.*, 1911, i, 672).

C. S.

**The Walden Rearrangement.** VIII. **Conversions of *d*-Glutamic Acid.** EMIL FISCHER and ANNIBALE MORESCHI (*Ber.*, 1912, 45, 2447—2453).—Natural *d*-glutamic acid is converted by nitrous acid into *l*-α-hydroxyglutaric acid. Nitrosyl chloride or hydrogen chloride and nitrous acid transform it into *l*-α-chloroglutaric acid, which, however, yields *d*-α-hydroxyglutaric acid. The last trans-

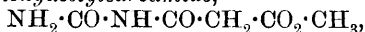
formation is effected either by boiling with water or by cold dilute sodium hydroxide, or by silver oxide and water at the ordinary temperature. In all three cases the hydroxy-acid obtained has the same rotatory power: this is contrary to observations in similar cases, especially that of chlorosuccinic acid.

The sodium salt of *l*-α-hydroxyglutaric acid forms a colourless, granular powder,  $[\alpha]_D^{19} - 8.65^\circ$ . The free acid has a very small laevorotation.

*l*-α-Chloroglutaric acid has m. p.  $99^\circ$  (corr.),  $[\alpha]_D^{18} - 12.5^\circ$ . It is converted into *d*-α-hydroxyglutaric acid,  $[\alpha]_D^{25} + 8.58^\circ$ , without any racemisation.

E. F. A.

**Preparation of Derivatives of Glycollic Carbamides.**  
ARNOLD VOSWINKEL (D.R.-P. 247270).—When bromoacetylcarbamide,  $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2\text{Br}$  (9.5 parts), is boiled for twelve hours with an alcoholic solution of anhydrous sodium acetate (4.1 parts), it furnishes carbomethoxyacetylcarbamide,



long, spear-like crystals, m. p.  $177^\circ$ ; the following analogous compounds were also obtained; from bromoacetylcarbamide with sodium isovalerate, m. p.  $165^\circ$ ; with sodium bromoisovalerate, glistening, mother-of-pearl scales, m. p.  $160^\circ$ ; with sodium benzoate, m. p.  $200^\circ$ , and with sodium salicylate, m. p.  $235^\circ$ ; these compounds are of therapeutic value.

F. M. G. M.

**Erysolin, a Thiocarbimidosulphone from Erysimum perowskianum.** WILHELM SCHNEIDER and HANS KAUFMANN (*Annalen*, 1912, 392, 1—15).—The seeds of *Erysimum perowskianum* contain a substance, probably a glucoside, from which a crystalline thiocarbimidosulphone, closely related to cheirolin (Abstr., 1910, i, 658), has been obtained, in 0.05% yield, calculated on the weight of the fresh seeds. The sulphone, which is called *erysolin*, is isolated in almost the same manner as cheirolin from wallflower seeds (*loc. cit.*).

*Erysolin*,  $\text{C}_6\text{H}_{11}\text{O}_2\text{NS}_2$ , m. p.  $59$ — $60^\circ$ , colourless prisms, is optically inactive. It reacts with alcoholic ammonia to form a thiocarbamide,  $\text{C}_6\text{H}_{14}\text{O}_2\text{N}_2\text{S}_2$ , m. p.  $143$ — $144^\circ$ , and is hydrolysed by boiling *N*-hydrochloric acid, yielding hydrogen sulphide, carbon dioxide, and a base,  $\text{C}_5\text{H}_{13}\text{O}_2\text{NS}$  (*hydrochloride*, m. p.  $160^\circ$ , colourless leaflets; *platinichloride*, decomp.  $205$ — $207^\circ$ ), the oxidation of which by nitric acid, D 1.5, at  $200^\circ$  yields methanesulphonic acid. A fuller examination of the natural *erysolin* has not been undertaken on account of lack of material, but the preceding facts, considered in conjunction with the close relation of *erysolin* to cheirolin, leave little doubt that *erysolin* is methyl-δ-thiocarbimidobutylsulphone,  $\text{CH}_3 \cdot \text{SO}_2 \cdot [\text{CH}_2]_4 \cdot \text{NCS}$ . This supposition has been verified by the synthesis of the latter. Methyl γ-cyanopropyl sulphide,  $\text{CN} \cdot [\text{CH}_2]_3 \cdot \text{SMe}$ , b. p.  $218^\circ$ , obtained from γ-chlorobutyronitrile and alcoholic sodium methylmercaptide at  $0^\circ$ , is reduced by sodium and boiling alcohol to methyl δ-aminobutyl sulphide,  $\text{NH}_2 \cdot [\text{CH}_2]_4 \cdot \text{SMe}$ , b. p.  $188$ — $190^\circ$ . This base, which has an odour resembling that of piperidine, forms a *hydrochloride*, m. p.  $153$ — $154^\circ$ , leaflets, *oxalate*, decomp.  $202^\circ$ , *picrate*, m. p.  $116$ — $118^\circ$ , yellow needles,

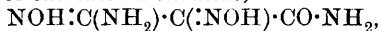
*picrolonate*, decomp. 172—174°, canary-yellow plates, *thiocarbamide*, m. p. 42—45°, and *NS-dimethiodide*,  $C_9H_{23}NSI_2$ , m. p. 142°, which is very stable. (The last fact is interesting in connexion with the non-existence of *NS*-dimethiodides of  $RS \cdot CH_2 \cdot CH_2 \cdot NH_2$  [this vol., i, 191] and the instability of the *NS*-dimethiodide of  $CH_3 \cdot S \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$  [Schneider, *loc. cit.*]).

Methyl  $\delta$ -aminobutyl sulphide in acetone is oxidised by concentrated hydrogen peroxide to *methyl- $\delta$ -aminobutylsulphoxide*,  $NH_2 \cdot [CH_2]_4 \cdot S(OMe)$ , which forms an *oxalate*, m. p. 174—179°, *picrate*, m. p. 149°, and *picrolonate*, m. p. 195° (decomp.). Methyl  $\delta$ -aminobutyl sulphide hydrochloride is oxidised by aqueous potassium permanganate to the *sulphone*,  $NH_2 \cdot [CH_2]_4 \cdot SO_2Me$ , m. p. 42°, b. p. 165°/4 mm., which is identical with the base obtained by the hydrolysis of *erysolin*. It forms a hydrochloride, m. p. 160°, platinichloride, decomp. 205—207°, *aurichloride*, m. p. 187—189°, yellow plates, *picrate*, decomp. 216°, *picrolonate*, m. p. 144°, decomp. 205°, yellow needles, *thiocarbamide*, m. p. 147°, and *dimethiodide*,  $C_8H_{20}O_2NSI$ , m. p. 138°, colourless needles.

By Braun's method (this vol., i, 693), the sulphone is converted into methyl- $\delta$ -thiocarbimidobutylsulphone, which proves to be identical with *erysolin*.  
C. S.

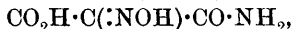
**Fulminic Acid. VI. Polymeric Fulminic Acids.** HEINRICH WIELAND and ARTUR BAUMANN (*Annalen*, 1912, 392, 196—213).—Of the three polymerides,  $C_3H_3O_3N_3$ , of fulminic acid, only the constitution of *isocyanilic acid* remains to be determined; *meta-fulminuric acid* is 4:5-dioximino-4:5-dihydroisooxazole (Abstr., 1909, i, 369), and *iso-fulminuric acid* is 3-hydroxyfurazan-4-carbonamide, as suggested by Nef, who obtained the substance by the action of ammonia on chloroformoxime. The authors have now thoroughly examined this reaction. A cold ethereal solution of chloroformoxime (obtained from silver fulminate and hydrochloric acid) is treated with *N*-ammonia. *iso*Fulminuric acid is not a direct product of the reaction. Doubtless fulminic acid is formed and immediately polymerises to *meta-fulminuric acid*. From this, by the action of the ammonia, the intermediate products of the reaction are obtained. These products are 3-hydroxyfurazan-4-carbonamidine, oximinomalonamideamidoxime, oximinomalonohydroxamidine (these three are the solid products of the reaction; the first two are the main products, and yield *isofulminuric acid* by warming with ammonia), a yellow oil, and 3-amino-4-oximinoisooxazolone (Abstr., 1909, i, 610). The separation of these substances is described.

The *amidoxime* of *oximinomalonamide*,



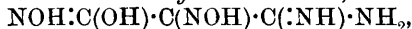
decomp. 170°, sulphur-yellow needles, forms colourless solutions in acids and yellow solutions in alkalis, and reacts with sodium nitrite in cold 15% hydrochloric acid to form nitrous oxide and a *substance*,  $C_3H_5O_3N_3$ , m. p. 215° (decomp.), colourless needles, which is isomeric, but not identical, with oximinomalonamide,  $\begin{matrix} NH \\ | \\ O \end{matrix} > C(CO \cdot NH_2)_2$ . This

substance is hydrolysed by boiling concentrated barium hydroxide, yielding oximinomalonic acid and *oximinomalonic acid*,

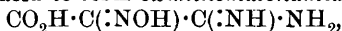


m. p. 137° (decomp.).

The *amidine* of *oximinomalonyhydroxamic acid*,



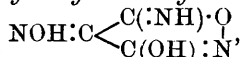
m. p. 177° (decomp.), colourless needles, is produced only in small quantity by the interaction of ammonia and chloroformoxime; together with the amidoxime, it is more conveniently obtained by allowing oximinocyanoacethydroxamic acid and an excess of aqueous ammonia to evaporate in the air. The amidine forms colourless solutions in acids and yellow solutions in alkalis, develops a bluish-violet coloration with dilute ferric chloride, forms an intensely yellow *silver* salt, and reacts with nitrous acid to form *oximinomalonamidine*,



decomp. 283°, colourless needles, which does not give a coloration with ferric chloride, but develops a deep violet coloration with ferrous sulphate and sodium acetate.

*iso*Fulminuric acid is best obtained by boiling the two products mentioned above with an excess of aqueous ammonia for three hours, and decomposing the resulting ammonium *isofulminate* by hydrochloric acid. It has m. p. 202° (decomp.), and is much less soluble in water or alcohol than Ehrenberg states. Reactions of the acid with metallic salts and so forth are mentioned. By hydrolysis with boiling barium hydroxide, it yields barium 3-hydroxyfurazan-4-carboxylate. *iso*-Fulminuric acid is also obtained from metafulminuric acid, either by its spontaneous decomposition in a sealed vessel (Scholvien's *β*-*iso*-fulminuric acid, m. p. 196°, stated to be so produced, is ordinary *iso*-fulminuric acid), or by heating it with a slight excess of sodium carbonate on the water-bath for a few minutes.

5-Imino-4-oximino-3-hydroxy-4:5-dihydroisooxazole,



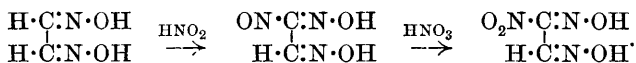
decomp. 143°, orange-yellow, crystalline powder, is obtained by warming metafulminuric acid for two to three minutes with *N*-sodium carbonate at 60—70°, cooling to 0°, and faintly acidifying with hydrochloric acid. It is unstable, gives no coloration with ferric chloride, and is converted into oximinomalonyhydroxamic acid by keeping with dilute hydrochloric acid. C. S.

**Mercury Fulminate.** ROBERT PHILIP (*Zeitsch. ges. Schiess- und Sprengstoffwesen*, 1912, 7, 109—112, 156—162, 180—182, 198—200, 221—225).—A series of papers dealing with different methods of preparing mercury fulminate, its purification, and analysis, with the theoretical considerations involved in these operations. F. M. G. M.

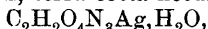
**Nitroglyoxime.** EUGEN BAMBERGER and UMETARO SUZUKI (*Ber.*, 1912, 45, 2740—2758).—The preparation and properties of nitroglyoxime have been investigated.

*Nitroglyoxime* is obtained in good yield by the regulated action of nitric acid (D 1·4—1·41) on glyoxime dissolved in a mixture of ether

and water. The presence of small quantities of nitrous acid appears essential to the success of the operation. It appears probable that the first stage of the reaction consists in the formation of nitroso-glyoxime, which is subsequently oxidised to nitroglyoxime, the nitrous acid simultaneously formed then acting on a further quantity of the original material:



Nitroglyoxime crystallises in white, silky needles, which swell up at 111°. The temperature is, however, largely dependent on external circumstances, such as rate of heating, width of capillary tube, etc. On further heating, a second more violent swelling occurs accompanied by evolution of gas. In the pure state it is stable. In aqueous solution, it gives a red coloration with ferric chloride, which, on keeping, increases in intensity and does not pass into ether when agitated with the latter. It yields a scarlet *ammonium* salt, a *potassium* salt,  $\text{C}_2\text{H}_2\text{O}_4\text{N}_3\text{K}$ , terra-cotta needles, a *silver* salt,



and a *copper* salt,  $(\text{C}_2\text{H}_2\text{O}_4\text{N}_3)_2\text{Cu}\cdot 2\text{H}_2\text{O}$ , dark green, almost black needles. The water of crystallisation in the two latter salts could not be directly determined, since they decompose in a vacuum at 50—60°. The *lead* salt,  $(\text{C}_2\text{H}_2\text{O}_4\text{N}_3)_2\text{Pb}\cdot\text{O}\cdot\text{Pb}(\text{C}_2\text{H}_2\text{O}_4\text{N}_3)$ , is formed as a yellow precipitate when aqueous solutions of lead acetate and nitroglyoxime are mixed, and is adapted for the detection of small quantities of the latter, since its aqueous suspension, when boiled, becomes colourless and almost clear.

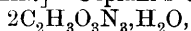
The *hydrazine* salt,  $\text{C}_2\text{H}_2\text{O}_4\text{N}_3(\text{NH}_3\cdot\text{NH}_2)$ , decomposing on rapid heating at 95°, when treated with acetone deposits white *needles*, decomposing at about 92°, according to the method of heating.

*Dibenzoylnitroglyoxime*, white needles decomposing at 151·5°, is obtained by the action of benzoyl chloride and potassium hydroxide on an aqueous solution of nitroglyoxime.

When a solution of nitroglyoxime in water is slowly distilled, decomposition occurs with the formation of nitrous oxide, nitrogen, nitric oxide, carbon dioxide, hydrocyanic acid, formic acid, oxalic acid, hydroxylamine, and ammonia, together with an oily acid *substance*, which has a powerful aldehydic odour. It is soluble in sodium hydroxide, but apparently unable to react with phenylhydrazine or *p*-nitrophenylhydrazine. It does not reduce ammoniacal silver nitrate or Fehling's solution. When allowed to remain in contact with water, it deposits a white *substance*, m. p. about 105°.

[With JUL. POTSCHIWAUSCHEG.]—Methazonic acid (Meister, Abstr., 1907, i, 885; Steinkopf, Abstr., 1909, i, 559) is transformed into nitroglyoxime when sulphuric acid is slowly added to a solution of the potassium salt and sodium nitrite at 0—4°.

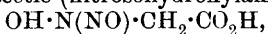
[With MARIE FINKELSTEIN.]—Ulpiani's compound,



prepared from glyoxime and nitrogen peroxide, proves to be a mixture of glyoxime and nitroglyoxime with small quantities of a third substance.

H. W.

**Reduction of Ethyl Diazoacetate.** II. AUGUST DARAPSKY and MORESHWAR PRABHAKAR (*Ber.*, 1912, 45, 2617—2625. Compare this vol., i, 543).—Hydrazinoacetic acid is obtained in good yield (65%) by reducing isonitroaminoacetic (nitrosohydroxylaminoacetic) acid,



with sodium amalgam in alkaline solution (compare Traube and Hoffa, *Abstr.*, 1897, i, 138 ; 1898, i, 235).

Ethyl nitrosohydrazinoacetate, which was previously described as an oil, has now been obtained in long, stout, colourless prisms, m. p. 33°. By reducing ethyl diazoacetate with zinc dust and acetic acid in ethereal solution, Curtius and Jay (*Abstr.*, 1889, 340) obtained a hydrazine compound, presumably the acetate of ethyl hydrazinoacetate. The authors have repeated the reduction, but from the product, only ethyl aminoacetate could be isolated.

Diazoacetic acid is readily reduced by zinc dust and sodium hydroxide to hydrazinoacetic acid, which is also obtained in good yield by reducing Pechmann's (*Abstr.*, 1895, i, 642) ethyl sulphohydrazimethylenecarboxylate with sodium amalgam in aqueous solution. The latter reaction is best interpreted on the assumption that the sulpho-compound has the structure  $\text{SO}_3\text{K}\cdot\text{NH}\cdot\text{N}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$ , and not the cyclic structure,

$$\text{SO}_3\text{K}\cdot\overset{\text{NH}}{\underset{\text{N}}{\text{C}}} \longrightarrow \text{CH}\cdot\text{CO}_2\text{Et}, \text{ proposed by Pechmann.}$$

Attempts to prepare the hydrazino-acid by reducing the hydrazone of glyoxylic acid proved fruitless. The semicarbazone, on the other hand, is readily reduced to  $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ , which, however, was not isolated, but hydrolysed by hydrochloric acid to hydrazinoacetic acid.

F. B.

**Estimation of Active Hydrogen in Organic Compounds by Magnesium Methyl Iodide.** TH. ZEREWITINOFF (*Ber.*, 1912, 45, 2384—2389).—In contrast to the results obtained by Hibbert (*Trans.*, 1912, 101, 328), the author finds that methyl, ethyl, and propyl alcohols yield practically the theoretical amount of methane by interaction with magnesium methyl iodide in pyridine.

From the results of experiments on the reaction between magnesium methyl iodide and ethylenediamine, *o*-, *m*-, and *p*-phenylenediamines, benzidine, *o*-tolidine, *oo'*-diaminostilbene, and 1:2-naphthylenediamine in pyridine or anisole, it is found that compounds containing two amino-groups yield two molecules of methane at the ordinary temperature and three molecules by warming; the fourth aminic hydrogen atom cannot be made to react with magnesium methyl iodide (compare *Abstr.*, 1908, i, 593). The abnormal behaviour of malonamide (*loc. cit.*), which by warming reacts with 4 molecules of magnesium methyl iodide, is due to the activity of one of the methylene hydrogen atoms.

Indene, fluorene, and  $\alpha\alpha'$ -dinaphthfluorene do not react with magnesium methyl iodide in pyridine at the ordinary temperature; however, by warming to 85°, one molecule of methane is evolved. Phenylfluorene and  $\alpha$ -naphthyldinaphthfluorene also only react when warmed. Phenylfluorenol and  $\alpha$ -naphthyldinaphthfluorenol partly react with magnesium methyl iodide at the ordinary temperature, but

must be heated to  $85^{\circ}$  in order that one molecule of methane may be liberated.

Only hydrocarbons of the fluorene type react with magnesium methyl iodide; diphenylmethane, triphenylmethane, dinaphthylmethane, and trinaphthylmethane ( $\alpha$  and  $\beta$ ) do not react either in the cold or by warming. C. S.

**Polymerisation of *cyclopentadiene*.** HANS STOBBE and FRITZ REUSS (*Annalen*, 1912, 391, 151—168).—By the spontaneous polymerisation of *cyclopentadiene*, *bicyclopentadiene* is the only product at temperatures up to  $100^{\circ}$ ; at higher temperatures, for example, at  $135^{\circ}$ , *polycyclopentadiene* is also formed.

In darkness at  $20^{\circ}$ , the polymerisation to the bicyclic compound is practically complete in thirty days, proceeding rapidly in the early stages and then more slowly as the process approaches completion. The rate of polymerisation is affected only very slightly by air or light. The course of the polymerisation is estimated by the change in the refractive index.

*cyclopentadiene* is prepared by the distillation of commercial *dicyclopentadiene* at  $166$ — $167^{\circ}$ , the fraction, b. p.  $41.5$ — $42^{\circ}$ , being redistilled until its refractive indices,  $n_D^{20}$  1.44113 and  $n_F^{20}$  1.45380, are constant. *Dicyclopentadiene*, m. p.  $32^{\circ}$ , b. p.  $70^{\circ}/24$  mm., is obtained by the spontaneous polymerisation of *cyclopentadiene*, and has  $n_D^{20}$  1.51047 and  $n_F^{20}$  1.52181. C. S.

**$\Delta^{1,3}$ -*cyclohexadiene*.** CARL D. HARRIES (*Ber.*, 1912, 45, 2586. Compare this vol., i, 343).—The hydrocarbon combines with bromine (one mol.) in chloroform solution, yielding the dibromide, m. p.  $108^{\circ}$ , described by Crossley (*Trans.*, 1904, 85, 1403). F. B.

**The Problem of Benzene Structure Reviewed from Thermochemical Standpoint.** WILLEBRORD TOMBROCK (*Chem. News*, 1912, 103, 155—156).—The heat liberated in the successive stages of the hydration of benzene is less than that set free in similar changes in open-chain compounds, and by ascribing the differences involved to the absorption of energy in the benzene ring, it is shown that information may be obtained in reference to the benzene structure. By assuming Kekulé's formula and correcting the heat of hydration for the influence of the ring structure, a value is obtained which agrees closely with the heat of hydration of open-chain compounds. When the centric formula is assumed, this concordance is no longer found.

H. M. D.

**Preparation of Nitrostyrene and of Arylnitroethanol Derivatives.** KARL W. ROSENEMUND (D.R.-P. 247817. Compare Abstr., 1905, i, 65; 1911, i, 34).—Pseudo-acids of the general formula



are readily obtained by the action of nitromethane on acylated hydroxyaryl aldehydes; these substances by treatment with acids furnish derivatives of nitrostyrene, which by subsequent hydrolysis with alkalis yield the corresponding hydroxy-compounds.

*Ethylcarbonatobenzaldehyde*, m. p.  $18^{\circ}$ , b. p.  $175-180^{\circ}$ /in a vacuum, when treated with nitromethane in sodium methoxide solution furnishes *ethylcarbonatonitrostyrene*,  $\text{OEt}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{NO}_2$ , yellow needles, m. p.  $110^{\circ}$ , and *ethylcarbonatophenylnitroethanol*  $\text{C}_2\text{H}_5\text{O}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NO}_2$ , yellow needles, m. p.  $91.5^{\circ}$ , whilst benzoylvanillin yields *vanillylnitroethylene*,  
 $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}\cdot\text{CH}\cdot\text{NO}_2$ ,  
 intensely yellow needles, m. p.  $161^{\circ}$ , and *vanillylnitroethanol*,  
 $\text{OH}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{NO}_2$ ,

a yellow oil:

*Dibenzoylprotocatechualdehyde*, m. p.  $96-97^{\circ}$ , yields *dibenzoyldioxy-nitrostyrene*,  $\text{C}_6\text{H}_5(\text{OBz})_2\cdot\text{CH}\cdot\text{CH}\cdot\text{NO}_2$ , yellow needles, m. p.  $143-144^{\circ}$ , which when treated with alcoholic alkaline hydroxides furnishes *nitro-dihydroxystyrene*,  $\text{C}_6\text{H}_3(\text{OH})_2\cdot\text{CH}\cdot\text{CH}\cdot\text{NO}_2$ , yellow needles, m. p.  $155^{\circ}$  (decomp.).  
 F. M. G. M.

**Phenanthrene-10-sulphonic Acid and Certain of its Derivatives.** HÅKAN SANDQVIST (*Annalen*, 1912, 392, 76-91).—*Phenanthrene-10-sulphonic acid*,  $\text{C}_{14}\text{H}_9\cdot\text{SO}_3\text{H}\cdot 2\text{H}_2\text{O}$ , m. p.  $134^{\circ}$  (decomp.) ( $174^{\circ}$  when anhydrous), leaflets or needles, is obtained in the form of the sodium salt in about 60% yield by the interaction of aqueous sodium sulphite and 10-bromophenanthrene at  $330-340^{\circ}$  for nine hours; the method is not satisfactory on the small scale. A process is described whereby the acid is obtained by the prolonged action of concentrated sulphuric acid on finely divided phenanthrene at the ordinary temperature. The molecular conductivities at  $18^{\circ}$  of the acid in aqueous solution,  $v = 34.25, 63.69, 127.8, 511.5$ , and  $1019$ , are  $319.4, 324.7, 329.2, 334.7$ , and  $334.7$  respectively.

The salts, obtained from the acid in aqueous solution and the hydroxide, oxide, or carbonate of the requisite metal, crystallise more readily and are much more soluble than most of the salts of other phenanthrenesulphonic acids. The following are described, the numbers in brackets denoting the weight of anhydrous salt which will dissolve in 100 grams of water at  $20^{\circ}$ : *potassium salt*, leaflets containing  $\text{H}_2\text{O}$  (0.84); *ammonium salt*, needles or leaflets containing  $1\frac{1}{2}\text{H}_2\text{O}$  (4.41); *sodium salt*, leaflets containing  $2\text{H}_2\text{O}$  (1.63); *calcium salt*, leaflets with  $2\text{H}_2\text{O}$  (0.30); *barium salt*, leaflets with  $3\text{H}_2\text{O}$  (0.13); *magnesium salt*, leaflets with  $5\text{H}_2\text{O}$  (0.22); *zinc salt*, leaflets and plates with  $6\text{H}_2\text{O}$  (0.15); *ferrous salt*, almost white leaflets with  $6\text{H}_2\text{O}$  (0.16); *lead salt*, needles or leaflets with  $4\text{H}_2\text{O}$ ; *copper salt*, green plates with  $4\text{H}_2\text{O}$  (0.26); *silver salt*, anhydrous leaflets (0.52).

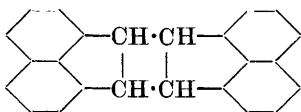
Phenanthrene-10-sulphonyl chloride, which is hydrolysed completely by water at  $230^{\circ}$ , is converted in benzene solution by concentrated aqueous ammonia into the *sulphonamide*, m. p.  $193.5^{\circ}$ , needles. *Methyl phenanthrene-10-sulphonate*, m. p.  $106^{\circ}$ , and the *ethyl ester*, m. p.  $108^{\circ}$ , are obtained from the potassium salt and the alkyl sulphate.

When heated at  $250-260^{\circ}$ , anhydrous ammonium phenanthrene-10-sulphonate is partly converted into ammonium phenanthrene-2-sulphonate and partly changed to phenanthrene and an ammonium phenanthrenedisulphonate.

Sodium phenanthrene-10-sulphonate yields phenanthraquinone by

oxidation with boiling chromic and acetic acids, but scarcely any quinone is formed when one part or more of potassium phenanthrene-3-sulphonate is present. C. S.

**Photochemical Changes of Acenaphthylene.** I. KARL DZIEWOŃSKI and G. RAPALSKI [and, in part, Z. LEYKO] (*Ber.*, 1912, 45, 2491—2495\*).—On exposure of yellow acenaphthylene in benzene solution to sunlight, it undergoes polymerisation, the new compound crystallising in slender, colourless needles of silky lustre, m. p. 306—307°; this is completely saturated, and does not dissolve in concentrated sulphuric acid. It has the composition  $(C_{12}H_8)_2$ , and, when oxidised with chromic acid, is converted almost quantitatively into naphthalic anhydride. This behaviour characterises it as *dinaphthylenecyclobutane* (annexed formula).



In view of the seven rings present, the name *heptacycene* is proposed.

In addition to the above an isomeric hydrocarbon crystallising in well formed, large, monoclinic prisms, m. p. 234°, is also formed. E. F. A.

**Fluoroanilines and Fluorophenols.** I. J. RINKES (*Chem. Weekblad*, 1912, 9, 778—783).—A number of fluoro-derivatives of aniline and phenol have been prepared. *p*-Fluoroaniline is obtained by reducing *p*-fluoronitrobenzene with iron-powder and sulphuric acid, (compare Wallach and Heusler, *Abstr.*, 1888, 362). It forms colourless crystals, m. p. -1.9°, b. p. 85°/19 mm. The *hydrochloride*, formed by the action of hydrogen chloride on the base in solution in carbon tetrachloride, has b. p. 167°/27 mm.

Diazotisation of *p*-fluoroaniline by Gattermann's method yields *p*-fluorophenol, white crystals, m. p. 46.0°, b. p. 81.5°/13 mm.

*o*-Fluoroaniline is prepared by reduction of *o*-fluoronitrobenzene with iron and very dilute sulphuric acid. Repeated distillation yields a product, m. p. -34.6°, b. p. 68.5°/14 mm. It is colourless, and has a faint aniline-like odour. On diazotisation, it resinifies, so that the corresponding phenol could not be prepared. A. J. W.

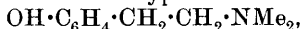
**Action of Formaldehyde on  $\beta$ -Phenylethylamine.** HERMAN DECKER and PAUL BECKER (*Ber.*, 1912, 45, 2404—2409).—A boiling alcoholic solution of  $\beta$ -phenylethylamine (*platinichloride*, m. p. 253—254°, yellow leaflets) reacts with methyl sulphate in the presence of sufficient sodium carbonate to keep the solution neutral, to form  $\beta$ -phenylethyltrimethylammonium iodide,  $CH_2Ph \cdot CH_2 \cdot NMe_3I$ , m. p. 227—230°, colourless leaflets; the corresponding *platinichloride* has m. p. 250°.  $\beta$ -Phenylethylamine hydrochloride and an excess of 40% formaldehyde at 130—140° for three hours yield the *hydrochloride*, white leaflets, of  $\beta$ -phenylethyltrimethylamine,  $CH_2Ph \cdot CH_2 \cdot NMe_3$ , b. p. 204—206°, which forms a *picrate*, m. p. 133—134°, yellow needles, and *platinichloride*, m. p. 206—208° (corr.), and yields the preceding quaternary ammonium iodide by methylation as above.

The base obtained by the decomposition of  $\beta$ -phenylethylglycine or its hydrochloride at their m. p.'s (*Abstr.*, 1911, i, 714) is  $\beta$ -phenylethyl-

\* and *Bull. Acad. Sci. Cracow*, 1912, A, 714—720.

*methylaminz*,  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NHMe}$ . This base, which forms a *hydrochloride* and *platinichloride*, m. p. 154—156° and 225—226° respectively, reacts with formaldehyde as above, to form  $\beta$ -phenylethyldimethylamine. C. S.

**Syntheses in the Fatty Aromatic Series. VIII. Phenol Bases.** JULIUS VON BRAUN and H. DEUTSCH (*Ber.*, 1912, 45, 2504—2522).—Compounds of the type of hordenine,

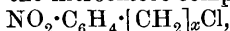


have been prepared, in which by the introduction of additional  $\text{CH}_2$  group the  $\text{NMe}_2$  is further removed from the benzene ring, in order to examine their pharmacological properties.

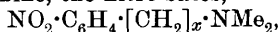
$\gamma$ -*o*-Hydroxyphenylpropyldimethylamine and the isomeric  $\gamma$ -*p*-hydroxyphenylpropyldimethylamine,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_3\cdot\text{NMe}_2$ , also  $\delta$ -*p*-hydroxyphenylbutyldimethylamine,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_4\cdot\text{NMe}_2$ , and  $\epsilon$ -*p*-hydroxyphenylamyldimethylamine,  $\text{OH}\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_5\cdot\text{NMe}_2$ , have been prepared by methods analogous to those used by Barger (*Trans.*, 1909, 95, 1123) in synthesising hordenine. The phenylalkyl chlorides,



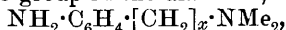
were cautiously nitrated, the nitrochloro-compounds,



acted on by dimethylamine, the nitro-bases,



reduced, and the amino-group in the diamines,



replaced by hydroxyl. Only in the propyl series is proof given that nitration takes place in the para-position. All four compounds act in the opposite manner to hordenine, since they lower the blood pressure; the effect of *o*-hydroxyphenylpropyldimethylamine is very small.

$\gamma$ -*o*-Hydroxyphenylpropyldimethylamine is a viscid, almost odourless, faintly yellow-coloured oil. The *hydrochloride* is colourless, m. p. 155—156°; the *platinichloride* forms small, yellow crystals, m. p. 160° (decomp.); the *methiodide* is colourless, m. p. 175°; the *picrate* separates in dark red, stout crystals, m. p. 127°. The *benzoyl* derivative is oily.

$\gamma$ -*p*-Nitrophenylpropyl chloride, prepared by nitration of  $\gamma$ -phenylpropyl chloride, has b. p. 176—180°. On reduction with tin and hydrochloric acid,  $\gamma$ -*p*-chloropropylaniline,  $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot[\text{CH}_2]_3\text{Cl}$ , is obtained. In addition chlorine enters the benzene ring, but this compound has not been isolated. The aniline is a brown oil with an odour of camphor; the *hydrochloride* has m. p. 174°; the *platinichloride* forms a yellow mass, m. p. 166°, which is decomposed even by cold water; the *benzoyl* derivative has m. p. 118°; the *phenylthiocarbamide* forms slender, colourless crystals, m. p. 125—126°.

The *phenylthiocarbamide* of tetrahydroquinoline, produced from the *o*-isomeride of the above, has m. p. 109°. The behaviour of *p*-chloropropylaniline on distillation and towards potassium hydroxide, carbonate or acetate establishes the absence of any *o*-chloropropylaniline from this product.

$\gamma$ -*p*-Hydroxyphenylpropyl chloride is a faintly yellow-coloured liquid,

b. p. 151—153°/8 mm. The *urethane*,  $\text{NHPh} \cdot \text{CO} \cdot \text{O} \cdot \text{C}_6\text{H}_4 \cdot [\text{CH}_2]_3\text{Cl}$ , forms a mass of crystalline threads, m. p. 124°.

$\gamma$ -p-*Hydroxyphenylpropyl alcohol* (*homotyrosol*),  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot [\text{CH}_2]_3 \cdot \text{OH}$ , forms colourless crystals resembling snow crystals, m. p. 55°; it gives an indigo-blue coloration with ferric chloride. It tastes only faintly bitter, and is without action on Fehling's solution. It is physiologically indifferent. The *dibenzoyl* derivative crystallises in colourless platelets, m. p. 72°.

$\gamma$ -p-*Nitrophenylpropyldimethylamine* has b. p. 168—170°/12 mm., 188—191°/22 mm., entirely without decomposition; it is yellow oil, non-miscible with water with a faintly basic odour. The *picrate* is sparingly soluble in alcohol; the *methiodide* separates in small, yellow crystals.

$\gamma$ -p-*Aminophenylpropyldimethylamine* is a colourless, mobile liquid of strong basic odour, b. p. 150—155°/10 mm., 155—160°/12 mm., with some decomposition. The benzoyl derivative and picrate are oily; the crystalline *hydrochloride* reddens on exposure, and blackens above 200° when heated. The *platinichloride* yields well-formed, yellow crystals, m. p. 201°.

*Homohordenine* separates in stunted, colourless crystals, m. p. 105—106°. The *picrate* crystallises in lustrous platelets, m. p. 164°; the *hydrochloride* forms plates, m. p. 142°; the *platinichloride* yields red platelets, m. p. 160°; the *methiodide* has m. p. 158°. The lethal dose of homohordenine for rabbits is 0.25 gram.

$\delta$ -p-*Nitrophenylbutyl chloride* is a yellow liquid of aromatic odour, b. p. 182—190°/7 mm.

$\delta$ -p-*Nitrophenylbutyldimethylamine* is a viscid, odourless oil, b. p. 166—168°/7 mm.; the *picrate* has m. p. 90—95°.

$\delta$ -p-*Aminophenylbutyldimethylamine* has b. p. 154—157°/7 mm., solidifying to a crystalline mass, m. p. 53°; the *picrate* has m. p. 120°; the *hydrochloride* blackens at 215°, m. p. 221°; the *platinichloride* blackens at 210°, m. p. 212°.

$\delta$ -p-*Hydroxyphenylbutyldimethylamine* separates in lustrous, colourless crystals, m. p. 97°; the *hydrochloride* has m. p. 154°; other derivatives analysed are the *picrate*, m. p. 124—125°, the *platinichloride*, m. p. 152°, and the *methiodide*, m. p. 214°. The lethal dose of the hydroxyphenylbutyldimethylamine is 0.01 gram.

$\epsilon$ -p-*Nitrophenylamyl chloride* is a pale yellow liquid, b. p. 190—195°/8 mm., with a pleasant sweet odour.

$\epsilon$ -p-*Nitrophenylamyl dimethylamine* has b. p. 190—192°/12 mm., and forms a *picrate*, m. p. 185°.

$\epsilon$ -p-*Aminophenylamyl dimethylamine* is a viscid liquid of a strongly basic odour, b. p. 179—185°/13 mm.

$\epsilon$ -p-*Hydroxyphenylamyl dimethylamine* crystallises in colourless, lustrous needles, m. p. 99°. The *hydrochloride* is oily; the *platinichloride* has m. p. 122°. The lethal dose of a slightly impure preparation was 0.02 gram.

E. F. A.

**Acetals Derived from Cyclic Alcohols.** MARCEL MURAT and CATHALA (*J. Pharm. Chim.*, 1912, [vii], 6, 289—292).—The condensa-

tion products of formaldehyde with *cyclohexanol* and the three methyl-*cyclohexanols* are described.

When hydrogen chloride is passed into *cyclohexanol*, dissolved in 40% formaldehyde solution, the product  $C_6H_{11}O \cdot CH_2 \cdot O \cdot C_6H_{11}$ , b. p. 279—280°/760 mm.,  $D_0^{24}$  0.9716,  $n_D$  1.470, is formed. It is a colourless liquid having a fruity odour and darkening on exposure to light with the liberation of some formaldehyde. It dissolves in sulphuric acid with a blood-red colour, forms substitution products with bromine, and is violently attacked by a mixture of sulphuric and nitric acids, producing adipic acid. When passed over thoria at 400°, it gives rise to hydrogen, ethylene, water, benzene, *cyclohexene*, and *cyclohexanone*.

2-Methyl*cyclohexanol* gives a similar product, b. p. 298°/760 mm. (corr.),  $D_0^{24}$  0.9627,  $n_D$  1.477, which with sulphuric and nitric acids yields chiefly *n*-pimelic acid,  $CO_2H \cdot [CH_2]_5 \cdot CO_2H$ . The corresponding substance from 3-methyl*cyclohexanol* has b. p. 301—303° (corr.),  $D_0^{24}$  0.9612,  $n_D$  1.470, whilst that from 4-methyl*cyclohexanol* has b. p. 301—303° (corr.),  $D_0^{24}$  0.968,  $n_D$  1.473, and with sulphuric and nitric acids yields  $\beta$ -methyladipic acid.

T. A. H.

**Behaviour of Phenols, Naphthols, and Phenolcarboxylic Acids Towards Quadrivalent Titanium.** OTTO HAUSER and A. LEWITE (*Ber.*, 1912, 45, 2480—2484).—Concentrated solutions of titanium oxide in cold fuming hydrochloric acid or strong sulphuric acid give an intense bluish-red coloration on heating with hydroxy-phenols, for example, phenol, the cresols, thymol, quinol, guaiacol, resorcinol, orcinol,  $\alpha$ - and  $\beta$ -naphthol, etc. The reaction is a general one for the detection of hydroxy-groups. Catechol and pyrogallol give a yellow or deep red coloration with dilute solutions of the titanium salt. The two dihydroxynaphthalenedisulphonic acids show violet with the solution of titanium in strong sulphuric acid, but red with a dilute solution.

Halogen and nitrogen derivatives of the phenols do not show the reaction; the colour is not influenced by other organic substituents so long as the hydroxy-group remains intact.

Well characterised compounds of titanium with phenols or naphthols could not be obtained. More favourable results are given by the phenolcarboxylic acids, which give a yellow coloration with titanous acid.

Salicylic acid thus gives an intense reddish-yellow coloration in alcoholic solution; on evaporation, red flakes separate. On boiling and dilution with water, an amorphous, yellow precipitate is obtained. Probably the solution contains a complex, titanisalicylic acid, and the precipitates represent hydrolytic decomposition products.

By mixing a concentrated solution of titanous acid in cold fuming hydrochloric acid with an excess of salicylic acid and adding in small portions 5% ammonium solution, while the whole is warmed and stirred until the solution is only just acid, the ammonium salt of a dititanisalicylic acid,  $O:[Ti(O \cdot C_6H_4 \cdot CO_2 \cdot NH_4)(O \cdot C_6H_4 \cdot CO_2H)_2]_2$ , is obtained in yellowish-red, prismatic crystals.

The corresponding sodium salt crystallises in golden-yellow platelets.

The *ammonium* salt of *dititanio-o-cresotic acid*,  
 $\text{OTi}_2(\text{O}\cdot\text{C}_7\text{H}_6\cdot\text{CO}_2)_6(\text{NH}_4)_4\text{H}_2\text{O}$ ,  
 separates in well crystallised, yellowish-red prisms. E. F. A.

**Aminoacetates of Phenols.** CARL MANNICH and W. DRAUZBURG (*Arch. Pharm.*, 1912, 250, 532—538).—A number of aminoacetates of phenols have been prepared by Delépine's method (Abstr., 1895, i, 327; 1897, i, 394) and their properties are described.

*Phenyl iodoacetate*, m. p. 68°, obtained by the interaction of sodium iodide and phenyl chloroacetate dissolved in acetone, crystallises from ether in colourless prisms, and with hexamethylenetetramine gives the *additive product*,  $\text{OPh}\cdot\text{CO}\cdot\text{CH}_2(\text{C}_6\text{H}_{12}\text{N}_4)\text{I}$ , m. p. 164° (decomp.), which when gently warmed with hydrochloric acid in alcohol yields *phenyl aminoacetate hydrochloride*, m. p. 206—208°, crystallising from acetone in colourless leaflets; the free ester decomposes immediately on liberation from its salts by alkalis.

*Guaiacyl bromoacetate*,  $\text{OMe}\cdot\text{C}_6\text{H}_4\text{O}\cdot\text{CO}\cdot\text{CH}_2\text{Br}$ , m. p. 45°, b. p. 181°/25 mm., obtained by the action of bromoacetyl bromide on guaiacol, crystallises from ether in colourless needles. It combines with hexamethylenetetramine, but gives an impure product containing the tetramine hydrobromide. *Guaiacyl iodoacetate*, m. p. 36°, obtained by treating the chloroacetate with sodium iodide in acetone, crystallises from ether in needles and decomposes when distilled even under reduced pressure. Its *additive product* with hexamethylenetetramine forms colourless leaflets, m. p. 157—158° (decomp.), and is hydrolysed by warm hydrochloric acid in alcohol to *guaiacyl aminoacetate hydrochloride*, m. p. 196°, which separates in colourless crystals; the free ester is an oil. *Eugenyl chloroacetate*, m. p. 23°, b. p. 187—193°/13 mm., was obtained by the action of chloroacetyl chloride on eugenol in presence of pyridine. *o-Nitrophenyl chloroacetate*, m. p. 63°, similarly prepared, crystallises in colourless needles, and gives no additive product with hexamethylenetetramine.

T. A. H.

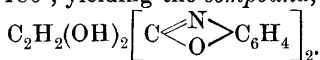
**Preparation of Complex Compounds from Halogenated Phenols and their Homologues.** SCHÜLKE & MAYR and PAUL FLEMMING (D.R.-P. 247410).—When halogenated phenols or their homologues are boiled with an alkali hydroxide or carbonate in an anhydrous solvent (such as benzene), crystalline complex salts are formed; the patent describes the preparation of *compounds* from *p*-chloro-*m*-cresol, *p*-chloro- and *p*-bromo-phenols, and from 2:4:6-tribromophenol; these compounds find employment as disinfectants.

F. M. G. M.

**Salts of Aminophenols with Dibasic Acids.** ROBERT MEDINGER (*J. pr. Chem.*, 1912, [ii], 86, 345—359. Compare Suida, Abstr., 1911, i, 284).—The author has examined the behaviour of the three isomeric aminophenols towards malic, tartaric, succinic, oxalic, and phthalic acids in aqueous or acetone solution, and finds that the tendency to form salts is most pronounced in the case of the ortho-compound, which yields only normal salts. With *m*- and *p*-aminophenols the acid salts are

formed most readily; only in a few cases could normal salts be isolated.

*o*-Aminophenol tartrate,  $C_{16}H_{20}O_8N_2$ , small, white needles (decomp.  $211^\circ$ ), loses water at  $180^\circ$ , yielding the compound,



The acid tartrate of *m*-aminophenol,  $C_{10}H_{13}O_7N$ , forms white needles (decomp.  $175^\circ$ ); the para-isomeride is converted at  $180$ – $200^\circ$  into *p*-hydroxytartranil, which forms slender, white, asbestos-like needles, m. p. above  $250^\circ$ . The normal tartrate of *p*-aminophenol decomposes at  $220^\circ$ .

The acid malates of *m*- and *p*-aminophenol decompose at  $111^\circ$  and  $115^\circ$  respectively; the acid succinates at  $155^\circ$  and  $151^\circ$ . The normal succinate of *o*-aminophenol (decomp.  $144^\circ$ ) is resolved by crystallisation from water into its components.

Of the normal oxalates, the ortho-compound forms leaflets (decomp.  $167.5^\circ$ ), the para-compound, lustrous, slender needles (decomp.  $290^\circ$ ); the meta-compound decomposes at  $180^\circ$ , and the acid oxalates of *m*- and *p*-aminophenol at  $176^\circ$  and  $220^\circ$  respectively. The interaction of *o*-aminophenol and phthalic acid in hot aqueous solution yield the normal phthalate, m. p.  $147.5^\circ$ , and di-*o*-hydroxyphthalanilide, m. p.  $227.5^\circ$ .

The acid phthalate of *m*-aminophenol is transformed by boiling with water into *m*-hydroxyphthalanil, m. p.  $220^\circ$ ; that of *p*-aminophenol (decomp.  $250^\circ$ ) into *p*-hydroxyphthalanil, m. p.  $250^\circ$ .

Attempts to prepare additive compounds of the aminophenols with ethyl succinate and benzyl tartrate proved fruitless.

Benzyl tartrate is obtained as a viscid, yellow oil by heating benzyl alcohol and tartaric acid with potassium hydrogen sulphate at  $130^\circ$ .  
F. B.

**Preparation of Pure *m*-Cresol.** F. HOFFMANN, LA ROCHE & Co. (D.R.-P. 247272. Compare this vol., i, 549).—When commercial *m*-cresol (1000 parts) containing about 90% *m*- and 10% *p*-cresol is dissolved in 900 parts of concentrated sulphuric acid and sulphonated at a temperature below  $100^\circ$ , *m*-cresolsulphonic acid separates on cooling and can subsequently be converted into pure *m*-cresol.  
F. M. G. M.

**Action of Oxygen on Quinol and a Sulphite.** JOHANNES PINNOW (*Zeitsch. Wiss. Photochem.*, 1912, 11, 289–304).—The changes which occur when oxygen is absorbed by aqueous solutions containing quinol and sodium sulphite have been investigated by quantitative measurements of the quinol, sulphite, and sulphate present at different stages of the oxidation process. Comparative experiments were also made with (1) quinol in the absence of sulphite; (2) potassium quinolmonosulphonate and sulphite; (3) potassium quinoldisulphonate and sulphite. From the data thus obtained it appears that, if sulphite is present in considerable excess, the quinol and sulphite disappear in the molar ratio 1 : 2. At the same time, one molecule of benzoquinonemonosulphonic acid and one of sulphate are produced. On the assumption

that the traces of copper present in the sulphite act catalytically, the changes which occur in the solutions may be represented by the equations : (1)  $\text{C}_6\text{H}_4(\text{OH})_2 + 2\text{CuO} = \text{C}_6\text{H}_4\text{O}_2 + \text{Cu}_2\text{O} + \text{H}_2\text{O}$  ; (2)  $\text{Cu}_2\text{O} + \text{O}_2 = \text{Cu}_2\text{O}_3$  ; (3)  $\text{C}_6\text{H}_4\text{O}_2 + \text{Na}_2\text{SO}_3 + \text{H}_2\text{O} = \text{C}_6\text{H}_3(\text{OH})_2\cdot\text{SO}_3\text{Na} + \text{NaOH}$  ; (4)  $\text{Cu}_2\text{O}_3 + \text{Na}_2\text{SO}_3 = \text{Na}_2\text{SO}_4 + 2\text{CuO}$  ; (5)  $\text{Cu}_2\text{O}_3 + \text{C}_6\text{H}_4(\text{OH})_2 = \text{C}_6\text{H}_4\text{O}_2 + 2\text{CuO} + \text{H}_2\text{O}$ .

Although quinol in pure aqueous solution is not oxidised at a measurable rate, the increase in the hydroxyl ion concentration resulting from the addition of disodium phosphate is sufficient to cause the reaction to take place quite readily. If the quinol in the sulphite solution is replaced by its monosulphonate, the oxidation of the sulphite is retarded, and this is still more marked if the disulphonate is introduced.

H. M. D.

### Iron Compounds of Phenols. III. Iron Guaiacol Derivatives.

RUDOLF F. WEINLAND and KARL BINDER (*Ber.*, 1912, 45, 2498—2502. Compare this vol., i, 445).—By the reaction in alcoholic solution of ferric acetate, guaiacol, and alcoholic ammonia or alkali hydroxide, complex salts of a monobasic *tetraguaiacolferric acid* are obtained, having the constitution  $[\text{Fe}(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})_4]\text{H}$ . In these, one guaiacol residue is attached by an auxiliary valency to the iron.

The *ammonium* salt forms a dark reddish-black, lustrous, crystalline powder, consisting of microscopic, rectangular prisms. The *sodium* salt forms a similar powder, composed of four- or six-sided microscopic plates, which are red or violet by transmitted light. The *potassium* salt appears under the microscope as bundles of four-sided prisms with straight cut ends.

These salts are stable when dry, but decomposed by boiling water.

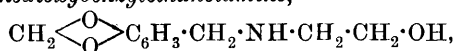
Guaiacol reacts with anhydrous ferric chloride in ethereal solution to form a substance,  $\text{FeCl}_2\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ . This constitutes a brownish-black powder of a dark bronze lustre, consisting of microscopic, well formed, transparent platelets. In alcohol it dissolves ; at first blue, the solution then becomes deep green, and on the addition of more alcohol a dirty brown colour is produced.

E. F. A.

**Benzylamine Derivatives.** CARL MANNICH and R. KUPHAL (*Arch. Pharm.*, 1912, 250, 539—547).—The following substances were prepared in the course of various unsuccessful attempts to synthesise isoquinoline derivatives from substituted benzylamines, containing the skeleton  $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{NH}\cdot\ddot{\text{C}}\cdot\text{C}\cdot$  (compare Fischer, *Abstr.*, 1893, i, 427 ; Rügheimer and Schön, *Abstr.*, 1909, i, 605).

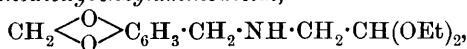
*Benzylmethylethanamine*,  $\text{CH}_2\text{Ph}\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$ , b. p. 133—135°/14 mm., obtained by the action of ethylene chlorohydrin on benzylmethylamine in a closed vessel at 110°, is a colourless oil, yielding a crystalline *hydrochloride* and *platinichloride*, m. p. 173°. When heated with phosphoric oxide in a closed vessel at 200°, it gives *benzylvinylmethylamine*, the *hydrochloride* of which crystallises from a mixture of alcohol and ethyl acetate in colourless needles, m. p. 218—220°, and yields a *platinichloride*, m. p. 215—216° (decomp.), in orange-yellow leaflets.

## 3 : 4-Methylenedioxybenzylethanamine,



b. p. 198—205°/14 mm., similarly obtained, gives a *hydrochloride*, m. p. 150—151°, crystallising in colourless leaflets.

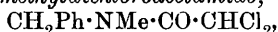
## 3 : 4-Methylenedioxybenzylaminoacetal,



b. p. 197—202°/12 mm., obtained by the action of chloroacetal on 3 : 4-methylenedioxybenzylamine at 140° in closed vessels, is a colourless liquid; the *hydrochloride*, m. p. 160° (decomp.), crystallises from dilute alcohol.

*Benzyl*dichloroacetamide,  $\text{CH}_2\text{Ph} \cdot \text{NH} \cdot \text{CO} \cdot \text{CHCl}_2$ , m. p. 95—96°, obtained by the action of ethyl dichloroacetate on benzylamine, crystallises from dilute alcohol.

3 : 4-Methylenedioxybenzyl*dichloroacetamide*,  $\text{CH}_2 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CHCl}_2$ , m. p. 136—137°, similarly prepared, crystallises in long, colourless needles from acetone or from dilute alcohol.



*Benzyl*methyl*dichloroacetamide*, m. p. 63°, forms stellate groups of slender needles from dilute alcohol.

Oxamethane reacts at 0° with 3 : 4-methylenedioxybenzylamine to furnish the compound,  $\text{CH}_2 \begin{array}{c} \diagup \text{O} \diagdown \\ \diagdown \text{O} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH}_2$ , small leaflets, m. p. 205—206°, and with benzylmethylamine to give the substance,  $\text{CH}_2\text{Ph} \cdot \text{NMe} \cdot \text{CO} \cdot \text{CO} \cdot \text{NH}_2$ , m. p. 86—87°, which crystallises from ether.

All attempts to condense these compounds to *isoquinoline* derivatives were unsuccessful.

T. A. H.

**Condensation of Chloroacetone with Phenols.** EDUARD LIPPMANN (*Ber.*, 1912, 45, 2489—2491).—*Trihydroxy-αβ-triphenylpropane*,  $\text{CH}_3 \cdot \text{C}(\text{C}_6\text{H}_4 \cdot \text{OH})_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , prepared by heating chloroacetone with three molecules of phenol and fuming hydrogen chloride, has been so far only obtained as a colloid, decomp. 175°. The *acetyl* derivative forms a colourless, lustrous mass, decomp. 155°.

*Hexahydroxy-αβ-triphenylpropane*, prepared in a similar manner from resorcinol, gives a colourless or faintly red-coloured substance, m. p. 180°.

E. F. A.

**Reduction of Disulphides by Dextrose. Preparation of Mercaptans.** MAX CLAASZ (*Ber.*, 1912, 45, 2424—2828).—*oo'*-Dinitrodiphenyl disulphide is reduced to *o*-nitrophenyl mercaptan very easily and conveniently by heating an alcoholic suspension of the substance and dextrose with aqueous sodium hydroxide; by heating the alkaline solution with chloroacetic acid, an almost quantitative yield of *o*-nitrophenylthiolacetic acid is obtained (compare this vol., i., 389).

This method of reducing disulphides to mercaptans is apparently general; thus dithiosalicylic acid yields thiosalicylic acid, and diphenyl disulphide yields phenyl mercaptan, which readily yields phenylthiolacetic acid by condensation with chloroacetic acid in warm alkaline solution.

C. S.

**The Action of Light on Sulphoxides and Sulphides.** OSCAR HINSBERG (*Ber.*, 1912, 45, 2337—2339).—The author withdraws his statement (*Abstr.*, 1908, i, 257) as to the existence of an isomeric form of benzyl disulphide. Further experiments have hitherto failed to reveal the existence of isomeric disulphides other than those previously described.

A weak solution of  $\beta$ -naphthyl disulphide in acetic acid containing a trace of iodine, when exposed to direct sunlight for several weeks, gives a small amount of dinaphthylene disulphide,  $C_{10}H_6 \begin{smallmatrix} S \\ \diagup \quad \diagdown \\ S \end{smallmatrix} C_{10}H_6$  (compare Fries and Volk, *Abstr.*, 1909, i, 406).

Benzyl sulphide under similar treatment in acetic acid solution also undergoes oxidation, giving a little benzyl sulphoxide. In this and the previous case the oxidation is attributed to the atmosphere.

Benzyl disulphoxide, if dissolved in acetic acid together with a little iodine, on exposure to sunlight is partly reduced to benzyl disulphide; the presence of the iodine as catalyst is essential to the action.

D. F. T.

**Sulphonylides.** RICHARD ANSCHÜTZ (*Ber.*, 1912, 45, 2378—2380).—By the name *sulphonylides* the author designates a new class of cyclic esters of phenol-*o*-sulphonic acids.

*o*-Phenylenesulphonylide,  $C_6H_4 \begin{smallmatrix} O \cdot SO_2 \\ \diagup \quad \diagdown \\ SO_2 \cdot O \end{smallmatrix} C_6H_4$ , m. p. 236.5—237.5°, stout needles, is obtained by treating an ethereal solution of *o*-acetoxybenzenesulphonyl chloride with gaseous ammonia or with diethylamine.

*Tolylene-3:4-sulphonylide*,  $C_6H_3Me \begin{smallmatrix} O \cdot SO_2 \\ \diagup \quad \diagdown \\ SO_2 \cdot O \end{smallmatrix} C_6H_3Me$ , m. p. 279—286°, is obtained in a similar manner, or, better, by treating *p*-cresol-3-sulphonic acid with phosphoryl chloride. These aromatic sulphonylides are very stable, but yield the alkali salts of phenol-sulphonic acids by treatment with concentrated alkalis.

C. S.

**Aromatic Telluride Dihaloids and their Basic Fission Products.** KARL LEDERER (*Annalen*, 1912, 391, 326—347).—Whilst diaryl telluride dihaloids,  $TeAr_2X_2$ , and the corresponding oxides,  $TeAr_2O$ , have long been known, the intermediate basic salts,  $OH \cdot TeAr_2X$ , have hitherto not been described. Diphenyl telluride dichloride, which is obtained almost quantitatively by passing oxygen through a mixture of its ethereal solution and concentrated hydrochloric acid, is converted by boiling water into basic *diphenyl telluride chloride*,  $OH \cdot TePh_2Cl$ , m. p. 233—234°, from which the *anhydride*,  $O(TePh_2Cl)_2$ , m. p. 233—234°, is obtained at 145—150°. Basic *diphenyl telluride bromide*,  $OH \cdot TePh_2Br$ , m. p. 264—265°, obtained from diphenyl telluride dibromide in a similar manner, yields the *anhydride*,  $O(TePh_2Br)_2$ , m. p. 264—265°, at 160—170°. *Diphenyl telluride di-iodide*,  $TePh_2I_2$ , m. p. 237—238° (decomp.), red crystals, obtained from diphenyl telluride and iodine in ether, is not converted by boiling water into the basic *iodide*. The latter, however, is obtained by treating a neutral solution of the basic

bromide or chloride with an alkali iodide. It is a canary-yellow, microcrystalline powder, m. p. 214—215°, easily decomposes into the oxide and di-iodide, and yields the *anhydride*, m. p. 216—217°, at 180°.

The following substances are also described: *Di-p-tolyl telluride dichloride*, m. p. 166—167°, monoclinic needles or triclinic leaflets; basic *di-p-tolyl telluride chloride*, m. p. 261—263°, and its *anhydride*, m. p. 261—263°; basic *di-p-tolyl telluride bromide*, m. p. 269—270°, and its *anhydride*; *di-p-tolyl telluride di-iodide*, m. p. 218—219°; basic *di-p-tolyl telluride iodide*, m. p. 203—204° (decomp.); *di-p-tolyl telluride oxide*,  $(C_6H_4Me)_2TeO$ , m. p. 166—167°; *di-p-tolyl telluride dihydroxide*,  $(C_6H_4Me)_2Te(OH)_2$ ; *di-o-tolyl telluride dichloride*, m. p. 183°, and the basic *anhydride*,  $O[TeCl(C_6H_4Me)_2]_2$ , m. p. 220—222°; *di-o-tolyl telluride dibromide*, and the basic *anhydride*, m. p. 224—225° (decomp.); *di-o-tolyl telluride di-iodide*, m. p. 175—176°; *di-o-tolyl telluride oxide*, m. p. 205—206° (decomp.). C. S.

**Synthesis of Tyrosol and its Conversion into Hordenine.** FELIX EHRLICH and P. PRITSCHIMUKA (*Ber.*, 1912, 45, 2428—2437).—Tyrosol is obtained in about 40% yield by the prolonged boiling of  $\beta$ -*p*-hydroxyphenylethylamine hydrochloride and an excess of potassium nitrite in neutral or faintly acid solution. It is obtained very conveniently as follows.  $\beta$ -*p*-Nitrophenylethylamine, readily obtained in 45% yield, together with 18% of the meta-isomeride, by the action of concentrated sulphuric acid and nitric acid, D 1.5, at  $-10^\circ$  on  $\beta$ -phenylethylamine, is converted by potassium nitrite and 10% sulphuric acid into  $\beta$ -*p*-nitrophenylethyl alcohol,  $NO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot OH$ , m. p.  $64^\circ$ , yellow needles, which is then reduced by tin and hydrochloric acid. The resulting *hydrochloride*, m. p.  $171^\circ$ , of  $\beta$ -*p*-aminophenylethyl alcohol is converted by hydrochloric acid and potassium nitrite into  $\beta$ -*p*-hydroxyphenylethyl alcohol, which is identical with tyrosol.

Tyrosol has also been obtained, although in poor yield, by reducing  $\beta$ -*p*-nitrophenylethylamine hydrochloride to  $\beta$ -*p*-aminophenylethylamine *dihydrochloride*, m. p. about  $296^\circ$  (decomp.), and treating this with nitrous acid. Tyrosol (this vol., ii, 590) has b. p.  $195^\circ/18$  mm., crystallises in the rhombic system, and reduces ammoniacal silver oxide solution, but not Fehling's solution, even by boiling. By heating with hydrochloric acid, D 1.19, at  $100^\circ$  for three hours, it yields  $\beta$ -*p*-hydroxyphenylethyl chloride, from which hordenine is obtained by the action of 33% alcoholic dimethylamine at  $100^\circ$  for three hours.

C. S.

**Triphenylcarbinols. IV.** HUGO KAUFFMANN and FELIX KIESER (*Ber.*, 1912, 45, 2333—2337. Compare Kauffmann, this vol., i, 351, 397).—2:4:2':4'-Tetramethoxy- and 2:4:2':4':2'':4''-hexamethoxytriphenylcarbinol are strongly basic substances, and exhibit halochromy in a marked manner.

4-Iodoresorcinol dimethyl ether, m. p.  $40^\circ$ , b. p.  $163^\circ/14$  mm., obtained by the action of iodine and mercuric oxide on resorcinol dimethyl ether, gives with magnesium and ether an organo-magnesium compound, which reacts with carbon dioxide, giving  $\beta$ -resorcylic acid, m. p.  $108^\circ$ , and with benzophenone giving 2:4-dimethoxytriphenylcarbinol

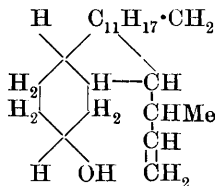
(compare Kauffmann and Pannwitz, Abstr., 1910, i, 393); in a similar manner, it reacts with 2:4-dimethoxybenzophenone, producing 2:4:2':4'-tetramethoxytriphenylcarbinol,  $\text{OH}\cdot\text{C}(\text{Ph})[\text{C}_6\text{H}_3(\text{OMe})_2]_2$ , m. p.  $134\cdot5^\circ$ , which gives a bluish-red colour with acids, and then dyes wool pale red; the carbinol is reduced by zinc dust and acetic acid to 2:4:2':4'-tetramethoxytriphenylmethane,  $\text{CHPh}[\text{C}_6\text{H}_3(\text{OMe})_2]_2$ , colourless needles, m. p.  $122^\circ$ , which give an orange-red solution in concentrated sulphuric acid.

2:4:2':4':2'':4''-Hexamethoxytriphenylcarbinol,  $\text{OH}\cdot\text{C}[\text{C}_6\text{H}_3(\text{OMe})_2]_3$ , obtained by the action of the above Grignard reagent on the dimethyl ether of ethyl  $\beta$ -resorcyate, and also in very small quantities as a by-product in the action of carbon dioxide on the same Grignard reagent, is a colourless, crystalline solid, m. p.  $149^\circ$ ; it dissolves in dilute acids, giving a carmine-red solution which dyes wool red. It is reduced by zinc and acetic acid to 2:4:2':4':2'':4''-hexamethoxytriphenylmethane, m. p.  $145^\circ$ , which gives a red solution in concentrated sulphuric acid.

D. F. T.

**Cholesterol. XV. New Degradation Products of Cholesterol.** ADOLF WINDAUS (*Ber.*, 1912, 45, 2421—2423).—By oxidation with chromic acid in 20% sulphuric acid on the water-bath, a glacial acetic acid solution of the cyclic ketonic acid,  $\text{C}_{24}\text{H}_{38}\text{O}_3$  (this vol., i, 449), yields a lactone,  $\text{C}_{24}\text{H}_{36}\text{O}_3$  (the analyses agree better with the formula  $\text{C}_{24}\text{H}_{38}\text{O}_3$ ), m. p.  $140^\circ$ , long needles subliming at about  $280^\circ/12$  mm., which is neutral, unchanged by aqueous potassium hydroxide, and soluble in concentrated alcoholic potassium hydroxide. It forms an oxime, m. p.  $136^\circ$ , and is oxidised to a crystalline acid, m. p.  $252^\circ$ , by chromic acid.

The tricarboxylic acid,  $\text{C}_{24}\text{H}_{38}\text{O}_6$ , which is also produced by the oxidation of the acid,  $\text{C}_{24}\text{H}_{38}\text{O}_3$  (*loc. cit.*), is oxidised by chromic, acetic, and 20% sulphuric acids to acetone and a tetracarboxylic acid,  $\text{C}_{21}\text{H}_{30}\text{O}_8$  (or  $\text{C}_{21}\text{H}_{32}\text{O}_8$ ), m. p.  $185^\circ$ , which contains a methyl group, since it yields acetaldehyde by oxidation with dilute sulphuric acid and potassium permanganate. At present the author is of opinion that cholesterol has the annexed formula.



C. S.

**Ferric Benzoates.** RUDOLF FRIEDRICH WEINLAND and ALFRED HERZ (*Ber.*, 1912, 45, 2662—2680).—The amorphous, flesh-coloured precipitate obtained by mixing dilute aqueous solutions of sodium benzoate (1.5 mols.) and ferric chloride (0.5 mol.) consists of an impure hexabenzototri ferric monobenzoate, (I)  $[\text{Fe}_3(\text{OBz})_6](\text{OBz})$ , which, when boiled with a solution of benzoic acid in acetone, separates as a lustrous, crystalline, dark reddish-orange powder, containing  $2\frac{1}{2}\text{H}_2\text{O}$ ; it has also been obtained crystallised with  $\frac{1}{2}\text{H}_2\text{O}$ . Hexabenzototri ferric tribenzoate,  $[\text{Fe}_3(\text{OBz})_6](\text{OBz})_3$ , prepared by boiling the original monobenzoate (I) with a saturated solution of

benzoic acid in chloroform, crystallises in thin, microscopic, hexagonal, orange leaflets.

Extraction of the monobenzoate (I) for several days with benzene, which has been saturated at the ordinary temperature with benzoic acid, yields a *dibenzoate*,  $\left[ \text{Fe}_3(\text{OBz})_6 \right] (\text{OBz})_2$ , crystallising in slender, light orange needles; if the extraction is carried out with an ethereal solution of benzoic acid, the dibenzoate is obtained in hexagonal, orange columns, containing  $2\text{H}_2\text{O}$ .

The following *compounds* of the mono- and di-benzoate are described:  $\left[ \text{Fe}_3(\text{OBz})_6 \right] (\text{OBz})_2$ ,  $\left[ \text{Fe}_3(\text{OBz})_6 \right] (\text{OBz})_2$ , microscopic, orange-red, four-sided, hemimorphic columns;

$\left[ \text{Fe}_3(\text{OBz})_6 \right] (\text{OBz})_2$ ,  $2 \left[ \text{Fe}_3(\text{OBz})_6 \right] (\text{OBz})_2 \cdot 2\text{H}_2\text{O}$ , lustrous, yellowish-orange needles, and

$\left[ \text{Fe}_3(\text{OBz})_6 \right] (\text{OBz})_2$ ,  $3 \left[ \text{Fe}_3(\text{OBz})_6 \right] (\text{OBz})_2 \cdot 6\text{H}_2\text{O}$ , which crystallises in reddish-orange, rectangular plates or short columns.

*Hexabenzototriferric perchlorate*,  $\left[ \text{Fe}_3(\text{OBz})_6 \right] \text{ClO}_4 \cdot 3\text{H}_2\text{O}$ , is obtained in parallel aggregates of long, flat plates or columns by the interaction of the monobenzoate (I) and perchloric acid in aqueous alcoholic solution; by varying the conditions under which the reaction takes place, the following *compounds* were isolated: *hexabenzototriferric benzoate perchlorate*,  $\left[ \text{Fe}_3(\text{OBz})_6 \right] \text{ClO}_4 \cdot (\text{OBz})_2 \cdot \text{H}_2\text{O}$ , stout, red, hexagonal plates;  $\left[ \text{Fe}_3(\text{OBz})_6 \right] \text{ClO}_4 \cdot \left[ \text{Fe}_3(\text{OBz})_6 \right] (\text{OBz})_2 \cdot 5\text{H}_2\text{O}$ , which forms yellowish-orange, rhombic or hexagonal plates, and

$2 \left[ \text{Fe}_3(\text{OBz})_6 \right] \text{ClO}_4 \cdot \left[ \text{Fe}_3(\text{OBz})_6 \right] (\text{OBz})_2 \cdot 6\text{H}_2\text{O}$ , crystallising in brown, hexagonal columns capped with pyramids.

The *platinichloride*,  $\left[ \text{Fe}_3(\text{OBz})_6 \right] \text{PtCl}_6 \cdot 4\text{H}_2\text{O}$ , crystallises in long, brown, rectangular plates.

The following *compounds* of the nitrate and nitrate benzoate were obtained by the action of nitric acid on the monobenzoate (I) in alcoholic and aqueous alcoholic solution respectively:

$\left[ \text{Fe}_3(\text{OBz})_6 \right] \text{NO}_3 \cdot \left[ \text{Fe}_3(\text{OBz})_6 \right] (\text{OBz})_2 \cdot 3\text{H}_2\text{O}$ , stout plates of rhombohedral habit, and

$3 \left[ \text{Fe}_3(\text{OBz})_6 \right] \text{NO}_3 \cdot \left[ \text{Fe}_3(\text{OBz})_6 \right] (\text{OBz})_2 \cdot 7\text{H}_2\text{O}$ , which crystallises in parallel aggregates of reddish-yellow plates.

When boiled for several hours with acetone, the monobenzoate (I) loses benzoic acid, yielding *pentabenzototriferric monobenzoate*,

$\left[ \text{Fe}_3(\text{OBz})_5 \right] (\text{OBz})_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ ,

which forms brownish-orange cubes, and has also been obtained

crystallised with  $1\text{H}_2\text{O}$ . The pentabenzoato-compound forms with hexabenzoatotriferric monobenzoate the *compounds*,

$$\left[ \text{Fe}_3 \begin{smallmatrix} (\text{OBz})_5 \\ (\text{OH})_3 \end{smallmatrix} \right] (\text{OBz}), \left[ \text{Fe}_3 \begin{smallmatrix} (\text{OBz})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] (\text{OBz}), 2\text{H}_2\text{O}$$
 and  $3 \left[ \text{Fe}_3 \begin{smallmatrix} (\text{OBz})_5 \\ (\text{OH})_3 \end{smallmatrix} \right] (\text{OBz}), \left[ \text{Fe}_3 \begin{smallmatrix} (\text{OBz})_6 \\ (\text{OH})_2 \end{smallmatrix} \right] (\text{OBz}), \text{H}_2\text{O}$ , and on treatment with chloroplatinic acid and perchloric acid is converted into the above-mentioned platinichloride and perchlorate of the hexabenzoato-base.

When boiled with 75% alcohol and the product crystallised from acetone, the original monobenzoate (I) yields *tribenzoatotriferric monobenzoate*,  $\left[ \text{Fe}_3 \begin{smallmatrix} (\text{OBz})_3 \\ \text{O} \\ (\text{OH})_3 \end{smallmatrix} \right] (\text{OBz})$ , which crystallises in dark brown, hexagonal columns capped with pyramids. F. B.

**Preparation of Aminobenzoyl Compounds.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 247818).—*m*-Aminobenzoyl-*m*-nitroanilide,  $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , yellow crystals, m. p.  $183^\circ$ , is readily prepared from *m*-nitrobenzoyl-*m*-nitroanilide by reduction with sodium hydrogen sulphide in boiling 90% alcohol. F. M. G. M.

**Hagemann's Esters and their Analogues.** WALTER DIECKMANN (*Ber.*, 1912, 45, 2689—2697).—Further insight into the isomerism exhibited by ethyl 2:6-diphenylcyclohexene-4-one-1-carboxylate (Abstr., 1911, i, 450) has been obtained by titration with bromine (Meyer, Abstr., 1911, i, 350; Meyer and Kappelmeier, *ibid.*, i, 832). Neither ketonic ester absorbs bromine in cold dilute alcoholic solution, whereas the enolic ester proves to be a mixture of the enolic and ketonic forms containing, when freshly prepared, 20—25% of the former. Similar experiments have been carried out with ethyl 6-phenyl-1-methyl- $\Delta^2$ -cyclohexene-4-one-1-carboxylate, with the corresponding methyl ester and with ethyl 2-methylcyclohexene-4-one-1-carboxylate (Hagemann's ester).

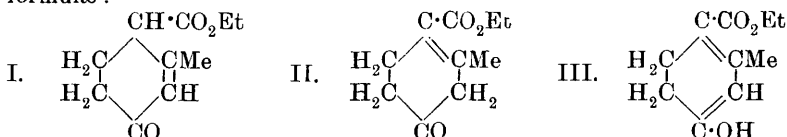
Ethyl 6-phenyl-2-methyl- $\Delta^1$ -cyclohexene-4-one-1-carboxylate is transformed into ethyl 6-phenyl-2-methyl- $\Delta^2$ -cyclohexene-4-one-1-carboxylate when boiled in alcoholic solution with sodium acetate and subsequently distilled. When dissolved in an alcoholic solution of sodium alkoxide and poured into benzenediazonium acetate, it yields a *phenylhydrazone*, m. p.  $98$ — $99^\circ$ .

Relationships between the isomerides are more readily observed with the corresponding methyl esters. Methyl 6-phenyl-2-methyl- $\Delta^2$ -cyclohexene-4-one-1-carboxylate, colourless, prismatic needles, m. p.  $89$ — $90^\circ$ , b. p.  $220$ — $225^\circ/20$  mm., is obtained by prolonged heating of a methyl-alcoholic solution of methyl benzylidenebisacetate (m. p.  $183^\circ$ ) with sodium methoxide or directly from the ethyl ester by means of methyl alcohol and sodium methoxide. It does not unite with bromine, and gives no coloration with ferric chloride. When heated at  $150^\circ$  or boiled in alcoholic solution during twelve hours, it only forms traces of the enolic ester. The *semicarbazone* has m. p.  $183^\circ$ . The ester is soluble in methyl-alcoholic sodium methoxide

with the formation of an intensely yellow *sodium* salt, which, on acidification, yields an impure enolic ester (containing from 10–20% of the enolic form). This solidified ester, after crystallisation from methyl alcohol, deposits the isomeric labile, ketonic ester (methyl 6-phenyl-2-methyl- $\Delta^1$ -cyclohexene-4-one-1-carboxylate, m. p.  $60^\circ$ ), which behaves towards ferric chloride and bromine in the same manner as the stable ester. The *semicarbazone*, m. p.  $210^\circ$ , is slowly formed when the aqueous alcoholic solution of the labile ester is mixed with semicarbazide acetate, a certain amount of transformation into the stable ester occurring simultaneously. Distillation or protracted heating of an alcoholic solution of the labile ester—particularly readily in the presence of alkaline reagents—produces an equilibrium mixture in which the stable ester predominates.

The *sodium* salt formed from the above ketonic esters readily couples with benzenediazonium acetate to form a *compound*, m. p.  $102^\circ$ .

With Hagemann's ester (ethyl 2-methyl- $\Delta^2$ -cyclohexene-4-one-1-carboxylate, formula I) similar behaviour is observed (compare Hagemann, Abstr., 1893, i, 393; Callenbach, *ibid.*, 1897, i, 271; Rabe and Rahm, *ibid.*, 1905, i, 348; Merling, *ibid.*, 1905, i, 349). Neither the above ester nor the labile ketonic isomeride (formula II) contains more than a trace of the enolic form. By means of sodium methoxide, a *sodium* salt is obtained, which, on acidification, yields an ester mixture containing from 10–20% of the enolic form (formula III). The labile ester appears to be rather more readily soluble in alkali than the stable ester. Attempts to prepare isomeric semicarbazones were fruitless.  $\gamma$ -Acetobutyric acid is formed when either ester is oxidised by potassium permanganate. The relationships are shown in the following formulæ:



Apparently the keto-ester (II) formed from the enol ester readily passes into the keto-ester (I). Hence, probably, Callenbach's acid ester is a mixture of keto-ester (II) with varying amounts of keto-ester (I), whilst the neutral ester is either the keto-ester (I) or an equilibrium mixture of the two keto-esters in which the ester (I) is present in by far the greater quantity.

The sodium salt of the above esters readily couples with benzenediazonium acetate with the formation of a *phenylhydrazone*, m. p.  $83\text{--}84^\circ$ .

H. W.

**Alkylation of cycloHexanone-4-carboxylic Esters and the Constitution of the Mentheneone Derived from Hagemann's Ester.** WALTER DIECKMANN (*Ber.*, 1912, 45, 2697—2707).—The mentheneone derived from the *isopropyl* derivative of Hagemann's ester (see previous abstract) has been variously regarded as 1-methyl-2-*isopropyl*- $\Delta^6$ -cyclohexene-5-one (Kötz and Auger, Abstr., 1911, i, 309)

and as 1-methyl-4-isopropyl- $\Delta^6$ -cyclohexene-5-one (Merling and Welde, Abstr., 1909, i, 479). The author's views on the constitution of the enolic form of Hagemann's ester lead him to consider the ketone as 1-methyl-2-isopropyl- $\Delta^1$ -cyclohexene-3-one. Attempts to obtain an insight into the mechanism of the alkylation of similar substances were not completely successful. Ethylation of ethyl 2:6-diphenyl- $\Delta^1$ -cyclohexene-4-one-1-carboxylate gave a 40% yield of ethyl 2:6-diphenyl-3-ethyl- $\Delta^2$ -cyclohexene-4-one-1-carboxylate, but action did not occur completely in one direction.

*Ethyl 2:6-diphenyl-3-ethyl- $\Delta^2$ -cyclohexene-4-one-1-carboxylate*, needles, m. p. 102°, obtained by the action of ethyl iodide and alcoholic sodium ethoxide on ethyl 2:6-diphenyl- $\Delta^1$ -cyclohexene-4-one-1-carboxylate, was slowly transformed by boiling mineral acids into 1:5-diphenyl-2-ethyl- $\Delta^1$ -cyclohexene-3-one, needles, m. p. 102—103° (semicarbazone, m. p. 205°). The same ester was also obtained by elimination of water from *ethyl 2:6-diphenyl-3-ethylcyclohexane-4-one-1-carboxylate*, m. p. 150—160° (obtained from ethyl benzoylacetate and styryl propyl ketone (compare Abstr., 1911, i, 451).

*Ethyl 2:4-diphenyl-1-ethyl- $\Delta^4$ -cyclohexene-6-one-1-carboxylate*, prisms, m. p. 138°, was obtained by the action of ethyl iodide on the sodio-salt of ethyl 2:4-diphenyl- $\Delta^4$ -cyclohexene-6-one-1-carboxylate (obtained from phenyl styryl ketone and ethyl acetoacetate), or, in poor yield, by the action of sodium ethoxide on a mixture of phenyl styryl ketone and ethyl ethylacetoacetate. Boiling dilute sulphuric acid scarcely attacked it, but hydrochloric or hydrobromic acid in glacial acetic acid solution gradually transformed it into 2:4-diphenyl-1-ethyl- $\Delta^4$ -cyclohexene-6-one, needles, m. p. 83° (semicarbazone, m. p. 208—209°).

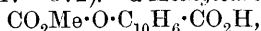
Hagemann's ester was converted into the isopropyl derivative, from which the corresponding menthenone was obtained according to Callenbach's directions (Abstr., 1897, i, 271). Oxidation of the ketone by means of potassium permanganate yielded  $\gamma$ -acetobutyric acid (identified as semicarbazone) and isobutyric acid. The oxime, m. p. 104°, appeared in all respects identical with that obtained by Callenbach, but the oxime, m. p. 90—91°, described by Kötze and Auger (Abstr., 1911, i, 310) could not be isolated. Contrary also to the experience of the latter chemists, the hydrochloride of this oxime, m. p. 135°, was hydrolysed by water. Further discrepancies were also observed with regard to the semicarbazone, which according to Kötze and Auger (*loc. cit.*) occurs in two forms melting at 138° and 152° respectively. The author has observed only one semicarbazone, m. p. 167—168°, which could be preserved unchanged for months. H. W.

**Combination of Phenolcarboxylic Acids.** FERDINAND MAUTHNER (*J. pr. Chem.*, 1912, [ii], 86, 432).—A correction. The author has described (Abstr., 1911, i, 725; this vol., i, 267) a number of compounds obtained by the reaction of certain acid chlorides and phenolic esters in the presence of sodium hydroxide. It is now found that the phenolic esters take no part in the reaction, and therefore the compounds cannot have the structure previously assigned to them. F. B.

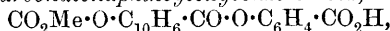
**Sodium Phenyl Carbonate as an Intermediate Product in Kolbe's Synthesis of Salicylic Acid.** S. TIJMSTRA (*Ber.*, 1912, 45, 2837—2838).—A reply to Sluiter (this vol., i, 189), re-stating and explaining the views already expressed (*Abstr.*, 1905, i, 209, 439).

T. A. H.

**Methylcarbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetic Operations. VII. Didepsides of Hydroxynaphthoic, Ferulic, and *o*-Coumaric Acids. Methyl Derivatives of Orsellic Acid.** EMIL FISCHER and KURT HOESCH (*Annalen*, 1912, 391, 347—372).— *$\alpha$ -Methylcarbonato- $\beta$ -naphthoic acid*,



m. p. 127—128° (decomp. corr.), is obtained by treating a cold suspension of  *$\alpha$ -hydroxy- $\beta$ -naphthoic acid* in benzene and dimethylaniline (2 mols.) with methyl chlorocarbonate and subsequently acidifying. The corresponding *chloride*,  $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_{10}\text{H}_6\cdot\text{COCl}$ , m. p. 96°, colourless prisms, dissolved in acetone, is added to a solution of *p*-hydroxybenzoic acid in *N*-sodium hydroxide (2 mols.) at 0°; by acidification, the mixture yields *4- $\alpha$ -methylcarbonatonaphthoiloxybenzoic acid*,



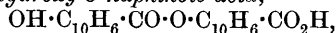
m. p. 231—232° (decomp. corr.). By hydrolysis in acetone by *N*-ammonium hydroxide (3 mols.), the latter yields *4- $\alpha$ -hydroxynaphthoiloxybenzoic acid*, m. p. 247° (decomp. corr.).

The preceding method with acetone is the most convenient process for preparing didepsides, and has been employed in the following cases.

*Methylcarbonatoferulic acid*,  $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , m. p. 186—187° (decomp. corr.), long needles, obtained from methyl chlorocarbonate and ferulic acid in cold alkaline solution, yields a *chloride*,  $\text{C}_{12}\text{H}_{11}\text{O}_5\text{Cl}$ , m. p. 147° (corr.), which forms with *p*-hydroxybenzoic acid by the acetone method *4-methylcarbonatoferuloyloxybenzoic acid*,  $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ , m. p. 246° (decomp. corr.). The hydrolysis of the last by aqueous ammonia and pyridine yields *4-feruloyloxybenzoic acid*,  $\text{C}_{17}\text{H}_{14}\text{O}_6$ , m. p. 233° (corr.), glistening leaflets. The preceding acid chloride reacts with ferulic acid in the acetone process to form *methylcarbonatodiferulic acid*,  $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_3(\text{OMe})\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , m. p. 230° (decomp. corr.), the hydrolysis of which yields *diferulic acid*,  $\text{C}_{20}\text{H}_{18}\text{O}_7$ , m. p. 241—242° (decomp. corr.). *Methylcarbonatodi-*o*-coumaric acid*,  $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$ , m. p. 170° (corr.), obtained in a similar manner from *o*-coumaric acid and methylcarbonatocoumaroyl chloride, yields *di-*o*-coumaric acid*, m. p. 188° (decomp. corr.), by hydrolysis with aqueous ammonia.

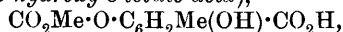
*2-Methylcarbonato-3-naphthoic acid*,  $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$ , m. p. 174—175° (decomp. corr.), forms a *chloride*,  $\text{C}_{13}\text{H}_9\text{O}_4\text{Cl}$ , m. p. 107° (corr.), which does not yield a didepside by the acetone method, but condenses with 2-hydroxy-3-naphthoic acid in benzene in the presence of dimethylaniline to form *2:2'-methylcarbonato-3'-naphthoiloxy-3-naphthoic acid*,  $\text{CO}_2\text{Me}\cdot\text{O}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}\cdot\text{O}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$ , m. p. 215° (decomp. corr.); the hydrolysis of the latter by aqueous ammonia and

acetone yields *di-2-hydroxy-3-naphthoic acid*,



m. p. 245° (decomp. corr.).

Orsellinic acid and methyl chlorocarbonate (1·1 mol.) in cold *N*-sodium hydroxide (2 mols.) yield *methylcarbonato-orsellinic acid* (*5-methylcarbonato-3-hydroxy-o-toluic acid*),



m. p. 153—154° (corr.), which is converted by further treatment with sodium hydroxide and methyl chlorocarbonate into *dimethylcarbonato-orsellinic acid*,  $\text{C}_{12}\text{H}_{12}\text{O}_8$ , m. p. 133° (decomp. corr.). All attempts to prepare the chloride of the latter acid have been unsuccessful, so that the synthesis of lecanoric acid (orsellic acid), the longest known lichen acid, has been frustrated.

*Methyl methylcarbonato-orsellinate*,  $\text{CO}_2\text{Me} \cdot \text{O} \cdot \text{C}_6\text{H}_2\text{Me}(\text{OH}) \cdot \text{CO}_2\text{Me}$ , m. p. 80—81° (corr.), is obtained from methyl orsellinate and methyl chlorocarbonate in alkaline solution. Like the preceding methylcarbonato-derivative, it develops a reddish-violet coloration with alcoholic ferric chloride.

Orsellinic acid is generally regarded as 3:5-dihydroxy-*p*-toluic acid. The authors are of opinion that it is 3:5-dihydroxy-*o*-toluic acid for the following reasons. Diazomethane methylates phenolcarboxylic acids preferentially in the para-position; ethyl orsellinate and ethereal

diazomethane yield an  $\alpha$ -methyl ether,  $\text{CO}_2\text{Et} \cdot \text{C} \begin{smallmatrix} \text{C}(\text{OH}) \cdot \text{CH} \\ \text{CMe} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{OMe}$ ,

m. p. 72—75°, which gives with ferric chloride a reddish-violet coloration resembling that developed by salicylic acid. Also methyl chlorocarbonate attacks phenolcarboxylic acids preferentially in the para-position. The preceding methyl methylcarbonato-orsellinate, therefore, has the methylcarbonato-group in position 5, and consequently develops a characteristic coloration with ferric chloride. Now, when methylcarbonato-orsellinic acid is treated with ethereal diazomethane, it yields *methyl methylcarbonato-orsellinate- $\beta$ -methyl ether*,  $\text{CO}_2\text{Me} \cdot \text{C} \begin{smallmatrix} \text{C}(\text{OMe}) \cdot \text{CH} \\ \text{CMe} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{O} \cdot \text{CO}_2\text{Me}$ , m. p. 86° (corr.), which

does not develop a coloration with ferric chloride. The hydrolysis of the ester by concentrated sulphuric acid at 25° yields *methylcarbonato-orsellinic acid- $\beta$ -methyl ether*,  $\text{CO}_2\text{H} \cdot \text{C} \begin{smallmatrix} \text{C}(\text{OMe}) \cdot \text{CH} \\ \text{CMe} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{O} \cdot \text{CO}_2\text{Me}$ ,

m. p. 145° (corr.), which also does not develop a coloration with ferric chloride. The hydrolysis of the last substance by *N*-sodium hydroxide yields *orsellinic acid- $\beta$ -methyl ether*,  $\text{CO}_2\text{H} \cdot \text{C} \begin{smallmatrix} \text{C}(\text{OMe}) \cdot \text{CH} \\ \text{CMe} \cdot \text{CH} \end{smallmatrix} \text{C} \cdot \text{OH}$

(decomp. 175°), which develops a yellowish-red coloration with ferric chloride. Were the old formula of orsellinic acid correct, the  $\beta$ -methyl ether would be a derivative of salicylic acid, and should develop its characteristic coloration with ferric chloride; moreover, the  $\alpha$ - and the  $\beta$ -methyl ethers would be identical, not isomeric, as is actually the case.

Orsellinic acid- $\alpha$ -methyl ether is shown to be identical with everninic acid by direct comparison of the m. p., colorations with ferric chloride, crystalline form, and properties of the ethyl esters. C. S.

**Number of Isomerides of Merotropic and Desmotropic Compounds. IV. Isomeric Modifications of Ethyl Formylphenylacetate.** ARTHUR MICHAEL (*Annalen*, 1912, 391, 235—274).—The author has re-commenced an investigation of the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -modifications of ethyl formylphenylacetate, since the constitutions of the first two, and the existence of the last, are still subjects of discussion. According to the author, ethyl formylphenylacetate exists in three modifications: the  $\alpha$ -ester, b. p. 125—126°/9 mm. (decomp.),  $\beta$ -ester, m. p. about 40°, and  $\gamma$ -ester, m. p. about 100°. All of these are enolic, since they react with aliphatic tertiary amines (compare Michael and Smith, *Abstr.*, 1908, i, 943), and also with phenylcarbimide; in the latter case, all three yield the carbanilide, m. p. 117—118° (*Abstr.*, 1906, i, 179), the  $\alpha$ -ester giving, in addition, an *isomeride*,  $C_{18}H_{17}O_4N$ , m. p. 59°, which is converted quantitatively into the anilide, m. p. 117—118°, by heat.

The preparation of  $\alpha$ -,  $\beta$ -, and  $\gamma$ -ethyl formylphenylacetates requires great care, and the original paper must be consulted for details. Briefly, they are obtained as follows. Ethyl formate and ethyl phenylacetate in ether are treated with sodium according to Wislicenus' directions. The aqueous extract of the product is freed from ether by air, kept at 0° for three to four hours, acidified by sulphuric acid, D at least 1.36, and the mixture kept at 0° for about four hours before removing the precipitated  $\gamma$ -ester.

The  $\beta$ -ester is obtained by passing carbon dioxide into the preceding aqueous alkaline extract, and keeping the product at 0° for some hours. The solid, m. p. 44—54°, is dissolved in dilute potassium hydroxide at 0°, and carbon dioxide is passed immediately through the solution; once again the mixture is kept at 0° for some hours before the  $\beta$ -ester is removed.

The liquid  $\alpha$ -ester is obtained by Wislicenus' method, and is purified through the copper derivative. The ester must be heated at 120° in a sealed tube for two to three hours, and subsequently distilled in a vacuum in order to obtain a product free from the solid modifications. The  $\alpha$ -ester cannot be kept without isomerising; in air, it undergoes a profound change, and finally does not develop a coloration with alcoholic ferric chloride.

The  $\beta$ - and the  $\gamma$ -ester change to the  $\alpha$ - by fusion. Neither gives directly a coloration with ferric chloride, but does so after being kept in solution for some time (change to the  $\alpha$ -modification).

Wislicenus'  $\beta$ -modification, m. p. about 70°, is most probably a mixture of the two preceding solid modifications. C. S.

**Number of Isomerides of Merotropic and Desmotropic Compounds. V. Isomeric Enolic Modifications of Ethyl Formylphenylacetate.** ARTHUR MICHAEL and G. PRESCOTT FULLER (*Annalen*, 1912, 391, 275—308. Compare preceding abstract).— $\alpha$ -Ethyl formylphenylacetate is recovered unchanged after being kept for a short time in methyl or ethyl alcohol, but, after prolonged keeping, an additive compound of the ester and the alcohol is obtained, which does not develop a coloration with ferric chloride. The  $\beta$ - and the  $\gamma$ -esters yield apparently the same additive compound after

prolonged keeping in either of these solvents; when rapidly recovered, however, each is obtained as a mixture of both.

The  $\alpha$ -ester is recovered unchanged from most solvents; a transitory formation of a solid mixture is observed in acetone, methylal, or pinacolin. The  $\beta$ -ester changes to the  $\alpha$  in most solvents, even in the cold; in bromoform, it changes almost completely to the  $\gamma$ -ester within fifteen minutes, the  $\alpha$ -ester being finally obtained after prolonged keeping. The  $\gamma$ -ester changes to the  $\alpha$  in all solvents.

The preceding results show that, contrary to the opinion of Wislicenus, there is no simple relation between the dielectric constant of an organic solvent and its capacity of producing isomerisation of one form of ethyl formylphenylacetate into another.

Mixtures of the solid  $\beta$ - and  $\gamma$ -esters in known proportions give an m. p. curve which indicates that the substances, m. p. about  $50^\circ$  and about  $70^\circ$  respectively, which are so frequently isolated in the preparation of the various modifications of ethyl formylphenylacetate, are not individual; these substances and the corresponding artificial mixtures behave alike physically.

The molecular weight of the  $\gamma$ -ester in cold benzene indicates that the compound is unimolecular. The determination of the molecular weight of the  $\beta$ -ester is difficult, because the substance changes so rapidly to the  $\gamma$ -ester in solution. Experiments on a sample, m. p.  $55^\circ$ , in benzene and in acetic acid gave values corresponding with the unimolecular formula, whilst the % of  $\gamma$ -ester had increased by only about 20% during the estimation.

The action of sodium ethoxide on an ethereal solution of the  $\alpha$ -ester gives a homogeneous  $\alpha$ -sodium derivative. When this solid is acidified with sulphuric acid, an oily ester is obtained, together with a little solid ester. By acidifying a cold dilute aqueous solution of the  $\alpha$ -sodium derivative, the oil obtained solidifies the more rapidly the greater is the concentration of the acid used. The m. p. of the solidified oil is  $90$ — $100^\circ$ , and is independent of the concentration of the acid. Excepting phosphoric and oxalic acids, there is an approximate relation between the % of  $\gamma$ -ester in the solidified oil and the affinity constant of the acid used in precipitating it.

The sodium derivative, whether solid or in aqueous solution, yields the bluish-violet ferric salt with ferric chloride. The  $\alpha$ -ester and alkaline copper acetate give at once the green  $\alpha$ -copper derivative, which is also obtained, more slowly, from the  $\beta$ - and the  $\gamma$ -esters. The bluish-green precipitate obtained from the  $\alpha$ -sodium salt and cold aqueous copper sulphate is a mixture of an inorganic copper salt, the green  $\alpha$ -copper derivative, and an oil. Copper chloride also produces the green  $\alpha$ -derivative; cuprous chloride gives a green precipitate, from which a mixture of the liquid and solid esters is obtained by acidification with sulphuric acid. These results do not support the theory of the existence of isomeric metallic derivatives of ethyl formylphenylacetate.

C. S.

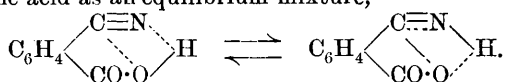
The Lactone of  $\alpha$ -*o*-Methoxyphenyl-*o*-hydroxy-*p*-tolylacetic Acid. H. STOCKMANN (*Ber.*, 1912, 45, 2547—2548).—The divergence of the m. p. ( $116$ — $119^\circ$ ) given for the above substance by Stoermer

and Friemel (this vol., i, 45) from that given by earlier workers (120—121°) is due to impurity arising from the presence of *p*-cresol in the *m*-cresol used. A carefully purified specimen of *m*-cresol when treated by Stoermer and Friemel's method gave a product of the higher m. p.

D. F. T.

***o*-Cyanobenzoic Acid.** JOHANNES SCHEIBER [and, in part, A. DEUTSCHLAND] (*Ber.*, 1912, 45, 2398—2403).—Several investigators have prepared *o*-cyanobenzoic acid by methods which leave no doubt as to its constitution. However, the acid behaves abnormally in several respects. For example, its dissociation constant is, contrary to expectation, smaller than that of *o*-chlorobenzoic acid, its tendency to liberate iodine from an iodide-iodate mixture is less than that of the weaker *m*-cyanobenzoic acid, and the absorption spectra of *o*- and of *m*-cyanobenzoic acids exhibit differences which are not found in the spectra of other *o*- and *m*-substituted benzoic acids.

The author is of opinion that these abnormalities can be explained by assuming a more intimate connexion between the cyano- and the carboxyl groups than is indicated by the ordinary formula, and represents the acid as an equilibrium mixture,



C. S.

**Fluorescence in the Terephthalic Acid Series.** HUGO KAUFFMANN and LEOPOLD WEISSEL (*Annalen*, 1912, 393, 1—29).—Continuing their investigations of the auxochromic influence of nitrogen in fluorescent substances, the authors find that, whilst methyl terephthalate is not fluorescent even in the ultra-violet, methyl aminoterephthalate and the 2:5- and 2:6-diamino-esters are fluorescent in the solid state and in solution. The phenomenon is due to the auxochromic influence of the amino-group, because, whilst the preceding diamino-esters fluoresce in the orange, the fluorescent band shifts towards the violet when the amino-groups are replaced by weaker auxochromes; thus methyl 2:5-dihydroxyterephthalate and 2:5-dimethoxyterephthalate fluoresce respectively in the blue and the violet. An alkaline alcoholic solution of the dihydroxy-ester fluoresces orange, because the auxochromic character of the hydroxyl groups is strengthened by salt formation. Methyl aminoterephthalate shows yellow fluorescence in the solid state and violet blue in solution; its acetyl derivative fluoresces blue in the solid state and violet in solution. Here again is illustrated the shift of the fluorescent band towards the violet when the auxochromic character of the amino-group is weakened by acetylation. Other examples of the same kind are quoted.

The orientation of the auxochromes also has a great influence on the fluorescence; amongst other examples, the fact is mentioned that the fluorescent band of methyl 2:6-diaminoterephthalate in any solvent is always nearer the violet than that of the 2:5-diamino-ester in the same solvent.

The influence of the solvent on the fluorescence is particularly

marked in the case of methyl 2:6-diaminoterephthalate. A comparison of many examples shows that the change in the fluorescent colour produced by a solvent is greater the more marked is the auxochromic character of the group causing the fluorescence. An important deduction from this is that the solvent must have some influence on the auxochromic group. The fluorescent colour of a substance is deepened most by dissociating solvents. Thus methyl 2:6-diaminoterephthalate, which exhibits a green or greenish-yellow fluorescence in hexane, benzene, ether, or chloroform, fluoresces orange-yellow in pyridine and orange in alcohol, acetic acid, or isobutyl alcohol. Carbon disulphide is remarkable in that substances which exhibit intense fluorescence in other solvents, show a scarcely appreciable fluorescence in this solvent.

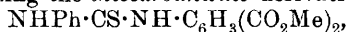
Methyl dimethylaminoterephthalate is remarkable in that it is non-fluorescent in almost all solvents. In hexane, carbon tetrachloride, and perchloroethylene it exhibits a violet to blue fluorescence. The authors are of opinion that this ester may be used to ascertain the character of a solvent; any solvent in which it forms a fluorescent solution is a non-dissociating, indifferent solvent. Such, for example, is tin tetra-ethyl, in which the ester shows a feeble blue fluorescence.

Methyl 2:5-diaminoterephthalate is easily obtained as follows. Methyl terephthalate is nitrated by fuming sulphuric and nitric acids below 5°. The resulting methyl nitroterephthalate, m. p. 76°, which is freed from a little accompanying *methyl dinitrohydroxyterephthalate*,  $\text{OH}\cdot\text{C}_6\text{H}(\text{NO}_2)_2(\text{CO}_2\text{Me})_2$ , m. p. 124°, by treatment with aqueous sodium carbonate, is reduced by stannous chloride and 25% methylalcoholic hydrogen chloride to methyl aminoterephthalate, the acetyl derivative of which is then nitrated by fuming nitric and concentrated sulphuric acids at about 0°. The main product is *methyl 2-nitro-5-acetylaminoterephthalate*, m. p. 142°, yellow prisms, which is non-fluorescent; the by-product, m. p. 128°, is probably *methyl 3-nitro-5-acetylaminoterephthalate*, but it has not been obtained free from the preceding isomeride. By hydrolysis with boiling methylalcoholic sulphuric acid, methyl 2-nitro-5-acetylaminoterephthalate yields *methyl 2-nitro-5-aminoterephthalate*, m. p. 187° (the corresponding acid has decomp. about 260°), the reduction of which by stannous chloride and methylalcoholic hydrogen chloride yields *methyl 2:5-diaminoterephthalate*, m. p. 185°, long, orange-red prisms. This ester exhibits a magnificent orange fluorescence in the solid state, and forms a *dibenzoyl* derivative, m. p. 268° (bluish-green fluorescence in solid state viewed through a blue screen; violet to blue fluorescence in solution), *acetyl* derivative, m. p. 198°, yellow needles (faint orange-yellow fluorescence in solid state; blue to green fluorescence in solution), *diacetyl* derivative, m. p. 284°, pale yellow needles (faint yellow fluorescence in solid state: violet to blue fluorescence in solution), and *benzoylacetyl* derivative, m. p. 248°, pale yellow crystals. *Methyl 5-amino-2-hydroxyterephthalate*, m. p. 144°, obtained by the electrolytic reduction of methyl nitroterephthalate in sulphuric acid and subsequent esterification, forms deep yellow crystals, which exhibit a faint yellow fluorescence behind a blue screen, and yields bluish-green to yellowish-green fluorescent solutions.

2 : 6-Diamino-*p*-toluic acid, which is obtained free from any isomeride by the reduction of 2 : 6-dinitro-*p*-toluic acid by tin and concentrated hydrochloric acid, forms a *methyl* ester, m. p. 129°, brown crystals, which exhibits peculiar fluorescent phenomena on account of the orientation of the amino- and the carbomethoxy-groups. Solutions of the ester in alcohol, acetic acid, petroleum, ether, or benzene are non-fluorescent. By treating its alcoholic solution with a little mineral acid, an intense violet-blue fluorescence is produced, which disappears by the addition of an excess of acid.

2 : 6-Diacetylaminop-*p*-toluic acid, m. p. above 280°, colourless needles, dissolved in water containing sodium carbonate, is treated with magnesium sulphate and then heated with potassium permanganate. The resulting 2 : 6-diacetylaminoterephthalic acid, m. p. above 280°, yields by boiling with methyl alcoholic hydrogen chloride, *methyl* 2 : 6-diaminoterephthalate,  $C_6H_3(NH_2)_2(CO_2Me)_2$ , m. p. 162°, yellow crystals, solutions of which exhibit intense violet to green fluorescence. Its *diacetyl* derivative, m. p. 204°, shows a faint blue fluorescence in the solid state and forms violet to blue fluorescent solutions. The *dibenzoyl* derivative, m. p. 248°, fluoresces greenish-white in the solid state and violet in solution.

Methyl aminoterephthalate reacts abnormally in some respects. It does not react with benzaldehyde, and only very slowly with phenylthiocarbimide, yielding the *thiocarbanilino*-derivative,

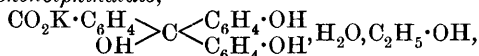


m. p. 211°, which is not fluorescent in solution. By treating its diazotised solution with alkaline  $\beta$ -naphthol, *methyl* 2- $\beta$ -naphtholazoterephthalate,  $C_6H_3(CO_2Me)_2 \cdot N_2 \cdot C_{10}H_6 \cdot OH$ , red needles, is obtained, which is not fluorescent.

By heating with methyl sulphate on the water-bath, methyl aminoterephthalate yields a mixture of methyl dimethylaminoterephthalate, m. p. 70.5° (Wegscheider and Black give 66—68°: this vol., i, 263), and methyl methylaminoterephthalate, m. p. 93° (not 89—90°: *loc. cit.*), which is separated by converting the latter into its *nitroso*-compound, m. p. 80°.

Phenolphthalein and its Colourless Salts. III. Preparation of Monobasic Phenolphthalates. PHILIP A. KOBER, J. THEODORE MARSHALL, and E. N. ROSENFELD (*J. Amer. Chem. Soc.*, 1912, **34**, 1424—1433. Compare Abstr., 1911, i, 300, 984).—The dynamics of phenolphthalein reactions are discussed, and the conclusion is drawn that in ordinary phenolphthalein the quinonoid dibasic salt is essentially primary and the carbinol form secondary.

*Potassium phenolphthalate*,

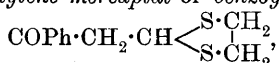


may be prepared by passing carbon dioxide into a solution of the tripotassium salt in absolute alcohol, filtering the product, and precipitating with dry ether. The corresponding *sodium* salt can be obtained in the same manner. These monobasic salts crystallise in long, colourless, hexagonal prisms with truncated ends, and are slowly hydrolysed by water at the ordinary temperature with the develop-

ment of colour and the separation of phenolphthalein. When the salts are crystallised from acetone, the alcohol of crystallisation is wholly, or in part, replaced by the former solvent. E. G.

**Crystallographic Study of 3:4:5-Trimethoxyphthalic Acid.** ARISTIDE ROSATI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 358—359).—This acid of m. p. 174° (decomp.) (compare Bargellini and Molina, this vol., i, 773) crystallises in the pinacoidal class of the triclinic system [ $a:b:c=0.3728:1.02994$ ,  $\alpha 77^\circ 4'$ ,  $\beta 111^\circ 32'$ ,  $\gamma 134^\circ 40'$ ]. R. V. S.

**Ketoaldehydes. Mercaptals of Benzoyl- and Thienoyl-acetaldehyde.** C. KELBER and A. SCHWARZ (*Ber.*, 1912, 45, 2484—2489).—The *ethylene mercaptal of benzoylacetaldehyde*,

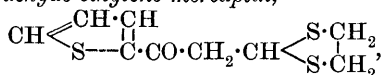


prepared by condensing the components in presence of hydrogen chloride, crystallises in thin, colourless platelets, m. p. 80°, which become brown on exposure to light.

*Benzoylacetaldehyde ethyl mercaptal*,  $\text{COPh} \cdot \text{CH}_2 \cdot \text{CH}(\text{SEt})_2$ , crystallises in thin, colourless needles, m. p. 46—47°.

*Thienoylacetaldehyde*,  $\text{CH} \begin{array}{l} \text{CH} \cdot \text{CH} \\ \text{S} \cdot \text{C} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CHO} \end{array}$ , obtained by condensing thienyl methyl ketone and ethyl formate by means of sodium ethoxide, is a viscid, yellow oil. The *sodium salt*, which is stable when dry, gives a deep red coloration with ferric chloride. In aqueous solution it gives precipitates with calcium, strontium, and magnesium chlorides, and also with mercuric chloride. The *mono-oxime* crystallises in flat tablets of silvery lustre, m. p. 106—107°. In solution a yellow coloration is obtained with ferric chloride, which is changed to blue on adding sodium acetate.

*Thienoylacetaldehyde ethylene mercaptal*,



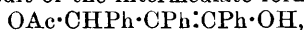
crystallises in stunted crystals, m. p. 98—99°.

When thienoylacetaldehyde is left overnight, it condenses to *trithienoylbenzene*,  $\text{C}_6\text{H}_3(\text{CO} \cdot \text{C}_4\text{H}_3\text{S})_3$ , the oil becoming converted into a reddish-yellow mass. The purified crystals form flat needles, m. p. 212—213°. E. F. A.

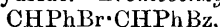
**Reduction of  $\Delta^2$ -Ketones and Formation of Indene Derivatives.** JOHANNES THIELE and P. RUGGLI (*Annalen*, 1912, 393, 61—80).—By reducing unsaturated ketones of the type  $\text{CHR}:\text{CH}:\text{COR}'$  with zinc dust and a mixture of acetic anhydride, acetic acid, and concentrated sulphuric acid, the authors have obtained evidence of the intermediate production of compounds of the type  $\text{CH}_2\text{R} \cdot \text{CH}:\text{CR}'\cdot\text{OH}$ .

Phenyl styryl ketone, anisylideneacetophenone, and benzylidene-deoxybenzoin have been examined. The usual reducing agents convert these normally into the saturated ketones, but with the preceding mixture at or below 0° the following results have been obtained.

Phenyl styryl ketone yields a brown mass, from which have been isolated a little  $\alpha\delta$ -dibenzoyl- $\beta\gamma$ -diphenylbutane and a substance,  $C_{80}H_{24}O$ , m. p. 168—169°, yellow powder, which is probably 2-benzoyl-1:3:4-triphenyl- $\Delta^1$ -cyclopentene, produced from the former by loss of water. By treatment with the preceding reducing mixture, benzylidenedeoxybenzoin yields a mixture of substances. The same mixture is also obtained in the absence of zinc dust, so that the reaction is one of addition of acetic acid (or anhydride), not of hydrogen. By a tedious fractional crystallisation from glacial acetic acid, three substances have been isolated from the mixture. Two of these,  $C_{23}H_{18}O_2$ , m. p. 170—172°, and  $C_{23}H_{20}O_3$ , m. p. sharply between 140° and 171° (decomp.), according to the conditions of heating, are substances of unknown constitution, but the third,  $C_{23}H_{18}O_2$ , m. p. 166—167°, is 1-acetoxy-2:3-diphenylindene,  $C_6H_4 \begin{smallmatrix} \text{CH(OAc)} \\ \text{---CPh} \end{smallmatrix} \text{CPh}$ . This substance is produced as the result of the intermediate formation of



not  $OAc \cdot CHPh \cdot CHPh \cdot CPh$ , from benzylidenedeoxybenzoin and acetic acid, because the second substance, *acetoxybenzyldeoxybenzoin*, m. p. 127.5—128.5°, colourless prisms, obtained from bromobenzyldeoxybenzoin and silver acetate, is not converted into an indene derivative by concentrated sulphuric acid either alone or mixed with acetic acid and acetic anhydride. *Bromobenzyldeoxybenzoin*,



m. p. 158° (decomp.), colourless needles, is obtained by treating a cold solution of benzylidenedeoxybenzoin in acetyl bromide with a little concentrated sulphuric acid; its constitution follows from the fact that it is reconverted into benzylidenedeoxybenzoin by boiling pyridine.

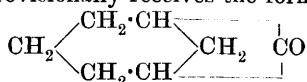
By treatment with hydrogen bromide in glacial acetic acid at 100°, 1-acetoxy-2:3-diphenylindene is converted into 1-bromo-2:3-diphenylindene,  $C_6H_4 \begin{smallmatrix} \text{CHBr} \\ \text{---CPh} \end{smallmatrix} \text{CPh}$ , decomp. 158°, yellow crystals, from which the acetate is regenerated by silver acetate.

By reduction with zinc dust and glacial acetic acid at 50—80°, 1-bromo-2:3-diphenylindene yields 2:3-diphenylindene, m. p. 108—109°, almost colourless prisms, which develops an intense dark green coloration with concentrated sulphuric acid and forms an *oximino*-compound,  $C_6H_4 \begin{smallmatrix} \text{C(:NOH)} \\ \text{---CPh} \end{smallmatrix} \text{CPh}$ , m. p. 253—255° (decomp.), yellowish-brown prisms, by treatment with amyl nitrite and alcoholic sodium ethoxide; the same substance is obtained from diphenylindone and hydroxylamine, and yields diphenylindone by treatment with hydrogen bromide in glacial acetic acid containing a little copper oxide. C. S.

**Constitution of Phenyl-*o*-nitroindone [4-Nitro-2-phenylindone] and of its Ozonide.** MARUSSIA BAKUNIN and T. ANGRI-SANI (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1912, [iii], 18, 213—222. Compare Bakunin, this vol., i, 344).—The ozonisation of the nitrophenylindone in chloroform solution has been repeated with ozonised oxygen (7%). The ozonide of m. p. 157—158° previously mentioned

was obtained, together with benzoic acid and ethyl 3-nitro-2-aldehydobenzoate, m. p. 133°. The two last-named substances are also obtained when the ozonide is subjected to prolonged boiling with water, alcohol or sodium carbonate, and this confirms the constitution previously assigned to it. The formation of this ozonide confirms the presence of a double linking in the phenylnitroindone. R. V. S.

**Synthesis of Meta-bicyclic Systems. Synthesis of a Demethylated Pinone.** OTTO STARK (*Ber.*, 1912, 45, 2369—2374).—*cyclo*Hexene-1 : 3-dicarboxylic acid is readily obtained in quantity by reducing isophthalic acid with sodium amalgam by Baeyer and Villiger's method to the tetrahydro-acid, and then treating an aqueous solution of this easily soluble acid with hydrogen and colloidal palladium as in the Paal-Skita process. From the product, the *cis*-anhydride is obtained by means of acetyl chloride, and converted into calcium *cis-cyclo*-hexenedicarboxylate. By distillation in a current of carbon dioxide, the finely powdered salt yields a liquid, the fraction, b. p. 60—100°/18 mm., of which contains a ketone,  $C_7H_{10}O$ , b. p. 157—158° (decomp.) or 60—70°/18 mm.,  $D^{20}_D$  0.9322,  $n^{20}_D$  1.4731 (*semicarbazone*, m. p. 179—180°), which provisionally receives the formula :



on account of its exalted molecular refraction. The ketone is attacked substitutively by bromine, and is not stable to alkaline potassium permanganate. C. S.

**Alkylation of Benzoylacetone and Desmotropy of Methyl- and Ethyl-benzoylacetone.** WALTER DIECKMANN (*Ber.*, 1912, 45, 2685—2689).—Previous attempts to alkylate benzoylacetone have led to the isolation of the decomposition products of the alkyl derivatives (Claisen and Lowman, *Abstr.*, 1888, 692; Auwers, *this vol.*, i, 486). The author shows that the methyl and ethyl derivatives may be readily prepared by use of the corresponding alkyl iodides if excess of sodium alkoxide is carefully avoided.

*Methylbenzoylacetone* ( $\alpha$ -phenyl- $\beta$ -methylbutane- $\alpha$ -*dione*),  
COPh·CHMe·COMe,

b. p. 150—152°/20 mm., is an almost colourless liquid, which does not solidify in a freezing mixture. Ferric chloride imparts a blue coloration to its solution in alcohol, which becomes more intense on standing. The freshly prepared alcoholic solution contains 6.4% of the substance in the enolic form, whilst a 1% solution in alcohol, after establishment of equilibrium, has 9% of the substance in this state, a similar solution in hexane having 11%. Addition of copper acetate to an alcoholic solution of methylbenzoylacetone causes the gradual precipitation of a green, crystalline *copper salt*,  $(C_{11}H_{11}O_2)_2Cu$ , m. p. 230°  
 $\gamma$ -Benzoyl- $\Delta^2$ -buten- $\beta$ -ol, COPh·CMe·CMe·OH, m. p. 45—50°, is formed by the cautious acidification of a methyl-alcoholic solution of sodium-methylbenzoylacetone. When freshly prepared it contains 97% of the enolic form, gives an immediate precipitate with copper acetate, and an intense blue coloration with ferric chloride. It gradually passes into the oily equilibrium mixture, the velocity of change being

greatly increased by addition of traces of alkaline reagents, such as piperidine.

*Ethylbenzoylacetone* ( $\alpha$ -phenyl- $\beta$ -ethylbutanedione), b. p. 155—157°/20 mm., strongly resembles the above methyl compound. In the free state, about 3% of the enolic modification is present, whilst in 1% solution in ethyl alcohol or hexane, the corresponding figures are 7% and 9% respectively. The copper salt,  $(C_{12}H_{13}O_2)_2Cu$ , is a microcrystalline, greyish-green powder, m. p. 220°.

$\gamma$ -Benzoyl- $\Delta^{\beta}$ -penten- $\beta$ -ol has m. p. 32°.

H. W.

**Keto-enolic Isomerism of Indandione and Oxindone Derivatives.** ARTHUR HANTZSCH (*Annalen*, 1912, 392, 286—301. Compare following abstracts).—Colourless, or at most yellowish, diketones of the type of 2-alkylindandiones form intensely coloured metallic derivatives, which are formulated as oxindone derivatives,  $C_6H_4 \begin{array}{c} \text{CO} \\ \diagdown \quad \diagup \\ \text{C(OM)} \end{array} \text{CR}$ , or

possibly  $C_6H_4 \begin{array}{c} \text{C=O} \\ \diagdown \quad \diagup \\ \text{C-O} \end{array} \text{CR} \cdot M$ . A chemical proof of enolisation during

salt-formation is afforded by the facts of (i) the occasional isolation of coloured, labile-free enols (oxindones) and also of the colourless or yellowish, isomeric ketones (indandiones), and (ii) the occasional existence of coloured *O*-ethers (oxindone ethers) together with the colourless, isomeric alkylindandiones. An optical proof of the enolisation during salt-formation is furnished by the spectrometric method. The absorption spectra of the constitutively unchangeable 2:2-dialkylindandiones exhibit only general absorption, which is affected only slightly by the nature of the solvent or of the substituents. The enolic salts and ethers of 2-alkylindandiones show strong selective absorption, independent of the nature of the solvent.

Enolisible indandiones are, like ethyl acetoacetate, extraordinarily optically variable according to the nature of the solvent and of the substituent. Thus 2-phenylindandione is colourless in ether and chloroform, but forms orange-red solutions in alcohols and deep red solutions in alkalis; the colourless solutions show only general absorption, whilst the coloured solutions exhibit selective absorption which is stronger the more intense is the colour. The coloured solutions are equilibrium mixtures of the keto- and the enolic modifications. Corresponding with this, it is found that 2-phenylindandione has a variable molecular refraction in different solvents, and exhibits an abnormally high exaltation during salt-formation.

The reasons for ascribing constitutions containing the 6-ring,

$\cdot CR \begin{array}{c} \text{C} \cdot O \\ \diagdown \quad \diagup \\ \text{C} \cdot O \end{array} M$ , to the metallic oxindone derivatives are, in the main,

similar to those quoted in the case of conjugated *aci*-nitro-compounds (Hantzsch and Voigt, this vol., i, 151).

Two classes of coloured, metallic oxindone derivatives have been obtained. Metallic derivatives of 2-alkyl- or aryl-oxindones are red, and exhibit pronounced selective absorption with persistent bands. Metallic derivatives of oxindones containing a carbonyl group in

the side-chain, for example, 2-acetyloxindone, are yellow, and exhibit feebler selective absorption and shallow bands. Both classes of salts are conjugated oxindone derivatives, but contain different 6-rings; the red salts contain that given above, whilst the yellow salts are

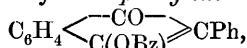
formulated thus:  $\text{CO}-\text{C} \cdot \text{CR} \begin{smallmatrix} \nearrow \text{O} \\ \vdots \\ \text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{OM} \end{smallmatrix}$ .

C. S.

**Simple Indandione and Oxindone Derivatives.** ARTHUR HANTZSCH and FRITZ GAJEWSKI (*Annalen*, 1912, 392, 302—318).—The following constitutively unchangeable indandiones have been prepared.

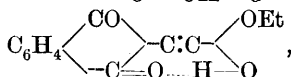
*2-Chloro-2-methylindandione*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \nearrow \text{CO} \\ \searrow \text{CO} \end{smallmatrix} \text{CClMe}$ , m. p. 79°, colourless leaflets, from chlorine and aqueous sodiomethyloxindone; *2-iodo-2-methylindandione*, m. p. 125°, pale yellow needles decomposed by light, prepared in a similar manner; *2-benzoyl-2-methylindandione*, m. p. 127—128°, colourless crystals, from sodiomethyloxindone and benzoyl chloride in chloroform on the water-bath. The ketonic nature of the last substance is shown, not only by its general absorption, but also by its behaviour with alkalis, whereby a complex decomposition ensues, not a simple formation of benzoic acid and an oxindone derivative as in the case of phenyloxindone benzoate. 2-Phenylindandione and its chloro- and bromo-derivatives, which have been described as yellow, are obtained in colourless crystals from benzene.

All conjugated oxindone salts,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \nearrow \text{C} \cdot \text{O} \\ \vdots \\ \searrow \text{C}(\text{OM}) \end{smallmatrix} \text{CR}$ , where R is an alkyl or aryl group, are deep red, never yellow; by interaction with alkyl haloids, they yield, not coloured *O*-ethers (compare following abstract), but disubstituted indandiones. However, 2-phenyloxindone salts and benzoyl chloride yield *2-phenyloxindone benzoate*,



an orange-red substance which yields benzoic acid and the potassium derivative of 2-phenyloxindone by hydrolysis with alcoholic potassium hydroxide. Ethyl oxindonecarboxylates (so-called ethyl diketohydrindenecarboxylates),

$\text{C}_6\text{H}_4 \begin{smallmatrix} \nearrow \text{CO} \\ \searrow \text{C} \end{smallmatrix} \text{C} \begin{smallmatrix} \nearrow \text{CO} \\ \searrow \text{OH} \end{smallmatrix} \text{OEt}$  or

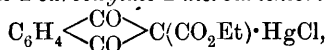


are intensely yellow, and, as enolic substances, react readily with bromine. Their metallic derivatives are always yellow. The sodium, potassium, rubidium, caesium, ammonium, lithium, barium, strontium, calcium, and silver derivatives of the preceding ester are described. The last derivative and methyl iodide at 0° yield *ethyl 3-methoxyindone-*

*2-carboxylate*,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \nearrow \text{CO} \\ \searrow \text{C} \end{smallmatrix} \text{C} \cdot \text{CO} \cdot \text{OEt}$ , m. p. 38—41°, yellow crystals,

together with the stable, colourless, isomeric ethyl 2-methylindandione-2-carboxylate. The former is not changed to the latter by heating, but yields indandione at 100°. The preceding silver salt and benzoyl chloride in boiling benzene yield *ethyl 3-benzoyloxindone-2-carboxylate*,  $C_6H_4 \begin{smallmatrix} \diagup & CO & \diagdown \\ & C(Obz) & \end{smallmatrix} > C \cdot CO_2Et$ , m. p. 146—148°, orange crystals, which yields benzoic acid and indandione by warming with sodium hydroxide.

Ethyl sodio-oxindone-2-carboxylate and aqueous mercuric chloride yield *ethyl indandione-2-carboxylate-2-mercurichloride*,



m. p. 240—245°, colourless prisms.

2-Acetylindandione, which is best obtained by condensing together ethyl phthalate and acetone by means of sodium, is faintly yellow, and exhibits practically only general absorption in indifferent solvents. In the solid state, therefore, it is a triketone. However, in aqueous-alcoholic solution it is yellow, instantly decolorises bromine, and exhibits strong absorption; in this solvent, therefore, it is partly

enolised. The metallic derivatives,  $C_6H_4 \begin{smallmatrix} \diagup & CO & \diagdown \\ & C & \end{smallmatrix} > C \cdot COMe$ , are yellow,

and are not hydrolysed by alkalis; the *sodium, potassium, rubidium, caesium, lithium, calcium, strontium, barium, silver, and thallium* salts are described. The *mercurichloride*,  $C_6H_4 \begin{smallmatrix} \diagup & CO & \diagdown \\ & C & \end{smallmatrix} > CAc \cdot HgCl$ , is colourless and microcrystalline.

Optically, real indandiones differ from the enolised oxindone derivatives by exhibiting general instead of selective absorption.

The molecular refraction,  $M_D^{20}$ , of the constitutively unchangeable 2-phenyl-2-methylindandione is 70·40 and 70·90 in benzene and acetone respectively, whereas 2-phenylindandione, which is enolisible, has the values 65·25 and 67·42 respectively in the same two solvents; the exalted molecular refraction of 2-phenylindandione in acetone is a sign that the substance has partly enolised to the phenyloxindone in this solvent. A still greater exaltation is shown by the sodium derivative in acetone.

C. S.

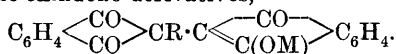
**Bisindandione and Bisoxindone Derivatives.** ARTHUR HANTZSCH and JOSEPH LISTER (*Annalen*, 1912, 392, 319—322).—

Corresponding with the structure,  $C_6H_4 \begin{smallmatrix} \diagup & CO & \diagdown \\ & CH \cdot CH & \end{smallmatrix} > \begin{smallmatrix} \diagup & CO & \diagdown \\ & C & \end{smallmatrix} > C_6H_4$ , ascribed to it by Gabriel and Leupold, bisindandione is colourless, and exhibits general absorption. There also exists, however, the isomeric

enolic modification, bisoxindone,  $C_6H_4 \begin{smallmatrix} \diagup & CO & \diagdown \\ & C(OH) & \end{smallmatrix} > C \cdot C \begin{smallmatrix} \diagup & C(OH) & \diagdown \\ & CO & \end{smallmatrix} > C_6H_4$ ,

which is brown, and exhibits selective absorption. Coloured metallic derivatives of the latter are known. Mono-substituted bisindandiones,  $C_6H_4 \begin{smallmatrix} \diagup & CO & \diagdown \\ & CR \cdot CH & \end{smallmatrix} > \begin{smallmatrix} \diagup & CO & \diagdown \\ & C & \end{smallmatrix} > C_6H_4$ , are colourless, and these have the

ketonic structure; they are enolised by alkalis, and thus yield metallic indandione-oxindone derivatives,



Dimethylbisindandione,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{CMe} \cdot \text{CMe} \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C}_6\text{H}_4$ , which is best prepared from the thallium salt and methyl iodide at  $100^\circ$ , is colourless and exhibits general absorption.

Bisindandione forms a reddish-brown *thallium* derivative, dark red *barium* and *calcium* derivatives, and a blue *lead* derivative. The *mercury* derivative is colourless, and therefore has the ketonic structure; by acidifying its solution in acetone, it yields the brown bisoxindone, not the colourless bisindandione. C. S.

**Bindone and *aci*-Bindone Derivatives.** ARTHUR HANTZSCH and J. ZORTMAN (*Annalen*, 1912, 392, 322—327).—The authors prefer the formula  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{CH} \cdot \text{C} \begin{array}{c} \diagup \text{CH}^- \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{CO}$  to Hoyer's formula,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C} : \text{C} \begin{array}{c} \diagup \text{CH}_2 \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{CO}$ , of bindone (anhydroindandione), because the former expresses clearly the great chemical analogy between bindone and enolisible indandiones containing the group  $\cdot \text{CO} \cdot \text{CHR} \cdot \text{CO} \cdot$ .

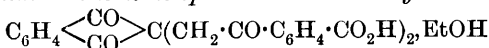
A complete optical comparison is possible between bindone, its metallic derivatives, and its isomeric alkyl derivatives, because both forms of the latter, namely, the red *O*-ethers and the hitherto unknown yellow *C*-ethers, are stable. Like 2-phenylindandione, bindone can be obtained in the form of a dark violet, amorphous *aci*-bindone by acidifying its violet salt solutions in the cold; the *aci*-compound, however, changes very rapidly to ordinary yellow bindone. An equilibrium mixture of the two forms must exist in alcoholic and in aqueous alcoholic solutions, since yellow bindone dissolves in these solvents with a violet-red colour. Of the *O*-ethers described by Hoyer, the methyl ether has m. p.  $213^\circ$ , not  $196^\circ$ , and the ethyl ether has m. p.  $164$ — $165^\circ$ , not  $159^\circ$ . The *benzoyl* derivative, m. p.  $211$ — $214^\circ$ , is a dark red substance. Solutions of these three compounds are converted by alcoholic potassium hydroxide into violet solutions of the *aci*-bindone salt.

*C-Methylbindone*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{CH} \cdot \text{C} \begin{array}{c} \diagup \text{CMe} \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} \text{CO}$ , m. p.  $174^\circ$ , yellow crystals, is obtained by heating bindone with methyl iodide and methyl alcoholic sodium methoxide for many hours; its alkaline solution is red, like those of the *aci*-bindone ethers.

The absorption spectrum of bindone shows a band in the ultra-violet. *aci*-Bindone salts and ethers are optically very similar, and show selective absorption in the visible region of the spectrum. C. S.

**Tris- and Hydroxytris-indandiones.** ARTHUR HANTZSCH and WALDEMAR FISCHER (*Annalen*, 1912, 392, 328—347).—The formula of trisindandione stated by Liebermann and Flatow does not sat

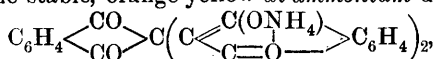
factorily explain why only a hydroxytrisindandione is obtained by oxidation. Moreover, trisindandione is easily converted by aqueous alkalis in the absence of air into two colourless carboxylic acids, from the alcoholic solution of which are obtained the *alcoholate*, m. p. 85—87°, of *indandionebisacetophenone-oo'-dicarboxylic acid*,



(the *acid* itself has m. p. 145—147°), and *bisindandioneacetophenone-o-carboxylic acid*,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C}(\text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}) \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C}_6\text{H}_4$ , m. p. 178°, colourless needles. A solution of these two acids reddens in the air and then contains hydroxytrisindandione. A solution of the two acids in concentrated sulphuric acid yields trisindandione by dilution with water.

Liebermann and Flatow's formula, however, explains satisfactorily the following behaviour of trisindandione and its derivatives.

Pure sodium and potassium derivatives of trisindandione cannot be isolated, because of their rapid oxidation to salts of hydroxytrisindandione. The stable, orange-yellow *di-ammonium* derivative,



however, is obtained by passing a mixture of dry oxygen and ammonia over trisindandione.

The almost colourless modification of hydroxytrisindandione is the ketonic form. The red *aci*-compound, which is best obtained by repeatedly digesting the ketonic form with a mixture of alcohol and acetone, has m. p. about 190°, not 218—219° (decomp.), as stated in the literature. The two forms, real acid and  $\psi$ -acid, cannot be distinguished by the gaseous ammonia test, because both yield ammonium salts with equal rapidity. They react differently, however, with bromine. The ketonic modification in glacial acetic acid yields

*bromohydroxytrisindandione* (annexed formula), m. p. 182°, almost colourless needles, whilst the *aci*-compound in carbon disulphide yields hypobromous acid and *bromotrisindandione*,  $\text{C}_{27}\text{H}_{13}\text{O}_6\text{Br}$ , m. p. 152° (decomp.). *Dibromotrisindandione*,  $\text{C}_{27}\text{H}_{12}\text{O}_6\text{Br}_2$ , m. p. 216°, colourless, microscopic prisms, is obtained from trisindandione and bromine containing a trace of iodine.

The dark red *potassium* derivative,  $\text{C}_{27}\text{H}_{13}\text{O}_7\text{K}$ , and *di-ammonium* derivative,  $\text{C}_{27}\text{H}_{12}\text{O}_7(\text{NH}_4)_2$ , of hydroxytrisindandione are described. Their constitutions correspond with that of *aci*-hydroxytrisindandione itself. In water or alcohol, however, these salts form orange *hydrates* or *alcoholates*,  $\text{C}_{27}\text{H}_{13}\text{O}_7\text{K} \cdot 2\text{EtOH}$  and  $\text{C}_{27}\text{H}_{12}\text{O}_7(\text{NH}_4)_2 \cdot 2\text{EtOH}$ , in which probably the hydroxylated indandione ring has been ruptured.

*aci-Hydroxytrisindandione diethyl ether*,  $\text{C}_{27}\text{H}_{12}\text{O}_7\text{Et}_2$ , m. p. 193—195°, a red substance, can only be prepared by treating the silver salt with ethyl iodide in darkness.

The absorption spectra of *aci*-hydroxytrisindandione, its potassium derivative, and its diethyl ether are identical. This furnishes another

proof of the statement that colour and absorption are unchanged if the constitution of an acid does not alter during its conversion into its salts or esters. The absorption spectra of the dimetallic derivatives of hydroxytrisindandione differ somewhat from those of the monometallic salts in alcohol, an explanation of which has been given above.

C. S.

**Transformation of Pyrogallol Triacetate.** GUSTAV HELLER and OTTO FRITSCH (*Ber.*, 1912, 45, 2389—2392. Compare this vol., i, 274).—By heating for two hours at 145—147° with its own weight of zinc chloride, pyrogallol triacetate loses one acetyl group; the other two migrate into the nucleus, and gallodiacetophenone is produced. By benzoylation in pyridine, the latter yields *tribenzoylgallodiacetophenone*,  $C_{31}H_{22}O_8$ , m. p. 189°.

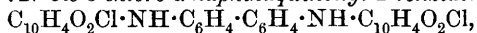
By heating with zinc chloride at 130—135° for one hour, pyrogallol triacetate is converted into *gallacetophenone diacetate*, m. p. 217—219°.

C. S.

**Oxidation of Anilinoquinones to Benzidine Derivatives.** KURT BRASS (*Ber.*, 1912, 45, 2529—2533).—As in an earlier investigation (Pummerer and Brass, *Abstr.*, 1911, i, 654) only one molecule of  $\alpha$ -naphthaquinone could be made to condense with benzidine, the author has attempted to prepare indirectly a substance which structurally shall be the symmetrical condensation product of two molecules of  $\alpha$ -naphthaquinone with one molecule of benzidine.

If 2-anilino- $\alpha$ -naphthaquinone is oxidised by manganese dioxide in concentrated sulphuric acid, the resultant liquid on pouring on to ice deposits dark brown flocks of *N:N'-bis- $\alpha$ -naphthaquinonyl-2-benzidine*,  $C_{10}H_5O_2 \cdot NH \cdot C_6H_4 \cdot C_6H_4 \cdot NH \cdot C_{10}H_5O_2$ .

The structure attributed to this substance is confirmed by the formation of benzidine on fusion with potassium hydroxide, and by the oxidation of 3-chloro-2-anilino- $\alpha$ -naphthaquinone in an analogous manner to *N:N'-bis-3-chloro- $\alpha$ -naphthaquinonyl-2-benzidine*,



red needles and prisms, m. p. 325° (decomp.); this substance dissolves in concentrated sulphuric acid with an intense bluish-violet colour; it is reduced by hyposulphite to a yellow vat, which dyes cotton a fast reddish-violet; on fusion with potassium hydroxide, it yields benzidine.

That in the formation of the above substances coupling occurs at the para-position is indicated by the failure to obtain any such oxidation product from 2-*p*-toluidino- $\alpha$ -naphthaquinone. D. F. T.

**Preparation of Anthracene Derivatives.** JACOB MEYER (D.R.-P. 247187).—When ketones of the general formula  $R \cdot CO \cdot CH_3$  (where R is an aliphatic, aromatic, or mixed residue) are heated at 120—130° during about an hour with anthraquinone derivatives in concentrated sulphuric acid solution, characteristic fluorescent condensation products are formed.

Anthraquinone (100 parts) acetone (50—60 parts) in 2000 parts of concentrated sulphuric acid furnishes a *compound*, orange-yellow

crystals, m. p. 252°, which crystallises from xylene and dissolves in concentrated sulphuric acid with a red fluorescence; when the anthraquinone is replaced by  $\beta$ -methylantraquinone, the *product* has similar properties.

The *compounds* from acetone and  $\alpha$ - or  $\beta$ -chloroanthraquinone are crystalline, orange powders, and decompose indefinitely when heated, whilst  $\alpha$ - and  $\beta$ -aminoanthraquinones yield orange-red and orange-yellow powders respectively, the former exhibiting yellowish-brown and the latter brick-red fluorescence in concentrated sulphuric acid, and are distinct from those previously obtained by similar condensations in alkaline solution.

A *compound*, greenish-yellow needles, m. p. 333°, is obtained from anthraquinone and acetophenone, whilst the same with *m*-nitroacetophenone forms pale brown needles. F. M. G. M.

**Reduction of Some Hydroxyanthraquinones.** YASUSABRO HIROSÉ (*Ber.*, 1912, 45, 2474—2480).—An attempt has been made to characterise more fully the reduction products of some hydroxyanthraquinones, using, in addition to the ordinary elementary analysis and determination of molecular weight, Zerewitinoff's method of determining free hydroxyl groups and the method of determining acetic acid in the acetyl derivatives.

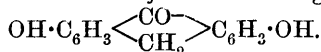
Anthrachrysone yields on reduction a product crystallising in yellowish-white, microscopic needles, m. p. 245°, which corresponds with either a penta-acetoxyanthracene or a tetra-acetoxy-anthranol or -anthrone.

*Trimethylanthrachrysone* forms yellow needles, m. p. 225°, and yields an *acetyl* derivative, crystallising also in yellow needles, m. p. 220°.

*Triacetyltrimethyldihydroanthrachrysone*, formed on reduction, separates in pale yellow needles, m. p. 241°; it is shown to contain three methyl and three acetyl groups, and a residue,  $C_{17}H_{16}O_6$ .

Quinalizarin is reduced by tin, acetic and hydrochloric acids to the oxanthranol stage,  $C_6H_2(OH)_2 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH(OH)} \end{smallmatrix} C_6H_2(OH)_2$ , the product crystallising in orange-yellow needles, m. p. 245°. The *tetra-acetyl* derivative forms pale yellow needles, m. p. 215°, which exhibit a blue fluorescence in solution. On repetition, the tetra- or penta-acetyl derivative of a compound with an oxygen atom less is obtained.

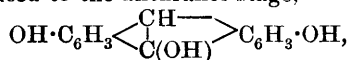
Anthrarufin is reduced to the hydranthone stage,



Using acetic anhydride, sodium acetate, and zinc dust to effect reduction, a *triacylated anthranol* of anthrarufin is obtained in colourless needles, m. p. 248—255°.

When diacetylanthrarufin is reduced, the process stops at the dianthranol stage,  $OAc \cdot C_6H_3 \begin{smallmatrix} \text{C(OH)} \\ \diagup \quad \diagdown \\ \text{C(OAc)} \end{smallmatrix} C_6H_3 \cdot OAc$ ; the product forms almost colourless platelets, m. p. 265—270°, which fluoresce strongly in solution.

Chrysazin is reduced to the anthranol stage,



the compound crystallising in yellow plates, m. p. 180°. Using acetic anhydride, the same product is obtained from chrysazin or its diacetyl derivative, namely:  $\text{OAc} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CH(OH)} \end{array} \text{C}_6\text{H}_3 \cdot \text{OAc}$ , m. p. 188—190°.

E. F. A.

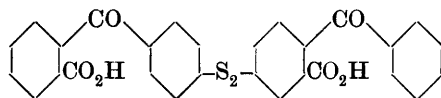
**Metallic Salt Precipitates of Dyes Containing Hydroxyl Groups.** P. BRUNO GUGGIARI (*Ber.*, 1912, 45, 2442—2447).—The composition of the metallic salt precipitates obtained with alizarin,  $\beta$ -nitroalizarin, quinizarin, naphthazarin, carminic acid, and anthragallol has been determined. The tendency is to form the normal salt, that is, that in which the acid groups of the dye are completely saturated by the basic groups of the metallic hydroxide. Difficulties are introduced by the retention of impurities in the flocculent precipitates.

The quinizarin precipitates have the same composition as those given by alizarin, but the former are much more sensitive towards weak acids, a few drops of acetic acid preventing precipitation.

E. F. A.

**Preparation of Anthraquinone Derivatives Containing Sulphur.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 247412).—Mercaptans of the anthraquinone series have been previously prepared from rhodanthraquinones, chloroanthraquinones, or anthraquinone-sulphonic derivatives. It is now found that they can be readily obtained in satisfactory yield from halogenated *o*-benzoylbenzoic acids or from diazo-*o*-benzoylbenzoic acids by condensation and subsequent reduction.

Sodium 4'-chloro-*o*-benzoylbenzoate (225 parts) is heated (with continual stirring) at 170° during four hours with a solution of sodium hydrogen sulphide (134 parts NaSH), and the 4'-thiol-*o*-benzoylbenzoic acid, after purification by several solutions in alkali, isolated



as a pale yellow or colourless powder; this acid when oxidised in alkaline solution furnishes *o*-benzoylbenzoic acid 4'-disulphide (annexed formula) as a pale yellow

powder. When the foregoing disulphide is heated at 150° during one and a-half hours with 10 parts of concentrated sulphuric acid, condensation occurs, yielding anthraquinone-2:2'-disulphide, and this when boiled with aqueous alkaline sodium sulphide furnishes  $\beta$ -thiolanthraquinone (*Abstr.*, 1909, i, 496).

F. M. G. M.

**Autoxidation of Phenanthraquinone in the Presence of Aromatic Hydrocarbons.** ALFRED BENRATH and ALEXANDER VON MEYER (*Ber.*, 1912, 45, 2707—2708. Compare Klinger, *Abstr.*, 1911, i, 633).—When phenanthraquinone suspended in toluene, or *o*-, *m*-, or *p*-xylene, is exposed to the action of light, diphenic acid is obtained, together with benzoic acid or the corresponding toluic acid. No phthalic acid could be detected. Oxidation occurs most rapidly

with the methyl derivatives of benzene, more slowly with ethylbenzene, still more slowly with cumene, whilst no oxidation could be detected in the presence of benzene. Aldehydes appear to be formed in small amount during the reactions.

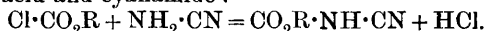
Since phenanthraquinone does not appear to undergo change when exposed to the action of air and water, the authors are led to the conclusion that the hydrocarbons unite with phenanthraquinone, and that the quinol ethers so obtained suffer oxidation. H. W.

[Preparation of Phenanthrene Derivatives Containing Sulphur.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 247415).—When nitrophenanthraquinones or their derivatives are heated with sulphur and an alkali sulphide, either with or without a diluting agent, they yield compounds which dye vegetable fibre a fast yellow to brown tone.

One hundred parts of 2:7-dinitrophenanthraquinone, m. p. 300° (Abstr., 1902, i, 797; 1904, i, 70), was heated at 180–220° with sulphur (200 parts), sodium sulphide crystals (300 parts), and water (500 parts) during eight to ten hours; the *product*, a black powder, is insoluble in water, acids, or alkalis, but soluble in sodium sulphide.

The analogous *compounds* from the isomeric 2:7-dinitrophenanthraquinone, m. p. 215–217° (*loc. cit.*), from 4:5-dinitrophenanthraquinone, and from *dibromodinitrophenanthraquinone*, m. p. above 300° (obtained by nitrating dibromophenanthraquinone, m. p. 284°), are also described in the original. F. M. G. M.

Preparation of Cyanoaminoformyl Esters. EMANUEL MERCK (D.R.-P. 247453).—Ethyl cyanoaminoformate has previously been prepared in ethereal solution (Abstr., 1878, ii, 214); the reaction is now found to take place in aqueous alkaline solution with an ester of chloroformic acid and cyanamide:



*Menthyl cyanoaminoformate* is obtained as an oil from menthylchloroformate and cyanamide; its *silver* salt forms microscopic needles, and the *sodium* salt, hygroscopic needles; the *guaiacyl* ester (from guaiacyl chloroformate) is a colourless oil; its *silver* and *sodium* salts form needles.

*Oxycamphor cyanoaminoformate*, colourless needles, m. p. 112° (indefinite), is prepared from oxycamphorchloroformate and cyanamide; its *silver* salt forms colourless aggregates; the *sodium* salt, needles, has m. p. 141°, or (after drying at 100°) decomposes at 260°.

F. M. G. M.

Preparation of Allophanic Acid Esters. EMANUEL MERCK (D.R.-P. 248164. Compare preceding abstract).—When cyanoaminoformyl esters are boiled with dilute mineral acids, they yield allophanic esters:  $\text{CO}_2\text{R}\cdot\text{NH}\cdot\text{CN} + \text{H}_2\text{O} = \text{CO}_2\text{R}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ ; by this means ethyl cyanoaminoformate is converted into ethyl allophanate; *guaiacyl allophanate*, colourless prisms, decomp. 176°, is obtained from guaiacyl cyanoaminoformate with 20% hydrochloric acid. *Oxycamphor allophanate*, colourless needles, m. p. 204°, is prepared in 50% sulphuric acid solution at 60–70°; *menthyl allophanate*, colourless needles, has

m. p. 215°. *Methyl salicylallophanate*, colourless needles, decomp. 175°, is obtained by treating cyanamide with methyl salicylchloroformate (Abstr., 1901, i, 697) in aqueous solution, and subsequently boiling with an acid. F. M. G. M.

**Terpenes and Ethereal Oils. CXI.** OTTO WALLACH (*Annalen*, 1912, 392, 49—75).—Pulegenolide is not inactive, as has hitherto been supposed, but has a very feeble rotatory power. Dihydropulegenolide, obtained by its reduction by Paal's method (Abstr., 1911, i, 469), has  $[\alpha]_D -56.85^\circ$  in methyl alcohol.

The reduction of *dl*-carvenolide by hydrogen and colloidal palladium in methyl alcohol yields *dl*-dihydrocarvenolide, which is proved to be identical with dihydropulegenolide by its m. p., 50—51°, and rotatory power,  $[\alpha]_D^{25} -57.57^\circ$ , and by the fact that both lactones yield the same hydroxy-acid. From this it follows that

both have probably the constitution  $\text{CH}_2 \begin{array}{c} \text{CHMe} \cdot \text{CH} \cdot \text{CO} \\ | \\ \text{CH}_2 - \text{CH} \cdot \text{CMe}_2 \end{array} \text{O}$ , and

whether this is correct or not, that pulegenolide and carvenolide are unsaturated compounds differing only in the position of the double linking.

The presence of a 5-ring in pulegenolide (or in its generator, pulegenic acid) has been established beyond doubt. Hence a change of a 6-ring to a 5-ring must have occurred during the conversion of tribromocarvone into carvenolide. The readily fusible by-product obtained during the reduction of pulegenolide (*loc. cit.*) is probably only impure dihydropulegenolide (dihydrocarvenolide).

By fusion with potassium hydroxide, *i*-carvenolic acid yields an acid,  $\text{C}_7\text{H}_{10}\text{O}_2$ , m. p. 130°, which is very probably 1-methyl- $\Delta^1$ -cyclopenten-2-carboxylic acid,  $\begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CMe} \end{array} \text{C} \cdot \text{CO}_2\text{H}$ . By hydrolysis with boiling

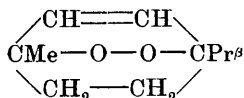
potassium hydroxide, *i*-dihydrocarvenolide yields *i*-dihydrocarvenolic acid,  $\text{C}_{10}\text{H}_{18}\text{O}_3$ , m. p. 87—88°, and *dl*-dihydrocarvenolide (dihydropulegenolide) yields *dd*-dihydrocarvenolic acid,  $\text{C}_{10}\text{H}_{18}\text{O}_3$ , m. p. 87—88°,  $[\alpha]_D^{17} +9.43^\circ$ . By slow, dry distillation, *i*-dihydrocarvenolic acid yields a hydrocarbon,  $\text{C}_9\text{H}_{16}$ , b. p. 135° (nitrosochloride, m. p. 104—105°, needles; nitrolpiperidide, m. p. 110—111°), and an acid (silver salt,  $\text{C}_{10}\text{H}_{15}\text{O}_2\text{Ag}$ ), which resembles pulegenic acid.

The reduction of *d*-pulegenamide in aqueous methyl alcohol by hydrogen and colloidal palladium proceeds with difficulty (probably on account of the presence of a semicyclic linking) and yields *d*-dihydropulegenamide,  $\text{C}_{10}\text{H}_{19}\text{ON}$ , m. p. 150°,  $[\alpha]_D^{20} +4.487^\circ$ , by the hydrolysis of which a liquid dihydropulegenic acid is obtained.

[With ERWIN MEYER.]—Pulegene is not reduced satisfactorily by Paal's process, but is so by Skita's modification thereof, yielding dihydropulegene (1-methyl-3-isopropylcyclopentane),  $\text{C}_9\text{H}_{18}$ , b. p. 142—144°,  $D_{20}^{22} 0.7730$ ,  $n_D 1.4236$ .

By reduction by Paal's method, ascaridole (Abstr., 1908, i, 667) rapidly absorbs four atoms of hydrogen and yields two products. The main product, which is only slightly volatile with steam, is a new 1:4-terpin,  $\text{OH} \cdot \text{CMe} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ | \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{CPr}^a \cdot \text{OH}$ , m. p. 116—117°, large,

glistening prisms. It is optically inactive, yields compounds of the terpinene series by treatment with hydrogen haloids, and is converted by warming with oxalic acid into 1 : 4-cineole (Abstr., 1907, i, 943) and a small quantity of an unsaturated *alcohol*. The latter could not be isolated in a pure state, but is proved to be  $\Delta^3$ -menthen-1-ol by oxidation by 1% potassium permanganate at 0°, whereby is obtained 1 : 3 : 4-trihydroxymenthane, which is converted by warm dilute sulphuric acid into *p*-cymene and  $\Delta^1$ -menthen-3-one. All these facts prove that the 1 : 4-terpin is a compound of the terpinene series. The second product of the reduction of ascaridole is an oil which is easily volatile with steam, and is a mixture of saturated and unsaturated substances. By further treatment with hydrogen and palladium, and subsequent removal of the still unsaturated impurities by potassium permanganate, the oil yields a substance,  $C_{10}H_{18} \cdot OH$ , b. p. 207—208°,  $D^{19}_D$  0.9080,  $n_D$  1.4656, which is converted by zinc chloride into a *hydrocarbon*,  $C_{10}H_{18}$ , b. p. 173.5—175.5°,  $D^{19}_D$  0.821,  $n_D^{19}$  1.4558; this hydrocarbon is probably a mixture of menthenes. The preceding facts are in harmony with the annexed formula of ascaridole, not with that proposed by Nelson (Abstr., 1911, i, 797).



[With HANS SCHLUBACH.]—1-Methyl-5-*isopropyl*- $\Delta^6$ -cyclohexen-2-one (*isocamphor*) and its reduction product have constitutions quite different from those previously ascribed to them (Abstr., 1911, i, 312) and indicated by the preceding name. It is now shown that the reduction product, which is easily obtained from *isocamphor* by Paal's method, is not 1-methyl-5-*isopropylcyclohexan*-2-one, but is identical with dihydropinolone (3-acetyl*isopropylcyclopentane*) (Abstr., 1911, i, 891). *isoCamphor* is certainly not identical with pinolone. The proof of the presence of a 5-ring in *isocamphor* is as follows. *isoCamphoroxime* in alcoholic solution is reduced by Paal's method (which excludes the possibility of any intramolecular change), and the products, after acidification with sulphuric acid and distillation with steam, are dihydropinolone and dihydropinolyamine (identical with the base obtained by the reduction of dihydropinoloneoxime by sodium and alcohol). Possibly *isocamphor* is an active modification of 3-acetyl*isopropyl*- $\Delta^2$ -cyclopentene (*loc. cit.*); an explanation is, as yet, not possible of the series of changes whereby the 5-ring is produced during the formation of *isocamphor* from fenchoneoxime or camphoroxime through the nitro-imines. C. S.

**Pinene Hydriodide. (3-Iodocamphane) and Camphane.** OSSIAN ASCHAN (*Ber.*, 1912, 45, 2395—2398).—The interaction of magnesium iodide and pinene hydrochloride for two hours in boiling ether and subsequently, after removal of the solvent, for three hours on the water bath, leads to the formation of pinene hydriodide, camphane and bornylene being obtained as by-products.

Pinene hydriodide and moist silver oxide, shaken for a long time with alcohol at about 50°, yield a substance,  $C_{10}H_{18}O$ , b. p. 207—211°, which is unsaturated, does not react with semicarbazide, and is apparently a new terpene alcohol.

Camphane is readily obtained from pinene hydriodide by treatment with 12% hydrogen chloride in glacial acetic acid and zinc dust.

The conversion of camphane into derivatives of camphor by passage through a dog is mentioned. C. S.

[Essential Oils.] ROURE-BERTRAND FILS (*Sci. Ind. Bull.*, 1912, [iii], 1, 3—160).—[JUSTIN DUPONT and LOUIS LABAUNE.]—A method for the estimation of geraniol in citronella oil is described, based on the fact that on treatment with hydroxylamine the citronellal is converted into the oxime, and that on further treatment with acetic anhydride the oxime is dehydrated, giving the corresponding nitrile, whilst the geraniol and other alcohols are acetylated. The quantity of esters thus formed can then be estimated in the usual way by hydrolysis with standard alkali. The results obtained by experiments on Java citronella oil indicate that the latter contains one or more alcohols of higher boiling point than geraniol; the new constituents *isoamyl* alcohol and *isovaleraldehyde* have also been noted in this oil.

*Cupressus lusitanica* branches gave 0.25% of bright yellow oil,  $D^{15}$  0.8723,  $\alpha_D + 9^\circ 10'$ , acid value 1.05, saponification value 9.8, soluble in 3 or more vols. of 90% alcohol.

*C. sempervirens fastigiata* branches gave 0.20% of brown oil,  $D^{15}$  0.8744,  $\alpha_D + 12^\circ 6'$ , acid value 0.7, saponification value 4.9, soluble in 3.5 or more vols. of 90% alcohol. The fruits of the same plant, freed from seeds, gave 0.41% of amber-tinted oil,  $D^{15}$  0.8739,  $\alpha_D + 29^\circ 52'$ , acid value 1.0, saponification value 9.8, soluble in 4 or more vols. of 90% alcohol. The seeds yielded only a trace of essential oil.

The aerial portion of parsnip (*Pastinaca sativa*) grown in Piedmont gave 0.1 per cent. of reddish-brown oil,  $D^{15}$  0.8970,  $\alpha_D + 0^\circ 6'$ , acid value 5.6, saponification value 228.9, soluble in 2 or more vols. of 80% alcohol.

Wild celery oil from Algeria, distilled from the entire mature plant, had  $D^{15}$  0.8467,  $\alpha_D + 69^\circ 18'$ , acid value 0, saponification value 14.7, and was miscible with 95% alcohol, but gave cloudy solutions with weaker alcohol.

Wild carrot oil from Puy-de-Dôme, distilled from the entire mature plant, had  $D^{15}$  0.9016,  $\alpha_D - 6^\circ 56'$ , acid value 2.7, saponification value 195.4.

The "Bulletin" also contain a critical résumé of recent work on essential oils and their constituents. T. A. H.

[Essential Oils.] SCHIMMEL & Co. (*Bericht*, October, 1912, pp. 22—200).—A comparison has been made of the various methods available for the estimation of citronellal and geraniol in citronella oil, including that due to Dupont and Labaune (see preceding abstract). It is pointed out that these constituents should be separately estimated, and that for geraniol the phthalic anhydride process probably gives the best results, whilst for citronellal Dupont and Labaune's method is satisfactory, as is also Kleber's phenylhydrazine process. Boulez's method (this vol., ii, 1105) gives good results for citronellal in Ceylon citronella oil. In determining the so-called "total geraniol" of the oil by acetylation, sodium acetate should always be used.

*Cymbopogon coloratus* oil, from Fiji, is golden-yellow to brown, has  $D^{15}$  0.9155—0.920,  $n_D - 7^\circ 43'$  to  $-8^\circ 40'$ , contains geraniol 15.6% and citronellal 45.7—49.5%, and is soluble in one or more volumes of 80% alcohol (compare *Bull. Imp. Inst.*, 1912, 10, 27). *Cymbopogon sennaarensis* (*C. Jwarancusa*, Abstr., 1911, i, 476), herb from the Sudan, gave on distillation 1.005% of oil,  $D^{15}$  0.9383,  $n_D^{20} + 34^\circ 14'$ , containing 17.3% of alcohols and 26—27% of constituents combining with sodium hydrogen sulphite. The principal constituent is a ketone resembling pulegone, and a dextrorotatory terpene is also present (*Bull. Imp. Inst.*, 1912, 10, 31).

The following new oils have been described by Baker and Smith (*J. Roy. Soc. N.S.W.*, 1911, 45, 267). *Eucalyptus acaciaeformis* leaves yield 0.197% of brown oil,  $D^{15}$  0.8864,  $n_D + 35.7^\circ$ ,  $n_D^{20}$  1.4713, containing *d*-pinene, a sesquiterpene, and geranyl acetate (?). *E. Andrewsii* leaves gave 1.27% of lemon-yellow oil,  $D^{15}$  0.8646,  $n_D - 41.5^\circ$ ,  $n_D^{15}$  1.4854, ester number 4.3, containing *l*-phellandrene, piperitone, and a sesquiterpene. *E. campanulata* leaves gave 0.851% of bright yellow oil,  $D^{15}$  0.8804,  $[a]_D - 25.8^\circ$ ,  $n_D^{18}$  1.4856, saponification number 7.6, containing phellandrene, cineole, piperitone, and eudesmol. *E. Bridgesiana* leaves gave 0.73 to 0.74% of oil,  $D^{15}$  0.9223 to 0.9246,  $n_D + 1.8^\circ$  to  $+1.9^\circ$ ,  $n_D^{20}$  1.4716—1.4729, saponification number 7.6 to 8.7, containing 73—78% of cineole. *E. laevopinea* oil has  $D^{15}$  0.8875,  $n_D - 30.7^\circ$  to  $-33.3^\circ$ ,  $D^{19}$  1.4691, and contains not more than 5% of cineole. *E. dextropinea* leaves gave 1.02% of oil,  $D^{15}$  0.8831,  $n_D + 24.2^\circ$ ,  $n_D^{21}$  1.4688, saponification number 22.1, containing 3.7% of geranyl acetate. *E. nova-anglica* oil had  $D^{15}$  0.9221 to 0.9301,  $n_D + 0.9^\circ$  to  $+5.8^\circ$ ,  $n_D^{15}$  1.4892—1.4944,  $n_D^{18}$  1.4857, saponification number 5.7—6.9, which is rich in sesquiterpenes, but contains only small amounts of cineole and phellandrene.

Silver fir seeds (*Abies pectinata*) after being crushed yielded 12—13% of oil,  $D^{15}$  0.8629—0.8668,  $n_D - 68^\circ 14'$  to  $-76^\circ 38'$ ,  $n_D^{20}$  1.47636 to 1.47812, acid number 0.5—1.8, ester number 0.9 to 3.7, soluble in 5—7 or more vols. of 90% alcohol.

"Lawang" bark from the Dutch East Indies, and probably derived from *Cinnamomum iners*, yields according to Mann (*Pharm. Journ.*, 1912, 89, 145) 0.5% of an oil,  $D^{15.5}$  1.0104,  $n_D^{20} - 6.97^\circ$ ,  $n_D^{20}$  1.5095, acid number 1.15, ester number 41.87, saponification number after acetylation 121.9, having an odour recalling those of nutmeg, saffras, and cloves.

The linalool oxide obtained from linaloe oil is now shown to be identical with that prepared by Prileschaeff (Abstr., 1910, i, 86), both giving the same *phenylurethane*, m. p. 58.5—59°, crystallising in colourless prisms from alcohol. The oxide is probably formed by saturation of the end group  $-\text{CH}:\text{CH}_2$  of linalool by one atom of oxygen.

Baker and Smith (*Proc. Roy. Soc. N.S.W.*, 1911, 45, 365) have described the following oils from *Melaleuca* spp. of Australia: *M. genistifolia* leaves and twigs gave 0.526% of bright yellow oil,  $D^{15}$  0.8807,  $n_D + 32.7^\circ$ ,  $n_D^{20}$  1.4702, saponification number 6.8, containing *d*- $\alpha$ -pinene (80 to 90%), cineole (2%), and a sesquiterpene. *M. gibbosa* leaves and twigs gave 0.158% of dark yellow oil,

D<sup>15</sup> 0.9138,  $\alpha_D + 4.5^\circ$ ,  $n_D^{20}$  1.4703, saponification number 9.9, containing cineole 61.5%,  $\alpha$ -pinene, a sesquiterpene, and terpinyl acetate (?). *M. pauciflora* leaves and twigs gave 0.3% of a viscous, dark amber-tinted oil, D<sup>15</sup> 0.9302,  $\alpha_D + 3.3^\circ$ ,  $n_D^{24}$  1.4921, saponification number 8.25, containing cineole, 8.7%, terpinyl acetate (?), terpineol (?), limonene (?), and at least 67% of a sesquiterpene giving a red colour with acetic and sulphuric acids and a blue coloration with bromine vapour.

An authentic sample of larch turpentine was pale yellow in colour, viscous, and had  $\alpha_D + 29.20'$ , acid number 69.5, ester number 55.9, and was soluble in three parts of 80% alcohol. On steam-distillation it yielded 13.5% of larch turpentine oil, D<sup>15</sup> 0.8649,  $\alpha_D - 8.15'$ ,  $n_D^{20}$  1.46924, acid number 0, ester number 5.9, and was soluble in six volumes or more of 90% alcohol. On fractionation it yielded 60% at 157—161°, 20% at 161—164°, and 6% at 164—168°.

*Juniperus phoenicea* oil, distilled in Cyprus from entire ground berries, had D<sup>15</sup> 0.8688,  $\alpha_D + 3.4'$ ,  $n_D^{20}$  1.47210, acid number 0.6, ester number 10.2, and was soluble in eight or more volumes of 90% alcohol with slight opalescence.

A critical survey of recent literature on the chemistry of essential oils is also published. T. A. H.

**The Constituents of Ethereal Oils (the Composition of Essential Oil of Vetiver).** FRIEDRICH W. SEMMLER, FELIX RISSE, and FRITZ SCHRÖTER (*Ber.*, 1912, 45, 2347—2457. Compare Genvresse and Langlois, *Abstr.*, 1903, i, 187).—Essential oil of vetiver was separated by fractional distillation under reduced pressure, and the fractions investigated chemically. A specimen obtained from a German firm showed marked differences in composition from oil distilled in Reunion, the variations being attributable to differences in the details of the method of extraction.

The highest fraction (b. p. 250—300°/12 mm.) from the German oil of vetiver contains an ester of a primary alcohol, *vetivenol*, C<sub>15</sub>H<sub>24</sub>O (distinct from the *vetivenol*, C<sub>15</sub>H<sub>26</sub>O, of Genvresse and Langlois), b. p. 170—174°/13 mm., D<sup>20</sup> 1.0209,  $n_D$  1.52437,  $\alpha_D + 34.5^\circ$ , with *vetivenic acid*, C<sub>15</sub>H<sub>22</sub>O<sub>2</sub>, b. p. 202—205°/13 mm., *methyl ester*, b. p. 170—173°/18 mm., D<sup>20</sup> 1.0372,  $n_D$  1.50573,  $\alpha_D + 42.2^\circ$ . Both the alcohol and the acid are tricyclic with one ethylenic linking, the former compound being reducible by hydrogen and platinum-black to *dihydrovetivenol*, b. p. 176—179°/17 mm., D<sup>20</sup> 1.0055,  $n_D$  1.51354,  $\alpha_D + 31^\circ$ ; *acetate*, b. p. 180—184°/19 mm., D<sup>20</sup> 1.0218,  $n_D$  1.50433,  $\alpha_D + 28.48^\circ$ .

The above *vetivenic acid* is also present in the fraction b. p. 190—250°/12 mm., but in this case as an ester with a *bicyclic* primary alcohol, *vetivenol*, C<sub>15</sub>H<sub>24</sub>O, b. p. 168—170°/14 mm., which could not be obtained quite pure.

Two hydrocarbon fractions also were isolated, of composition C<sub>15</sub>H<sub>24</sub> (*vetivene*), one apparently being a diolefinic bicyclic (b. p. 137—140°/16 mm.) and the other a mono-olefinic tricyclic compound (b. p. 123—130°/16 mm.).

In Réunion oil of vetiver, the ester of *vetivenic acid* with tricyclic

vetivenol is lacking, otherwise the constituents are the same as in the German sample; a portion of the tricyclic vetivenol separated was converted by phosphorus pentachloride into the *chloride*,  $C_{15}H_{23}Cl$ , b. p.  $140-147^{\circ}/10$  mm.,  $D^{20}_D$  0.9679,  $n_D^{20}$  1.52640,  $\alpha_D - 24^{\circ}$ , which by reduction with sodium and alcohol gave an artificial vetivene, the product varying in properties with the experimental details.

No indication of the vetivenol,  $C_{15}H_{26}O$ , described by earlier investigators was observed. D. F. T.

**Sterols from *Castilloa* and *Ficus-caoutchouc*.** A. J. ULTÉE (*Chem. Weekblad*, 1912, 9, 773-777).—*Castilloa*-caoutchouc contains about 20% of a resin, the alcoholic extract from which contains  $\beta$ -amyrin acetate, m. p.  $233-234^{\circ}$ ; lupeol acetate, m. p.  $213^{\circ}$ ;  $\alpha$ -amyrin, m. p.  $184-188^{\circ}$ ; and an acetate, m. p.  $121-122.5^{\circ}$ , probably identical with the compound obtained by Cohen from an African *Euphorbia*-rubber (Abstr., 1908, i, 884).

*Ficus-caoutchouc* yields a resin, from which alcohol extracts a substance, m. p.  $76^{\circ}$ , also obtained in small proportion from *castilloa*-caoutchouc.  $\alpha$ -Amyrin acetate, m. p.  $218^{\circ}$ , is also present, but this rubber is comparatively deficient in sterols. A. J. W.

**Resin Balsam of *Pinus cambodgiana*.** ARTHUR WICHMANN (*Arch. Pharm.*, 1912, 250, 472-477).—The resin balsam of *Pinus cambodgiana* is a yellowish-greyish-white substance of the consistence of honey. It has a pleasant, aromatic odour, and dries to an opaque resin by exposure to air in thin layers. It dissolves completely in the usual solvents except water, and has acid number 145.315 (direct) or 148.12 (indirect method). By distillation with steam, it yields a yellow, aromatic oil,  $D$  0.892,  $n^{21}_D$  1.48455, in 19.35% yield. By extracting the ethereal solution of the purified residue with 1% ammonium carbonate, *cambopinic acid*,  $C_{11}H_{18}O_2$ , is obtained. It is a colourless, odourless, tasteless, amorphous powder, m. p.  $78^{\circ}$ . The ethereal solution then yields to 1% sodium carbonate, *cambopinonic acid*,  $C_{16}H_{24}O_2$ , m. p.  $71^{\circ}$ , which resembles the preceding acid in physical characteristics. The ethereal solution then contains only *camboresen* in very small amount. C. S.

**The Main Constituent of Japanese Lac. III. Catalytic Reduction of Urushiol.** RIKŌ MAJIMA (*Ber.*, 1912, 45, 2727-2730. Compare Abstr., 1907, i, 1032; 1909, i, 402, 915).—Previous investigations of urushiol have failed to yield crystallisable products. The application of Willstätter's method of catalytic reduction has led to the isolation of well-crystallised derivatives of urushiol, diacetyl- and dimethyl-urushiol, from the constitution of which the molecular formula,  $C_{20}H_{30}O_2$ , for urushiol itself is established. Reduction appears to take place exclusively in the side-chain.

*Hydrourushiol*,  $C_{20}H_{34}O_2$ , was obtained in good yield by the action of hydrogen on an alcoholic solution of purified urushiol in the presence of platinum. It crystallises in needles, m. p.  $58-59^{\circ}$ , mol. wt. (in benzene solution) 302. Crude urushiol, when similarly treated,

yielded 68% hydrourushiol and 32% of an amorphous black residue. *Dimethylhydrourushiol*,  $C_{20}H_{32}(OCH_3)_2$ , prisms, m. p. 36—37°, and *diacetylhydrourushiol*, m. p. 50—51°, were similarly obtained from dimethylurushiol and diacetylurushiol respectively.

[With TEPPEI OKADA.]—The catalytic reduction of elæostearic acid (Abstr., 1909, i, 204) gives an almost quantitative yield of stearic acid, thus confirming the normal linking of the carbon chain in this substance (compare Kametaka, Trans., 1903, 83, 1042).

H. W.

**Synthesis of Phenolic Glucosides.** EMIL FISCHER and HERMANN STRAUSS (*Ber.*, 1912, 45, 2467—2474).—On shaking an alkaline solution of phloroglucinol with an ethereal solution of acetobromoglucose and removal of the acetyl groups, phloroglucinol-*d*-glucoside is obtained, identical with the compound prepared by Cremer and Seuffert from phloridzin by heating it with barium hydroxide. In a similar manner resorcinol glucoside is obtained. Both compounds are hydrolysed by emulsin.

Acetobromoglucose readily couples with tribromophenol, but the acetyl groups can only be removed by liquid ammonia at the ordinary temperature, other alkalis bringing about complete decomposition.

*Resorcinol-d-glucoside* crystallises in colourless, short needles, which sinter at 185°, m. p. 190° (corr.),  $[\alpha]_D^{24} - 70^\circ$ . It tastes bitter and is readily hydrolysed by boiling dilute mineral acids.

*Phloroglucinol-d-glucoside* crystallises in ray-like aggregates, m. p. 239° (corr.),  $[\alpha]_D^{22} - 74^\circ$ . *2:4:6-Tribromophenoltetra-acetyl-d-glucoside* crystallises in long, pliable needles, which sinter at 190°, m. p. 195—196° (corr.),  $[\alpha]_D^{25} - 8.8^\circ$ .

*2:4:6-Tribromophenol-d-glucoside* separates in slender, colourless needles, m. p. 207—208° (corr.),  $[\alpha]_D^{25} - 23.2^\circ$ . It is hydrolysed by emulsin.

[With JOSEF SEVERIN.]—*Allyl tetra-acetyl-d-glucoside* has m. p. 88—89°,  $[\alpha]_D^{21} - 26.3^\circ$ . On hydrolysis with barium hydroxide, *allyl-d-glucoside*, m. p. 102—103°,  $[\alpha]_D^{20} - 42.3^\circ$ , is obtained. The *dibromide* of the acetyl derivative has m. p. 87—88°,  $[\alpha]_D^{21} - 11.4^\circ$ . On treatment with bases, *monobromoallyl-d-glucoside* is obtained. E. F. A.

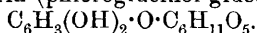
**Arbutin and its Synthesis.** CARL MANNICH (*Arch. Pharm.*, 1912, 250, 547—560).—It is shown that commercial arbutin invariably contains some methylarbutin, and although pure methylarbutin can be obtained from this source, it is impossible to isolate pure arbutin. A synthesis of the latter is described.

Five commercial specimens of arbutin were found to contain from 5 to 40% of arbutin methyl ether as ascertained by methoxyl determinations. This is due to variation in the source of the material, bearberry leaves from Tyrol giving a product containing much arbutin methyl ether, whilst Spanish bearberry leaves yield a product containing not more than 5% arbutin methyl ether. Herissey's method for the separation of pure arbutin from the commercial article (Abstr., 1910, i, 692) does not yield a pure substance. Better results are obtained by precipitating the arbutin as its *additive product*,

$C_{18}H_{18}O_7N_4 \cdot 2H_2O$ , with hexamethylenetetramine, or by acetylating the crude product and recrystallising the mixed acetates from dilute alcohol, when penta-acetyl-arbutin, m. p.  $143-144^\circ$ , needles, separates first, but even by these methods a pure product is not obtainable. From commercial arbutin containing at least 40% of arbutin methyl ether, the latter can be separated in a pure state by precipitating most of the arbutin with hexamethylenetetramine, evaporating the mother liquor, and recrystallising the residue from dilute sodium hydroxide solution. Arbutin methyl ether separates with  $1H_2O$  from water, or anhydrous from alcohol, melts at  $158-160^\circ$ , and re-melts at  $175^\circ$ . The *tetra-acetyl* derivative, m. p.  $95.5-96.5^\circ$ , crystallises from dilute alcohol in silky needles.

Acetylbromoglucose, prepared by van Charante's method (Abstr., 1902, i, 426), reacts with quinol in presence of alkali to give *tetra-acetyl-arbutin*, m. p.  $136^\circ$ , which crystallises from dilute alcohol in colourless prisms, and on acetylation yields penta-acetyl-arbutin, m. p.  $144-145^\circ$ , which on hydrolysis with baryta water yields arbutin. The latter crystallises from water with  $1H_2O$  in colourless needles, with a bitter taste, melts at  $163-164^\circ$ , re-melts at  $199.5-200^\circ$  (corr.), and has  $[\alpha]_D^{17.5} - 60.34^\circ$  in water (compare Herissey, *loc. cit.*). T. A. H.

**Phlorin, a Product of the Hydrolysis of Phloridzin.** MAX CREMER and R. W. SEUFFERT (*Ber.*, 1912, 45, 2565—2571).—When phloridzin is hydrolysed by dilute mineral acid, dextrose and phloretin are obtained, the latter substance being resolved by the action of potassium hydroxide solution into phloroglucinol and phloretic acid (*p*-hydroxy- $\alpha$ -phenylpropionic acid; Bougault, Abstr., 1900, i, 495). If, however, phloridzin is treated directly with an aqueous solution of an alkali (preferably barium hydroxide), the products of hydrolysis are phloretic acid and phlorin (phloroglucinol glucoside),



The last-mentioned substance, for which crystallographic details are given, is identical with the phloroglucinol glucoside synthesised by Fischer and Strauss (this vol., i, 884). D. F. T.

**Fagopyrum-Rutin.** JOSEF BRANDL and G. SCHÄRTEL (*Arch. Pharm.*, 1912, 250, 414—417).—Fagopyrum-rutin is very easily and rapidly obtained as follows. Fresh, blooming buckwheat is repeatedly extracted with 98% alcohol for many days. The combined extracts are concentrated and freed from chlorophyll by Willstätter's process (Abstr., 1907, i, 71); the rutin is then isolated by concentrating the solution.

The leaves, flowers, and stalks of buckwheat yield respectively 1.78%, 0.71%, and 0.09% of fagopyrum-rutin. The hydrolysis of the rutin to quercetin and sugars (compare Wunderlich, Abstr., 1908, i, 559) is readily effected by boiling 40—50% sulphuric acid. C. S.

**Saponin-like Glucosides from the Leaves of Polyscias nodosa and Hedera helix.** A. W. VAN DER HAAR (*Arch. Pharm.*, 1912, 250, 424—435).—From the mixture of amorphous saponinins,

dextrose, arabinose, and methylpentose obtained by the hydrolysis of the polyscias-saponins, the author has isolated a crystalline sapogenin, *polyscias-sapogenin*,  $C_{26}H_{44}O_4$ , m. p.  $324^\circ$ ,  $\alpha_D^{18}$   $75.58^\circ$  in pyridine. It is a lactone, develops a characteristic violet-red coloration with concentrated sulphuric acid, yields two *substances*, m. p.  $295^\circ$  (not sharply) and  $327^\circ$  respectively, by sublimation, and closely resembles, but is not identical with,  $\alpha$ -hederagenin described below.

The leaves of *Hedera helix* contain glucosides soluble in water and glucosides insoluble in water; the latter contain amorphous and crystalline components. From the last the author has isolated a crystalline glucoside,  $\alpha$ -*hederin*,  $C_{42}H_{66}O_{11}$ , m. p.  $256$ — $257^\circ$ ,  $\alpha_D^{10}$   $9.68^\circ$  in alcohol. It crystallises with  $2H_2O$ , and, unlike other saponins, does not foam on shaking with water; however, it develops the characteristic saponin reaction (violet-red coloration) with concentrated sulphuric acid. It contains five hydroxyl groups and one methoxy-group, and is hydrolysed with difficulty by boiling 4% sulphuric acid, yielding equal molecular quantities of  $\alpha$ -hederagenin, arabinose, and a methylpentose.

$\alpha$ -*Hederagenin*,  $C_{31}H_{50}O_4$ , m. p.  $325$ — $326^\circ$ , forms rhombic crystals, and has  $\alpha_D^9$   $81.2^\circ$  in pyridine. It contains two hydroxyl groups and behaves like a lactone. By distillation with zinc dust in a current of hydrogen, it yields water and an oil, a portion of which is easily volatile with steam. This portion contains a *sesquiterpene*,  $C_{15}H_{24}$ , b. p.  $245$ — $255^\circ$ ,  $n_D^{13}$   $1.5303$ , which is optically inactive and develops a violet-red coloration with sulphuric acid. The portion of the oil which is not volatile with steam contains a *substance*, which is probably a hydrocarbon,  $(C_5H_8)_x$ . C. S.

**Picrotoxin.** II. JOHANNES SIELISCH (*Ber.*, 1912, 45, 2555—2565. Compare this vol., i, 790).—Although acetone has been already observed as a degradation product of picrotoxin, it is obtainable more easily than hitherto suggested (compare Horrmann, this vol., i, 709). If picrotin, picrotoxinin, or picrotoxin is treated with *N*-potassium hydroxide solution at  $100^\circ$ , an equimolecular amount of acetone is formed. The hydrolysis of each of these substances can also be effected by concentrated hydrochloric acid, when the acetone is accompanied by a *substance*,  $C_{12}H_{24}O_2$ , m. p.  $84^\circ$ , b. p.  $162^\circ/12$  mm., which by treatment with hydriodic acid and phosphorus in a sealed tube yields a *hydrocarbon*,  $C_{12}H_{20}$ , b. p.  $90$ — $100^\circ$ .

Bromopicrotoxinin gives an *acetyl* derivative, needles, m. p.  $268^\circ$ . Although it is stable towards potassium permanganate, it is oxidised by nitric acid to a *substance* crystallising in needles, m. p.  $184^\circ$ ; *acetyl* derivative, needles, m. p.  $214^\circ$ . The action of concentrated hydrochloric or hydrobromic acid on bromopicrotoxinin gives a monobasic *bromopicrotoxinic acid*,  $C_{15}H_{19}O_8Br$  (termed  $\beta$  to distinguish it from the acid obtained by Meyer and Bruger, *Abstr.*, 1899, i, 226), colourless needles, m. p.  $223^\circ$ . The  $\alpha$ -bromopicrotoxinic acid (compare Meyer and Bruger) on heating with concentrated hydrochloric acid gives a *chlorobromopicrotoxinic acid*,  $C_{14}H_{17}O_5ClBr \cdot CO_2H, H_2O$ , leaflets, m. p.  $274^\circ$ ; in a similar manner,  $\alpha$ -bromopicrotoxininic acid, when heated with hydrobromic acid, adds a molecule of hydrogen bromide, yielding

*dibromopicrotoxinic acid*,  $C_{14}H_{17}O_5Br_2 \cdot CO_2H, H_2O$ , leaflets, m. p. 278° (decomp.). D. F. T.

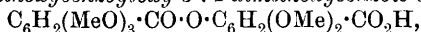
**Absorption of Ultra-violet Rays by  $\alpha$ - and  $\beta$ -Chlorophylls and Crystallised Chlorophyll.** CHARLES DHÉRE and W. DE ROGOWSKI (*Compt. rend.*, 1912, 155, 653—656).—The  $\alpha$ - and  $\beta$ -chlorophylls were obtained from the fresh leaves of *Taxus baccata* and the crystallised chlorophyll from those of *Galeopsis tetrahit*. The pure chlorophylls exhibit a remarkable transparency for the extreme ultra-violet rays. In ethereal solution, the natural chlorophylls only show one absorption band, which is exclusively ultra-violet, and is situated in the middle region of the ultra-violet spectrum considered ( $\lambda = 304\mu\mu$  approximately). W. G.

**Influence of Some Chemical Compounds on the Artificial Melanins.** MAURICE PIETTRE (*Compt. rend.*, 1912, 155, 594—597. Compare this vol., i, 42).—A study of some of the conditions governing the formation of artificial melanins. The yield of melanin varies with the weight of diastase or tyrosine used, but is not directly proportional to either. Mineral acids precipitate the melanins, 15 c.c. of *N*/10-hydrochloric acid per litre of solution being sufficient after forty-eight hours' contact with the diastase. Formic and acetic acid do not cause this precipitation. Alkalis produce no precipitation, but the hydroxides of the alkaline-earth metals bring about a rapid deposition of pigment. Hydrochloric acid precipitates the melanin without entering into combination, but with barium chloride there is a very considerable amount of barium in the precipitate, even after prolonged washing, and with the washing liquid, excess of barium hydroxide gives a yellow, flocculent precipitate containing a fairly constant percentage of barium. W. G.

**Tannin and the Synthesis of Similar Substances. II.** EMIL FISCHER and KARL FREUDENBERG (*Ber.*, 1912, 45, 2709—2726).—In continuation of their previous work (this vol., i, 471), the authors have investigated the action of pentamethyldigalloyl chloride on dextrose, and are led to the conclusion that the product obtained is a mixture, probably of two stereoisomeric penta-[pentamethyl-*m*-digalloyl] dextroses, the relative amounts of which depend on whether  $\alpha$ - or  $\beta$ -dextrose is employed as starting point. It shows a very close analogy with methylotannin, which is also a mixture, but the identity of the two products could not be fully established. They consider their conjecture that pentadigalloyldextrose is an important constituent of tannin to have received additional confirmation.

3:5-Dimethylcarbonato-4-hydroxybenzoic acid was readily prepared from gallic acid (1 mol.), methyl chlorocarbonate (2 mols.), and sodium hydroxide. It had m. p. 186—187° (corr. decomp.) instead of 180°, as previously stated (*Abstr.*, 1908, i, 892; 1911, i, 815). When, however, only 1 molecule of ethyl chlorocarbonate was employed for each molecule of gallic acid, a 36% yield of 3-methylcarbonato-4:5-dihydroxybenzoic acid, needles, m. p. 207° (corr. decomp.), was obtained. This acid, when treated with diazomethane and subsequently with sodium

hydroxide, yielded 5-hydroxy-3:4-dimethoxybenzoic acid, which, after purification by crystallisation of the *cadmium* salt, softened at 187° (corr.), and had m. p. 195—196° (corr.), whereas Herzig and Pollak found 189—192°. When heated in aqueous acetone solution with sodium hydroxide and 3:4:5-trimethoxybenzoyl chloride (m. p. 80°; Perkin and Weizmann, *Trans.*, 1906, 89, 1655, give 78°), it gave 5(3':4':5')-trimethoxybenzoyloxy-3:4-dimethoxybenzoic acid,



m. p. 194—195° (corr.). Phosphorus pentachloride transformed the latter in the presence of chloroform into the corresponding *chloride*, which softened at about 100° and had m. p. 110—111° (corr.), and from which the methyl ester, prisms, m. p. 129—130° (Mauthner, this vol., i, 267, gives 127—128°), was obtained by means of methyl alcohol. When the chloride was shaken with  $\alpha$ -dextrose in the presence of chloroform and quinoline, a *product* was formed which, on analysis, gave figures intermediate between those required for penta-[penta-methyl-*m*-digalloyl]-dextrose and tetra-[pentamethyl-*m*-digalloyl]-dextrose. From analogy with the benzoyl and cinnamoyl derivatives of dextrose (see later), the authors regard the former constitution as the more probable. The product is amorphous, and does not give a sharp m. p. It begins to soften at about 125°, and forms clear drops at about 135°, which, on further heating, flow together. It is apparently not uniform. The analysed product had  $[\alpha]_D^{25} + 15.1^\circ$  in benzene solution, whilst that recovered from the mother liquor showed  $[\alpha]_D^{25} + 28.1^\circ$ . Attempts to isolate a substance of constant specific rotation were unsuccessful. Analogous results were obtained with the *product* of the action of pentamethyldigalloyl chloride on  $\beta$ -dextrose, the specific rotation of which was lowered by repeated crystallisation from  $[\alpha]_D^{25} + 19.5^\circ$  to  $[\alpha]_D^{25} + 8.7^\circ$  in acetylene tetrachloride solution. For purposes of comparison, a specimen of methylotannin was treated in the same manner as the above substances. Its behaviour was similar,  $[\alpha]_D^{25} + 14^\circ$  observed for the original product sinking on repeated crystallisation to  $[\alpha]_D^{25} + 10.6^\circ$  in acetylene tetrachloride solution.

The quinoline method has also been applied to the benzylation of dextrose. Difficulty was experienced in obtaining substances of constant m. p.  $\alpha$ -Pentabenzoyldextrose,  $[\alpha]_D^{25} + 107.6^\circ$  in chloroform, began to soften at about 145°, formed a viscid syrup at 157°, and showed a distinct meniscus at about 177°.  $\beta$ -Pentabenzoyldextrose had  $[\alpha]_D^{25} + 23.71^\circ$  in chloroform, softened at about 155°, and was completely melted at 187° (corr.). It was probably identical with the pentabenzoyldextrose obtained by Fischer and Helferich (*Abstr.*, 1911, i, 802).

$\alpha$ -Pentacinnamoyldextrose, on the other hand, crystallised without difficulty, and had  $[\alpha]_D$  about +196° in chloroform, m. p. 225—226° (corr.).  $\beta$ -Pentacinnamoyldextrose,  $[\alpha]_D - 4.6^\circ$  in chloroform, melted to a thick syrup at 191° (corr.), and showed a distinct meniscus at 201°.

Sucrose, when benzyolated under similar conditions, appeared to yield an octabenzoyl derivative. H. W.

The Tannin of Chinese Galls. KARL FEIST and HEINRICH HAUN (*Chem. Zeit.*, 1912, 36, 1201—1202).—It was thought that the

conflicting results obtained by various authors (Fischer and Freudenberg, this vol., i, 471; Manning and Nierenstein, this vol., i, 566) in the hydrolysis of tannin might be due to the use of gallo-tannin prepared from the two different sources of this product, namely, Turkish galls and Chinese galls. Feist has shown already that the former contain glucogallic acid and yield a tannin, which gives dextrose on hydrolysis (this vol., i, 566). It is now shown that Chinese galls contain gallic acid and a tannin, which yields dextrose on hydrolysis. A small proportion of this tannin is hydrolysed by dilute sulphuric acid only with difficulty. No glucogallic acid is present. T. A. H.

**Active Principle of Iodotannin Solutions.** C. COURTOT (*J. Pharm. Chim.*, 1912, [vii], 6, 253—258).—The author has shown previously (*ibid.*, 1911, [vii], 4, 299) that the iodotannin solution of the French Codex after treatment with hide powder does not invert sucrose, and must therefore contain its soluble iodine in the form of an organic compound (iodotannin), and not as hydriodic acid. In support of this conclusion it is now shown that residues left by slow evaporation of iodotannin solutions, previously cleared with hide powder, show under the microscope characteristic crystals of an unstable compound of gallic acid and iodine. T. A. H.

**Isomerism of Some Unsaturated Lactonic Acids.** ERICH BESCHKE, GEORG KÖHRES, and LUDWIG STOLL (*Annalen*, 1912, 391, 111—150).—Beschke, Winograd-Finkel, and Köhres (*Abstr.*, 1911, i, 873) obtained by the interaction of zinc, benzil, and ethyl bromoacetate, the meso- and the racemic modifications of ethyl  $\beta\gamma$ -dihydroxy- $\beta\gamma$ -diphenyladipate. By treatment with acid, the latter yields  $\beta\gamma$ -diphenylpentadilactone, whilst the meso-form is converted into ethyl  $\beta$ -hydroxy- $\beta\gamma$ -diphenyl- $\gamma$ -butyrolactone- $\gamma$ -acetate, from which, through the intermediate formation of sodium  $\beta\gamma$ -diphenylmuconate, an unsaturated lactonic acid,  $C_{18}H_{14}O_4$ , was obtained. This acid was regarded as  $\beta\gamma$ -diphenyl- $\gamma$ -crotonolactone- $\gamma$ -acetic acid, because it yields undoubtedly the ester, m. p.  $93^\circ$ , of this acid by esterification with alcoholic hydrogen chloride. This view of the constitution of the acid is now shown to be erroneous, because the silver salt and ethyl iodide yield an ethyl ester,  $C_{20}H_{18}O_4$ , m. p.  $73^\circ$ .

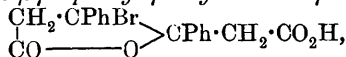
The real  $\beta\gamma$ -diphenyl- $\gamma$ -crotonolactone- $\gamma$ -acetic acid [5-keto-2:3-diphenyl-2:5-dihydrofuran-2-acetic acid],  $\begin{array}{c} \text{CO} \text{---} \text{O} \\ | \quad \diagup \\ \text{CH} : \text{CPh} \end{array} > \text{CPh} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p.  $184^\circ$  (which yields the ester, m. p.  $93^\circ$ , by both methods of esterification), has been obtained by warming the isomeric  $\beta\gamma$ -diphenylpentadilactone with glacial acetic acid and a little piperidine. It has also been prepared by hydrolysing by sodium hydroxide the racemic modification of ethyl  $\beta\gamma$ -dihydroxy- $\beta\gamma$ -diphenyladipate and acidifying the resulting sodium  $\gamma$ -hydroxy- $\beta\gamma$ -diphenyl- $\gamma\delta$ -dihydromuconate.

Ethyl  $\beta\gamma$ -diphenyl- $\gamma$ -crotonolactone- $\gamma$ -acetate yields the corresponding acid by hydrolysis by glacial acetic and hydrochloric acids, and the isomeric lactonic acid (previously described as  $\beta\gamma$ -diphenyl- $\gamma$ -crotonolactone- $\gamma$ -acetic acid) by hydrolysis by alkali.

This isomeric lactonic acid has the same m. p. and similar crystalline form and solubilities as  $\beta\gamma$ -diphenyl- $\gamma$ -crotonolactone- $\gamma$ -acetic acid, and is easily converted into it by hydrogen bromide in glacial acetic acid. Taking into account its formation from sodium  $\beta\gamma$ -diphenylmuconate, the most probable constitution is that of  $\gamma\delta$ -diphenyl- $\Delta^{\beta}$ -hexen- $\alpha\epsilon$ -olide-

$\epsilon$ -carboxylic acid,  $\text{CH} \begin{array}{c} \text{CPh} \cdot \text{CHPh} \\ \text{CO} \text{---} \text{O} \end{array} \text{CH} \cdot \text{CO}_2\text{H}$ . This constitution ex-

plains quite satisfactorily the previously described behaviour of the acid (*loc. cit.*). The molecule easily suffers rearrangement at the lactone group, and therefore reacts as though it were  $\beta\gamma$ -diphenylmuconic acid,  $\text{CO}_2\text{H} \cdot \text{CH} \cdot \text{CPh} \cdot \text{CPh} \cdot \text{CH} \cdot \text{CO}_2\text{H}$ . Thus the reduction of the acid by zinc and acetic acid or by sodium amalgam in neutral or alkaline solution gives mainly  $\beta\gamma$ -diphenyldihydromuconic acid, m. p.  $297^\circ$ , together with a little of the isomeride, m. p.  $185^\circ$  (not  $195^\circ$ , as given previously), which probably has the *cis*-configuration. These isomeric acids do not combine additively with hydrogen bromide or bromine. The latter, however, attacks the sodium salts in aqueous solution to form  $\beta$ -bromo- $\beta\gamma$ -diphenyl- $\gamma$ -butyrolactone- $\gamma$ -acetic acid,



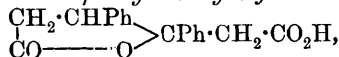
m. p.  $162^\circ$ , and  $\beta\gamma$ -dibromo- $\beta\gamma$ -diphenylbutane,  $\text{CPhMeBr} \cdot \text{CPhMeBr}$ , m. p.  $152^\circ$ .

Reduction of sodium diphenylmuconate by Paal's method gives the two isomeric  $\beta\gamma$ -diphenyladipic acids; the *cis*- and the *trans*-modifications of diphenyldihydromuconic acid have been treated in a similar manner, but only the former is attacked, yielding the diphenyladipic acid, m. p.  $272^\circ$ .

Diphenylcrotonolactone-acetic acid is scarcely attacked by zinc and acetic acid. It is reduced, however, by sodium amalgam, yielding  $\gamma$ -hydroxy- $\beta\gamma$ -diphenyladipic acid,

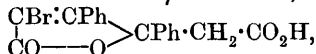


m. p.  $195$ — $198^\circ$ , in alkaline solution, and  $\beta\gamma$ -diphenylbutyrolactone- $\gamma$ -acetic acid [*5-keto-2:3*-diphenyltetrahydrofuran-2-acetic],



m. p.  $221^\circ$  (*ethyl* ester, m. p.  $116^\circ$ ), in neutral solution. The latter acid is converted into 2:8-diacetoxychrysene by acetic anhydride and concentrated sulphuric acid. The reduction of sodium diphenylcrotonolactone- $\gamma$ -acetate by hydrogen and colloidal palladium yields  $\beta\gamma$ -diphenylbutyrolactone- $\gamma$ -acetic acid, whilst diphenylhexenolidecarboxylic acid gives the two isomeric diphenyladipic acids by similar treatment.

Diphenylcrotonolactone- $\gamma$ -acetic acid and the hexenolide acid are only difficultly attacked by potassium permanganate, and do not reduce ammoniacal silver oxide. In glacial acetic acid containing sodium acetate, both are attacked by bromine on the water-bath, and yield  $\alpha$ -bromo- $\beta\gamma$ -diphenylcrotonolactone- $\gamma$ -acetic acid,

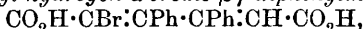


m. p.  $168^\circ$  (*ethyl* ester, m. p.  $119$ — $120^\circ$ ). The hexenolide acid and bromine in boiling  $\alpha$ -chloroform yield  $\beta$ -bromo- $\gamma\delta$ -diphenyl- $\Delta^{\beta}$ -hexen-

*αε-olid-ε-carboxylic acid*,  $\text{CBr} \begin{array}{c} \text{CPh} \cdot \text{CHPh} \\ \text{CO} \text{-----} \text{O} \end{array} \text{CH} \cdot \text{CO}_2\text{H}$ , m. p. 186°.

These two brominated compounds are more easily obtained by the action of aqueous bromine at 0° on the sodium salt of diphenylcrotonolactone-γ-acetic acid and of diphenylmuconic acid respectively. The *ethyl* ester, m. p. 143°, of the bromohexenolide acid is obtained from the silver salt of the acid and ethyl iodide, or by the action of bromine on a chloroform solution of ethyl hydrogen diphenylmuconate in sunlight.

An alcoholic suspension of the ethyl ester of either of these brominated acids, when gently warmed with sodium ethoxide and then acidified, yields *ethyl hydrogen α-bromo-βγ-diphenylmuconate*,

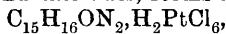


m. p. 152—153°. The *diethyl* ester,  $\text{C}_{20}\text{H}_{17}\text{O}_4\text{Br}$ , m. p. 122—123°, is obtained therefrom by alcoholic hydrogen chloride. C. S.

**Two New Methods of Formation of Dyes of the Pyronine Group.** JOACHIM BIEHRINGER [and R. GLÜCKSBERG and A. TANZEN] (*Annalen*, 1912, 391, 308—325).—An intimate mixture of benzil (1 mol.) and dimethyl-*m*-aminophenol (2 mols.) is heated for four to five hours on the water-bath in an atmosphere of carbon dioxide. The products are benzoic acid, benzoin, and a substance which is shown to be identical with Heumann and Rey's tetramethylrosamine (the tetramethylbenzorrhodamine of the Badische Co.), and with the tetramethylbenzopyronine obtained from benzaldehyde and dimethyl-*m*-aminophenol.

Dimethyl-*m*-aminophenol is heated with concentrated sulphuric acid at 160—170° for five to six hours. The aqueous solution of the product is neutralised by sodium carbonate, whereby a bluish-red colour base is obtained, which dissolves in dilute mineral acids with a bluish-red colour and orange-yellow fluorescence. By solution in dilute hydrochloric acid and treatment with a little ferric chloride, the colour base is converted into a dye, which is shown to be *s-dimethylformopyronine*,  $\text{NHMe} \cdot \text{C}_6\text{H}_3 \begin{array}{c} \text{CH} \\ \text{O} \end{array} \text{C}_6\text{H}_3 \cdot \text{NHMeCl}$ , by its

formation from alcoholic methyl-*m*-aminophenol and 30% formaldehyde. The zincchlorides of the dye prepared by the two methods show identical absorption spectra, whilst the *leuco-base*,  $\text{C}_{15}\text{H}_{16}\text{ON}_2$ , m. p. 192—193°, colourless needles, obtained by distilling a mixture of the dye, sand, zinc dust, and soda-lime, or by treating the dye with dilute hydrochloric acid and zinc dust, forms a *platinichloride*,



yellow needles.

C. S.

**Oxonium Compounds. I. Tricyclic Benzopyrylium Compounds.** WALTHER BORSCHKE and A. GEYER (*Annalen*, 1912, 393, 29—60).—Tricyclic benzopyrylium compounds in the form of their chlorides can be obtained in one operation by condensing *o*-hydroxylated benzaldehydes and cyclic ketones (which are capable of condensing

with aldehydes) by hydrogen chloride, or in two operations by obtaining first an unsaturated hydroxy-ketone from the two components in alkaline solution, and then dehydrating it by hydrogen chloride.

Thus equal molecular quantities of salicylaldehyde and methylcyclohexan-3-one in alcohol are kept with aqueous sodium hydroxide for about a week, whereby 4-salicylidene-1-methylcyclohexan-3-one,  $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{C} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CO} - \text{CH}_2 \end{smallmatrix} > \text{CHMe}$ , m. p.  $153^\circ$ , yellow needles, is obtained, the sodium salt of which is red. 6-Salicylidene-1:3-dimethyl- $\Delta^3$ -cyclohexen-5-one,  $\text{C}_{15}\text{H}_{16}\text{O}_2$ , m. p.  $179^\circ$ , dark yellow plates, is obtained in a similar manner from 1:3-dimethyl- $\Delta^3$ -cyclohexen-5-one. Under similar conditions, pulegone yields, not a similarly constituted compound, but the di-sodium derivative of dihydroxystyryl ketone, which owes its formation probably to a decomposition of the pulegone into acetone and methylcyclohexan-3-one.

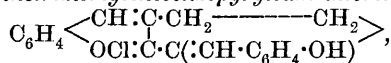
By keeping an alcoholic solution of cyclohexanone and salicylaldehyde with 20% sodium hydroxide for two days and then treating with carbon dioxide, 2:6-disalicylidene-cyclohexanone,  $\text{C}_{20}\text{H}_{18}\text{O}_3$ , m. p.  $150^\circ$ , yellow needles, is obtained. By heating alone or with dissociating solvents, it is rapidly changed to the trimethylenedibenzospiropyran, m. p.  $159^\circ$  (see below). In a similar manner, methylcyclohexan-4-one yields 3:5-disalicylidene-1-methylcyclohexan-4-one,  $\text{C}_{21}\text{H}_{20}\text{O}_3$ , m. p.  $159$ — $160^\circ$  (decomp.), pale yellow crystals, which is converted by boiling aqueous alcohol through the isomeric benzopyranol into the methyltrimethylenedibenzospiropyran (see below). By keeping with 20% sodium hydroxide for two weeks, an alcoholic solution of suberone and salicylaldehyde (2 mols.) yields the dark red disodium derivative of 2:7-disalicylidene-cycloheptanone,  $\text{C}_{21}\text{H}_{20}\text{O}_3$ , m. p.  $155^\circ$ , yellow leaflets, which cannot be converted into the corresponding dibenzospiropyran by boiling with dilute alcohol.

3-Methyl-1:2:3:4-tetrahydro-xanthylum chloride,



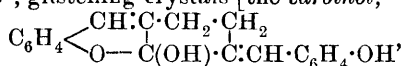
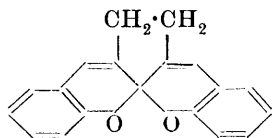
which is produced almost instantly by saturating a solution of 4-salicylidene-1-methylcyclohexan-3-one in cold glacial acetic acid with hydrogen chloride, can only be isolated from the acetic acid solution in the form of the ferrichloride,  $\text{C}_{14}\text{H}_{15}\text{OCl} \cdot \text{FeCl}_3$ , m. p.  $114$ — $115^\circ$  (decomp.), brownish-yellow needles, or the tri-iodide,  $\text{C}_{14}\text{H}_{15}\text{OI}_3$ , m. p.  $135^\circ$ , dark reddish-brown needles. By treating its acetic acid solution with aqueous sodium acetate, the chloride is converted into the benzopyranol,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH} : \text{C} \cdot \text{CH}_2 \cdot \text{CH}_2 \\ \text{O} - \text{C}(\text{OH}) \cdot \text{CH}_2 \end{smallmatrix} > \text{CHMe}$ , m. p. about  $90^\circ$ , green powder containing  $\text{H}_2\text{O}$ , which is stable to boiling 25% alcoholic sodium hydroxide, is re-converted into the xanthylum chloride by hydrogen chloride in glacial acetic acid, and yields 3-methylxanthene by distillation with zinc chloride.

2:3- $\alpha$ -Salicylidene-trimethylenebenzopyrylium chloride,



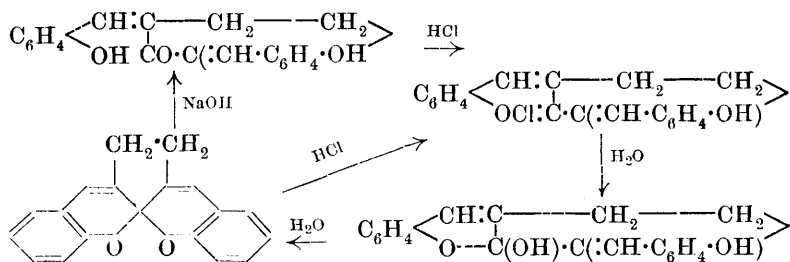
m. p.  $181$ — $183^\circ$  (decomp.), red crystals containing  $1\frac{1}{2}\text{H}_2\text{O}$ , is obtained

by treating a glacial acetic acid solution of 2:5-disalicylidene*cyclopentanone* with hydrogen chloride, or, much more conveniently, by similarly treating a cold solution of *cyclopentanone* and salicylaldehyde (2 mols.). By treating salicylidenetrimethylenebenzopyrylium chloride in almost boiling alcohol with aqueous sodium acetate, it is converted into 3:3'-*ethylenedibenzospiropyran* (annexed formula), m. p. 218—219°, glistening crystals [the *carbinol*,

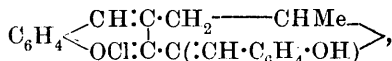
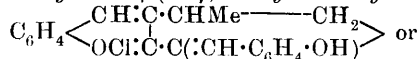


is obtained as a by-product], which is converted into salicylidenetrimethylenebenzopyrylium chloride by hydrogen chloride in glacial acetic acid, and into 2:5-disalicylidene*cyclopentanone* by warm alcoholic sodium hydroxide.

The changes which the preceding substances undergo, and are similar to those exhibited by the following compounds, are clearly illustrated by the scheme :

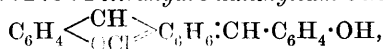


Methyl*cyclopentan-3-one* and salicylaldehyde (2 mols.) in glacial acetic acid react in the presence of hydrogen chloride to form 2:3-*α-salicylidene-β(or γ)-methyltrimethylenebenzopyrylium chloride*,



decomp. 142°, yellow crystals, which is converted by boiling aqueous alcoholic sodium acetate into the *carbinol*, and ultimately into 3:3'-*propylenedibenzospiropyran*,  $\text{C}_{20}\text{H}_{16}\text{O}_2$  (constitution similar to that above), decomp. 254—255°, colourless crystals.

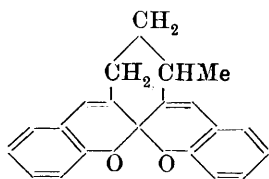
4-*Salicylidene-1:2:3:4-tetrahydro-xanthylium chloride*,



m. p. 155° (decomp.), dark brown plates containing  $1\frac{1}{2}\text{H}_2\text{O}$ , is obtained by treating 2:6-disalicylidene*cyclohexanone* in glacial acetic acid with hydrogen chloride or directly in a similar manner from *cyclohexanone* and salicylaldehyde, or by fission of the corresponding dibenzospiropyran by hydrogen chloride in warm glacial acetic acid. It forms a *ferrichloride*,  $\text{C}_{20}\text{H}_{17}\text{O}_2\text{Cl}\cdot\text{FeCl}_3$ , decomp. about

142°, dark red needles with green reflex, and is converted, by boiling its acetic acid solution with 90% alcohol, into 3:3'-*trimethylenedibenzo-spiropyran*,  $C_{20}H_{16}O_2$ , m. p. 159°, stout needles, which is re-converted into the xanthylium chloride and the disalicylidene*cyclohexanone* by the methods given above.

4-*Salicylidene-3-methyl-1:2:3:4-tetrahydro-xanthylium chloride*,  $C_{21}H_{19}O_2Cl, 1\frac{1}{2}H_2O$ , m. p. 119—120°, dark red, crystalline powder, obtained by condensing salicylaldehyde and *d*-methyl*cyclohexan-3-one*



in ether by hydrogen chloride, forms a *ferrichloride*,  $C_{21}H_{19}O_2Cl, FeCl_3$ , m. p. 152°, black needles with green reflex and red streak, and is converted by water into *as-methyl-3:3'-trimethylenedibenzo-spiropyran* (annexed formula), m. p. 147°, colourless needles, which is re-converted into the xanthylium chloride by hydrogen chloride

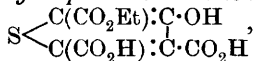
in ether or glacial acetic acid, but apparently does not yield 2:4-disalicylidene-1-methyl*cyclohexan-3-one* even by prolonged boiling with alcoholic sodium hydroxide.

Since 4-salicylidene-3-methyl-1:2:3:4-tetrahydro-xanthylium chloride is obtained by treating an ethereal solution of salicylaldehyde and 3-methyl-1:2:3:4-tetrahydro-xanthylium chloride with hydrogen chloride, it seems that in pyrylium salts the methylene group attached to the carbon atom adjacent to the quadrivalent oxygen atom can condense with ketones.

4-*Salicylidene-2-methyl-1:2:3:4-tetrahydro-xanthylium chloride*,  $C_{21}H_{19}O_2Cl, 1\frac{1}{2}H_2O$ , decomp. 155°, greenish-yellow crystals, is obtained from salicylaldehyde and methyl*cyclohexan-4-one* in the usual manner. Attempts to prepare a salicylidenebenzopyrylium chloride from salicylaldehyde and suberone by means of hydrogen chloride yielded an almost colourless substance,  $C_{21}H_{18}O_2$ , which is apparently 3:3'-*tetramethylenedibenzo-spiropyran*; however, it is not affected by hydrogen chloride in glacial acetic acid or by warm alcoholic sodium hydroxide.

C. S.

**Thiophen and Furan Derivatives.** OSCAR HINSBERG (*Ber.*, 1912, 45, 2413—2418. Compare Abstr., 1910, i, 334).—The prolonged action of ethyl thioglycollate, glyoxal, and alcoholic sodium ethoxide results in the formation, after acidification, of thiophen-2:5-dicarboxylic acid. In a similar manner, ethyl thioglycollate, alcoholic sodium ethoxide, and ethyl oxomalonate yield, after successive acidification and hydrolysis of the product by boiling 10% sodium hydroxide, 2-ethyl dihydrogen 3-hydroxythiophen-2:4:5-tricarboxylate,



m. p. 188°, colourless needles, which develops a cherry-red coloration with ferric chloride and forms a sodium salt,  $C_9H_7O_7SNa, H_2O$ , long needles, decomp. about 260°.

By boiling methyl 3:4-dihydroxythiophen-2:5-dicarboxylate with dilute alcoholic sodium hydroxide (4 mols.) and acidifying the product,

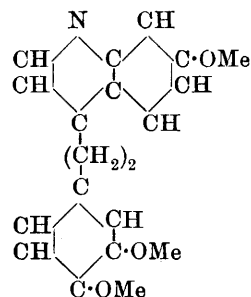
*methyl 3:4-dihydroxythiophen-2-carboxylate*,  $S \begin{matrix} \text{C}(\text{CO}_2\text{Me}) \cdot \text{C} \cdot \text{OH} \\ \text{CH} = \text{C} \cdot \text{OH} \end{matrix}$ , m. p. 108° (?), is obtained, which develops a blue coloration with ferric chloride; the corresponding *ethyl* ester has m. p. 76—78°.

Methyl thioidiglycollate, ethyl oxalate, and methyl alcoholic sodium methoxide yield ultimately *methyl 3:4-dihydroxyfuran-2:5-dicarboxylate*, m. p. 220°. Methyl thioidiglycollate, benzil, and sodium methoxide in a similar manner yield *3:4-diphenylfuran-2-carboxylic acid*, m. p. 231°. By a similar process with phenanthraquinone, *phenanthrafurandicarboxylic acid dihydrate*,  $\text{C}_{18}\text{H}_{14}\text{O}_7$ , decomp. 280°, is obtained, from which the two molecules of water are not expelled at 130°. C. S.

**Solubility of Alkaloids in Basic Solvents.** MAX SCHOLTZ (*Arch. Pharm.*, 1912, 250, 418—423).—The solubility of alkaloids in basic solvents, such as aniline, pyridine, piperidine, and diethylamine, has been determined; a table of the results is given. It has been found that alkaloids differ in a remarkable degree as regards their solubility in one and the same basic solvent. As an illustration, the following solubilities in pyridine are given, the numbers in brackets representing the parts by weight of the alkaloid dissolved by 100 parts by weight of pyridine at 20°: quinine (101), cinchonine (1·4), strychnine (1·5), brucine (28), morphine (19), narcotine (2·3), papaverine (8), thebaine (9), veratrine (175), cocaine (80), atropine (73). Some of the solubilities are extremely striking; thus the solubility of veratrine in diethylamine is 271, whilst strychnine, which is generally so sparingly soluble in most solvents, dissolves in only five times its weight of aniline at 20°. The solubilities of alkaloids in basic solvents at their b. p. are very much greater than at the ordinary temperature.

Although sodium and potassium hydroxides, as is well known, diminish the solubility of organic bases in water, the author finds that quinine, strychnine, and cinchonine are decidedly more soluble in 10% ammonia than in water. This is true, however, only with aqueous ammonia; the alkaloids are less soluble in alcoholic ammonia than in alcohol. C. S.

**Angostura Alkaloids.** JULIUS TRÖGER and W. KROSEBERG (*Arch. Pharm.*, 1912, 250, 494—531. Compare *Abstr.*, 1911, i, 482).—It



was found that mixtures of cusparine and galipine could be separated by conversion into the oxalates, cusparine oxalate being insoluble and galipine oxalate soluble in water. Making use of this method only three alkaloids, cusparine, galipine, and galipoidine, could be prepared from angostura bark extract, so that the supposed alkaloids, cusparidine and galipidine, are probably only mixtures of galipine and cusparine. On oxidation with permanganate, galipine yields veratric acid and a methoxyquinolinecarboxylic acid, and the annexed formula is provisionally assigned to this alkaloid.

*Nitrogallipine*,  $C_{20}H_{20}O_3N, NO_2$ , m. p.  $140^\circ$ , formed by the action of either dilute or concentrated nitric acid on galipine, crystallises in pale yellow needles, yields a *nitrate*, m. p.  $180^\circ$  (decomp.), crystallising in bright yellow, prismatic needles, a *hydrochloride*,  $B, HCl, \frac{1}{2}H_2O$ , m. p.  $180^\circ$  (decomp.), a *sulphate*,  $B_2, H_2SO_4, H_2O$ , m. p.  $191^\circ$  (decomp.), a *platinichloride*, m. p.  $227^\circ$  (decomp.), and an *aurichloride*, m. p.  $192^\circ$  (decomp.). On reduction with stannous chloride and hydrochloric acid in alcohol, *aminogallipine* is produced; this crystallises in grey needles, m. p.  $156^\circ$ , and yields a *platinichloride*, which darkens at  $192^\circ$ , and does not melt below  $300^\circ$ .

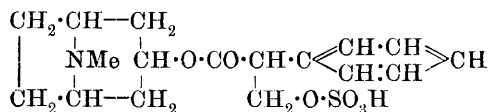
On oxidation with permanganate in alkaline solution, galipine sulphate yields veratric acid and an *acid*,  $C_{11}H_9O_3N, 2H_2O$ , m. p.  $194^\circ$  (anhydrous), crystallising in glancing needles, which contains one methoxyl group and is probably a methoxyquinolinecarboxylic acid, since on heating at  $190^\circ$  it gives a product from which a *platinichloride*, m. p.  $221^\circ$ , having the composition of a methoxyquinoline platinichloride, was prepared. With hydriodic acid, it gives an *acid* (? hydroxyquinolinecarboxylic acid),  $C_{10}H_7O_3N$ , m. p.  $273^\circ$  (decomp.), crystallising in long, slender, colourless needles.

Galipine on destructive distillation with zinc dust yields quinoline, which was identified by means of the platinichloride.

Galipine is colourless when pure, and yields colourless salts; the yellow colour usually ascribed to the salts is due to the presence of impurities.

T. A. H.

**Preparation of Sulphuric Acid Esters of Alkylamine Hydroxy-acid Esters.** F. HOFFMANN, LA ROCHE & Co. (D.R.P. 247455 and 247457).—The action of concentrated sulphuric acid on alkylamine hydroxy-acid esters has been described (Abstr., 1893,



i, 677; 1894, i, 153), and in this connexion the following compounds have been obtained.

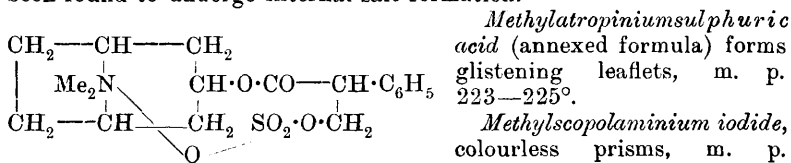
*Atropinesulphuric acid* (annexed formula), prisms,

m. p.  $238-239^\circ$ , is prepared by dissolving atropine sulphate (m. p.  $183-184^\circ$ ) in 97% sulphuric acid, and allowing it to remain during one hour at the ordinary temperature; the solution is diluted, and carefully treated with ammonium hydroxide, when the ester is precipitated in crystalline form.

The *compound*, slender needles, obtained when a solution of scopolamine in carbon tetrachloride is cooled and allowed to remain in contact with fuming sulphuric acid during half an hour, has m. p.  $225^\circ$ , whilst homoatropine hydrobromide, under similar conditions, furnishes *homoatropinesulphuric acid*, rhombic leaflets or prisms, containing  $H_2O$ , and m. p.  $245^\circ$  (when anhydrous). These esters crystallise from hot water. The second patent states that the sulphuric acid employed in the preceding reactions can be replaced by chlorosulphonic acid.

F. M. G. M.

**Preparation of Sulphuric Acid Esters of Alkylammonium Salts of Hydroxy-acid Esters of Alkylamines.** F. HOFFMANN, LA ROCHE & Co. (D.R.-P. 247456. Compare Abstr., 1903, i, 512, and preceding abstract).—The previously described atropine esters have been found to undergo internal salt formation.



action of methyl iodide on scopolamine in absolute alcoholic solution; on treatment with silver sulphate it yields *methylscopolaminium sulphate*, an amorphous mass, which furnishes *methylscopolaminiumsulphuric acid* (prismatic crystals, m. p. 238—241°) with fuming sulphuric acid.

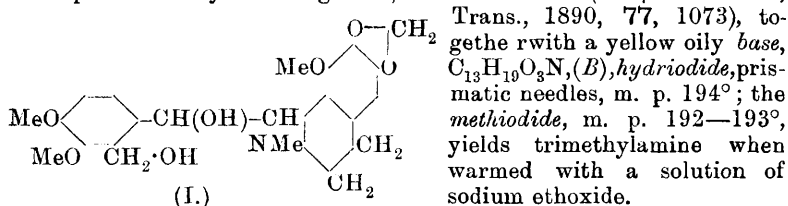
F. M. G. M.

**Nicotine and Water.** HUGO R. KRUYT (*Chem. Weekblad*, 1912, 9, 830—834).—The author could not find any trace of the change in the specific rotation of mixtures of water and nicotine, such as was described by Pribram (Abstr., 1887, 755). Distillation in an atmosphere of hydrogen under reduced pressure yields pure nicotine, but the alkaloid could not be obtained crystalline.

A. J. W.

**The Electrolytic Reduction of Narcotine.** CESARE FINZI and MARTIN FREUND (*Ber.*, 1912, 45, 2322—2333).—By the reduction of narcotine at a lead cathode, there has been obtained among other substances, hydrodeoxynarcotine,  $\text{C}_{22}\text{H}_{25}\text{O}_6\text{N}$ , m. p. 126° (Hammel, *Diss.*, 1910).

Attempts by the present authors to reproduce the same results have hitherto failed. The reduction of narcotine in dilute sulphuric acid at a lead cathode gave a mixture of a syrupy product with a crystalline substance, prisms, m. p. 128°, quite distinct from the above substance; its behaviour indicates it to be *tetrahydronarcotine*,  $\text{C}_{22}\text{H}_{27}\text{O}_7\text{N}$ ; *hydrochloride*, decomposes at 160—165°; *platinichloride*, yellow, amorphous powder. The *methiodide*, needles, m. p. 224° (decomp.), on treatment with silver oxide gives an oily base (A), which on further treatment with potassium hydroxide gives  $\psi$ -meconinic acid (compare Perkin,



Oxidation of the above tetrahydronarcotine with potassium dichromate and dilute sulphuric acid gives  $\psi$ -meconinic acid and cotarnine.

On heating with benzoic anhydride, tetrahydronarcotine is converted into an oily *dibenzoyl* derivative, the crystalline *platinichloride* of

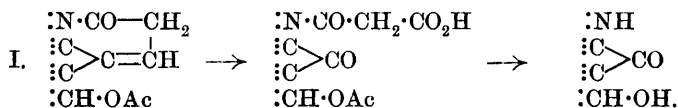
which on hydrolysis with alcoholic potassium hydroxide yields two molecules of benzoic acid.

From the above results the conclusion is drawn that the base *B* is 6-methoxy-4:5-methylenedioxy-1-methyl-2-dimethylaminoethylbenzene,  $\text{OMe} \cdot \text{C}_6\text{HMe}(\text{CH}_2\text{O})_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe}_2$ , whilst to tetrahydronarcotine is attributed the structure given in formula (I); the base *A* is the quaternary dimethylammonium hydroxide derived from this structure.

D. F. T.

**Methylation of Clupeine.** F. ROGOZIŃSKI (*Zeitsch. physiol. Chem.*, 1912, 80, 371—375).—Skraup and Krause (Abstr., 1909, i, 748), have shown that a profound change takes place in the protein molecule when methyl iodide acts on casein. Methyl sulphate is shown to have a similar effect on clupeine, the arginine nitrogen, which before treatment corresponded with 88% of the total, sinking after methylation to 37.7% and 28.8% in the methylated product. E. F. A.

**Strychnos Alkaloids. XV. Decomposition of Brucine into a Base, termed Curbine.** HERMANN LEUCHS and GEORGE PEIRCE (*Ber.*, 1912, 45, 2653—2662).—The acid,  $\text{C}_{23}\text{H}_{24}\text{O}_9\text{N}_2$  (acetylbrucinolic acid), isolated from the oxidation product of brucinolone acetate (Leuchs and Brewster, this vol., i, 210), is hydrolysed by hydrochloric acid to acetic acid, malonic acid, and a base, *curbine*,  $\text{C}_{18}\text{H}_{20}\text{O}_5\text{N}_2$ , which crystallises in slender needles, m. p. 322°, gives a red coloration with nitric acid, and has also been obtained by hydrolysing the substance,  $\text{C}_{22}\text{H}_{24}\text{O}_7\text{N}_2$ , formed by the removal of carbon dioxide from acetylbrucinolic acid; the *hydrochloride* crystallises in colourless needles, m. p. 270°, with previous darkening at 265°. In addition to the above compounds, a small amount of a *hydrochloride*, crystallising in yellow leaflets, m. p. 238—240° (decomp.), was isolated from the product of hydrolysis of acetylbrucinolic acid. From these results the authors draw the conclusion that brucinolone acetate contains the groups shown in (I) below, and represent its conversion into acetylbrucinolic acid and curbine by the following scheme:



The compound  $\text{C}_{22}\text{H}_{24}\text{O}_7\text{N}$  is the diacetyl derivative of curbine.

The oxidation of brucinolone acetate yields, in addition to acetylbrucinolic acid and the compound,  $\text{C}_{28}\text{H}_{22}\text{O}_6\text{N}_2$ , previously described (*loc. cit.*), a small amount of a substance, crystallising in yellow prisms, m. p. 230—235° (decomp.), together with a yellow, oily acid, the barium salt of which,  $\text{C}_{23}\text{H}_{22}\text{O}_{10}\text{N}_2\text{Ba}$  or  $\text{C}_{23}\text{H}_{24}\text{O}_{10}\text{N}_2\text{Ba}$ , crystallises in slender, white needles.

The by-product,  $\text{C}_{21}\text{H}_{24}\text{O}_6\text{N}_2$ , obtained by the action of sodium hydroxide on brucinolic acid, is converted by the further action of sodium hydroxide into brucinolone, which is accompanied by small amounts of the following substances: (1) A compound,  $\text{C}_{21}\text{H}_{22}\text{O}_5\text{N}_2$ , isomeric with brucinolone, and termed by the authors *crypto-*

*brucinolone*; it crystallises in lustrous, yellow, broad prisms, m. p. 188—190°, and yields a *hydrochloride*, crystallising in needles, m. p. 240°. (2) A substance,  $C_{21}H_{24}O_6N_2 \cdot 6H_2O$ , which forms lustrous, broad needles or leaflets, m. p. 227—228°, with previous sintering at 220°.

F. B.

**Pyrroline-2-carboxylic Acid.** EMIL FISCHER and FERDINAND GERLACH (*Ber.*, 1912, 45, 2453—2456. Compare Fischer and van Slyke, *Abstr.*, 1911, i, 1020).—By reduction of pyrrole-2-carboxylamide with phosphonium iodide and concentrated hydrogen iodide, a compound containing two hydrogen atoms more, namely, *pyrroline-2-carboxylic acid*, is obtained. This is very similar to proline, and the two acids may readily be mistaken for one another. It is proposed to make a special search for pyrroline-2-carboxylic acid among the products of protein hydrolysis. The free acid has m. p. 235° (corr.); the copper salt,  $C_{10}H_{12}O_4N_2Cu \cdot 2H_2O$ , consists of microscopic, irregular, intergrown, deep blue plates. The *methyl* ester resembles those of the aliphatic amino-acids.

E. F. A.

**2:3-Dimethylpyrrole.** OSCAR PILOTY and K. WILKE (*Ber.*, 1912, 45, 2586—2592).—Ethyl oxalacetate condenses with  $\beta$ -aminobutan- $\gamma$ -one in alkaline solution, yielding 4-ethyl hydrogen 2:3-dimethyl-

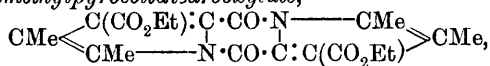
pyrrole-4:5-dicarboxylate,  $NH \begin{matrix} \swarrow CMe \\ \searrow C(CO_2H) \end{matrix} \begin{matrix} \swarrow CMe \\ \searrow C \cdot CO_2Et \end{matrix}$ , which crystallises

in small, stout prisms, m. p. 201°, and forms with potassium methoxide in methyl alcoholic solution a *potassium* salt, crystallising in snow-white needles of a pearly lustre. The acid ester is converted by methyl sulphate into the *methyl ethyl* ester, stout, colourless prisms, m. p. 152°, and is hydrolysed by aqueous potassium hydroxide to 2:3-dimethylpyrrole-4:5-dicarboxylic acid, which becomes red at 180°, sinters at 200°, and melts at 225° with evolution of carbon dioxide. When boiled with aqueous potassium hydroxide for twenty hours, it yields

2:3-dimethylpyrrole-4-carboxylic acid,  $NH \begin{matrix} \swarrow CMe \\ \searrow CH \end{matrix} \begin{matrix} \swarrow CMe \\ \searrow C \cdot CO_2H \end{matrix}$ , m. p.

188°, the *ethyl* ester of which has m. p. 110—111°, and is best prepared by heating the original monoethyl ester at 225° in an atmosphere of carbon dioxide.

*Ethyl tetramethylpyrocollidicarboxylate*,



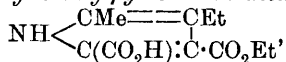
is obtained in long, pointed, light yellow, felted needles of a silky lustre, m. p. 169°, by boiling 4-ethyl hydrogen 2:3-dimethylpyrrole-4:5-dicarboxylate with acetic anhydride.

When heated with potassium and toluene, ethyl 2:3-dimethylpyrrole-4-carboxylate forms a *potassium* derivative, which reacts with acetyl chloride, yielding *ethyl 1-acetyl-2:3-dimethylpyrrole-4-carboxylate*, spherical aggregates of pale red needles, m. p. 65°.

2:3-Dimethylpyrrole, obtained together with a small amount of bis-2:3-dimethylpyrrole (compare this vol., i, 736; Dennstedt, *Abstr.*, 1899, 1209) by the distillation of 2:3-dimethylpyrrole in

a current of carbon dioxide at a temperature slightly above its m. p., forms a *potassium* derivative, which reacts with ethyl iodide, yielding an *ethyl* derivative, in which the ethyl group is probably attached to one of the carbon atoms of the ring.

4-Ethyl hydrogen 2-methyl-3-ethylpyrrole-4 : 5-dicarboxylate,



prepared by condensing ethyl oxaloacetate with  $\beta$ -aminopentan- $\gamma$ -one in alkaline solution, has m. p. 174—175°. F. B.

**An Attempt to Synthesise 2 : 3-Dimethyl-4-ethylpyrrole (Hæmopyrrole).** LUDWIG KNORR and KURT HESS (*Ber.*, 1912, 45, 2626—2631).—By the reduction of  $\beta$ -oximinobutan- $\gamma$ -one and the sodium salt of formylacetone with sodium amalgam in alcoholic solution, the authors have obtained 4-formyl-2 : 3 : 5-trimethylpyrrole instead of the expected 2 : 3-dimethyl-4-ethylpyrrole.

In the first attempts the usual method of reduction adopted in Knorr's synthesis of pyrrole derivatives was employed, namely, reduction with zinc dust and glacial acetic acid, but owing to the ease with which formylacetone condenses in the presence of acids to triacetylbenzene, no pyrrole compound was obtained. It was found subsequently that the pyrrole synthesis may be accomplished by reduction with sodium amalgam in alcoholic solution, and in illustration of the latter method of reduction the preparation of ethyl 2 : 4-dimethylpyrrole-3 : 5-dicarboxylate and 2-carbethoxy-3 : 5-dimethylpyrrole-4-carboxylanilide is described.

4-Formyl-2 : 3 : 5-trimethylpyrrole,  $\begin{array}{c} \text{CMe} \text{---} \text{C} \cdot \text{CHO} \\ | \quad | \\ \text{CMe} \cdot \text{NH} \cdot \text{CMe} \end{array}$ , has m. p. 80°,

b. p. 186.5°, reduces ammoniacal silver nitrate, and forms a *phenylhydrazone*, crystallising in yellow needles. F. B.

**Acetylpyrroles.** LUDWIG KNORR and KURT HESS (*Ber.*, 1912, 45, 2631—2635).—It has been shown previously (*Abstr.*, 1911, i, 1019) that the hydrazone of 3-acetyl-2 : 4-dimethylpyrrole when heated with sodium ethoxide yields 3-acetyl-2 : 4-dimethylpyrrole, whereas the azine is converted into a pyrrole, which closely resembles 3-acetyl-2 : 4-dimethylpyrrole, but differs from it in giving a picrate of much lower m. p. (Fischer and Bartholomäus, this vol., i, 50). With the object of discovering the cause of this difference in the behaviour, the authors have investigated the behaviour of the azines of 2-acetylpyrrole and 3-acetyl-2 : 4-dimethylpyrrole towards sodium methoxide and sodium ethoxide respectively, and find that with the azines the original acetyl group is not reduced to the ethyl group as in the case of the hydrazones, but is removed from the molecule, the further action of the alkyl oxide resulting in the introduction of an alkyl group in the 1-position.

The *azine* of 2-acetylpyrrole,  $\text{C}_{12}\text{H}_{14}\text{N}_4$ , prepared by boiling the pyrrole compound with hydrazine hydrate, crystallises in colourless, prismatic columns, m. p. 213° (corr.), and is converted by methylalcoholic sodium methoxide at 200—210° into 2-methylpyrrole.

The azine of 3-acetyl-2:4-dimethylpyrrole when heated with alcoholic sodium ethoxide yields 3:5-dimethyl-2-ethylpyrrole (Abstr., 1911, i, 1019). F. B.

**Action of Sodium Ethoxide on Pyrrole Derivatives. II.**  
HANS FISCHER and ERICH BARTHOLOMÄUS (*Zeitsch. physiol. Chem.*, 1912, 80, 6—16. Compare the vol., i, 384).—By the action of sodium ethoxide on trimethylpyrrole, crystalline tetramethylpyrrole has been obtained. In a similar manner with sodium propoxide, trimethylpropylpyrrole is formed, and has been isolated as picrate. A methylpropylpyrrole is stated by Marchlewski to be present in the hæmopyrrole mixture, but, on heating this with sodium methoxide, phyllopyrrole is practically the only product. This serves to negative Marchlewski's supposition.

When ethyl 2:5-dimethylpyrrole-3-carboxylate is heated with sodium ethoxide, the carbethoxy-group is eliminated. Similarly, from acetyldimethylpyrrole, dimethylpyrrole is obtained; this yields a characteristic crystalline picrate. When 2:4-dimethyl-5-ethylpyrrole is heated with sodium methoxide, the ethyl group in position 5 is replaced by methyl, and tetramethylpyrrole is obtained.

Methyl groups render the pyrrole nucleus unstable, dimethyl- and trimethyl-pyrrole being more sensitive than pyrrole. Acetyltrimethylpyrrole is stable; trimethylethylpyrrole is most unstable. The pyrrole-carboxylic acids are stable when pure.

The 2-azo-dyes of the pyrroles are similarly rendered more stable by the introduction of the acetyl or carboxyl group.

The picrates of the pyrroles are conveniently decomposed by shaking the suspension in ether with 25% hydrochloric acid.

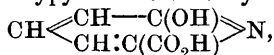
2:3:4:5-Tetramethylpyrrole,  $\text{NH} \begin{smallmatrix} \text{CMe}:\text{CMe} \\ | \\ \text{CMe}:\text{CMe} \end{smallmatrix}$  (compare Ciamician and Silber, this vol., i, 537), crystallises in colourless platelets, m. p. 111—112°; it has an odour like naphthalene. The yellow picrate has m. p. 127—128°.

2:4:5-Trimethyl-3-propylpyrrole,  $\text{NH} \begin{smallmatrix} \text{CMe}:\text{CPr} \\ | \\ \text{CMe}:\text{CMe} \end{smallmatrix}$ , was isolated as picrate, m. p. 80—91°.

2:4-Dimethylpyrrole picrate has m. p. 92—93°.

E. F. A.

**Conversion of Dihydrofurandicarboxylic Acid into Hydroxypyridinecarboxylic Acid.** EMIL FISCHER, KURT HESS, and ALEX. STAHLSCHMIDT (*Ber.*, 1912, 45, 2456—2467).—When 2:5-dihydrofuran-2:5-dicarboxylic acid, obtained from dehydromucic acid on reduction with sodium amalgam (Hill and Wheeler, Abstr., 1901, i, 556), is heated with aqueous ammonia in presence of ammonium bromide at 160°, 2-hydroxypyridine-6-carboxylic acid,



is formed.

When further heated this compound loses carbon dioxide, forming 2-hydroxypyridine. Phosphorus pentachloride converts it into a

chloropyridinecarboxylic acid, which is reduced by hydrogen iodide to picolinic acid.

The transformation from the furan to the pyridine ring takes place in several stages. When the heating is effected in the absence of ammonium bromide at  $150^{\circ}$ , dihydrofurandicarboxylic acid is converted into the half amide; this could not be transformed into hydroxypyridinecarboxylic acid.

$\alpha$ -Dihydrofurandicarboxylamide is prepared by the action of ammonia on the dichloride; here, also, dehydrating agents other than ammonia were without effect.

2 : 3-Dihydrofuran-2 : 5-dicarboxylic acid, which is obtained from the 2 : 5-isomeride on boiling with alkali, is readily converted by ammonia into the same hydroxypyridinecarboxylic acid.

2-Hydroxypyridine-6-carboxylic acid forms long, thin prisms or needles, which sinter at  $275^{\circ}$  (corr.), m. p.  $282^{\circ}$  (corr. decomp.). It tastes and reacts acid, and gives a yellowish-red colour with ferric chloride. The barium salt forms long, narrow prisms, obliquely cut and aggregated in bunches; the calcium salt crystallises in microscopic, prismatic needles; the copper salt forms microscopic, obliquely cut prisms.

2-Chloropyridine-6-carboxylic acid crystallises in colourless platelets, which sinter at  $180^{\circ}$  (corr.), m. p.  $190^{\circ}$  (corr.). The copper salt +  $4\text{H}_2\text{O}$  forms pale-coloured, microscopic columns; the silver salt appears as very slender, microscopic, thread-like needles; the calcium salt +  $\text{H}_2\text{O}$  forms short, interlaced, pointed needles.

The monoamide of 2 : 5-dihydrofuran-2 : 5-dicarboxylic acid,



crystallises in microscopic prisms, m. p.  $244^{\circ}$  (corr., decomp.).

2 : 5-Dihydrofuran-2 : 5-dicarboxyl chloride,  $\text{C}_4\text{H}_4\text{O}(\text{COCl})_2$ , is a colourless, strongly refractive, mobile oil of powerful odour, b. p.  $146^{\circ}/28\text{ mm.}$ , which darkens in colour on keeping.

2 : 5-Dihydrofuran-2 : 5-dicarboxylamide forms colourless, stunted crystals, mostly plates, m. p.  $211\text{--}212^{\circ}$  (corr.). E. F. A.

1 : 5-Naphthylenediamine. CHEMISCHE FABRIK R. SCHEUBLE & Co. (*Chem. Zeit.*, 1912, 36, 1226).—The unpleasant properties attributed to 1 : 5-diacetylnaphthylenediamine by Kunckell and Schneider (this vol., i, 811) are ascribed to chloroacetyl chloride and bromoacetyl chloride, each of which can cause an inflammation of the skin. Susceptibility to the action of these substances appears to be largely a personal matter, whilst persons who have recovered from one attack appear to be subsequently immune. In reply to this criticism, FRANZ KUNCKELL (*ibid.*, 1226—1227) points out that chloroacetyl chloride was employed during two years in his laboratory without unpleasant consequences. The latter were only observed when 1 : 5-naphthylenediamine was acetylated, and, since the amine itself is apparently harmless, they must be attributed to 1 : 5-diacetylnaphthylenediamine. H. W.

Ditertiary Hydrazines and Bivalent Nitrogen. HEINRICH WIELAND (*Annalen*, 1912, 392, 127—133).—Tetraphenylhydrazine

and its homologues, analogously to hexaphenylethane, dissociate in solution into radicals,  $\text{NAr}_2$  (Abstr., 1911, i, 570). The author's aims in the following papers are to trace as fully as possible the analogy between carbon and nitrogen as regards the existence of free radicals, and to examine the dependence of the stability of the hydrazine on the character of the substituting aryl groups. Confining the comparison to tetra-arylated hydrazines, it is found that the dissociability increases with the presence of positive groups. On the other hand, mixed dialkyldiarylhydrazines have been prepared, and are found to dissociate less readily than tetra-arylhydrazines.

C. S.

### Aromatic Hydrazines. XI. Dissociation of Tetrazens.

HEINRICH WIELAND and H. FRESSEL (*Annalen*, 1912, 392, 133—156).—Franzen and Zimmermann's observations regarding the conversion of tetrazens into ditertiary hydrazines (Abstr., 1906, i, 702) require amplification. Many tetrazens require boiling for some time for the complete expulsion of the azo-nitrogen, and the products are secondary amines and Schiff's bases, doubtless formed by the interaction of the  $\text{NR}_2$  groups, which are intermediate products. Tetraethyltetrazen, which in the pure condition is a pleasantly odorous liquid, b. p.  $79^\circ/12$  mm., decomposes when heated for some time under the ordinary pressure, and yields nitrogen, diethylamine, and ethyl ethylideneamine. The formation of  $\text{NEt}_2$  groups during the decomposition of the tetrazen is shown by passing a slow current of nitric oxide over the decomposing tetrazen, whereby nitrosodiethylamine is produced. *N*-Azopiperidine decomposes when heated for some time, and yields piperidine and tetrahydropyridine (?). It reacts with ethereal methyl iodide (3 mols.) to form dimethylpiperidinium iodide and an amorphous substance.

Tetrabenzyltetrazen is best obtained by oxidising a cold saturated alcoholic solution of *as*-dibenzylhydrazine with alcoholic *p*-benzoquinone at  $0^\circ$ . By being heated for six hours in boiling xylene, it yields dibenzylamine and benzylbenzylideneamine, whilst when heated with methyl iodide in benzene, it yields, amongst other products, *dibenzyltrimethylammonium iodide*, m. p.  $191^\circ$ .

*$\alpha\beta$ -Diphenyl- $\alpha\beta$ -dimethylhydrazine*,  $\text{NPhMe}\cdot\text{NPhMe}$ , b. p.  $138^\circ/1$  mm., is obtained, together with methylaniline and the Schiff base, by heating diphenyldimethyltetrazen in boiling xylene for one and a-half hours in an atmosphere of carbon dioxide. The dissociation of the hydrazine into  $\text{NPhMe}$  can be indicated, either by distillation in a vacuum, whereby methylaniline and polymerisation products of methylenedianiline are obtained, or by heating the substance in boiling xylene in a current of nitric oxide, whereby phenylmethylnitrosoamine is produced. Diphenyldimethylhydrazine behaves towards acids like its tetrazen (of course, nitrogen is not evolved); specially characteristic is the action of slightly warmed glacial acetic acid, which produces a violet coloration, changing to blue and green.  *$\alpha\beta$ -Diphenyl- $\alpha\beta$ -diethylhydrazine*, b. p.  $141^\circ/1$  mm., behaves like its methyl homologue, and is obtained in a similar manner. The formation of ammonia and

phenylcarbylamine by the decomposition of diphenyldimethyltetrazen in boiling xylene (Franzen and Zimmermann, *loc. cit.*) has not been observed by the authors. The diphenyldibenzylhydrazine described by these two investigators (*loc. cit.*) is probably a mixture of benzylaniline and benzylideneaniline.

Unsuccessful attempts have been made to prepare ditertiary hydrazines by the action of metals on secondary *N*-chloroamines.

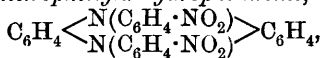
C. S.

**Aromatic Hydrazines. XII, Dissociation of Tetra-arylhydrazines and of Diarylnitrosoamines.** HEINRICH WIELAND and HANS LECHER (*Annalen*, 1912, 392, 156—169).—Rapidly in boiling xylene, or after some months in chloroform or benzene in darkness at the ordinary temperature, tetraphenylhydrazine decomposes into diphenylamine (2 mols.) and 5:10-diphenyldihydrophenazine (1 mol.).

*s*-Diphenyldi-*p*-tolylhydrazine,  $C_6H_4Me \cdot NPh \cdot NPh \cdot C_6H_4Me$ , m. p.  $123^\circ$ , colourless crystals, obtained by the oxidation by potassium permanganate of phenyl-*p*-tolylamine in acetone at  $10$ — $20^\circ$ , decomposes in a similar manner in boiling toluene in thirty minutes, or in chloroform or benzene in darkness after three months, the products being phenyl-*p*-tolylamine and a diphenyldimethyldihydrophenazine,  $C_{26}H_{22}N_2$ , m. p. above  $315^\circ$ , darkening at  $267^\circ$ . On the contrary, tetra-*p*-tolylhydrazine can be kept in benzene in darkness for three months without appreciable change; in chloroform, however, under similar conditions, it decomposes into *p*-ditolyldihydrotolazine, m. p.  $274^\circ$ , not  $269^\circ$  (Abstr., 1908, i, 1014), and di-*p*-tolylamine.

Tetra-*p*-anisyltetrazen decomposes in boiling benzene in an atmosphere of carbon dioxide, yielding the anisazine, m. p.  $292^\circ$  (not  $290^\circ$ , *loc. cit.*), and presumably di-*p*-anisylamine.

Diarylnitrosoamines decompose in boiling xylene in an atmosphere of carbon dioxide, yielding nitric oxide and products similar to those obtained above by the decomposition of tetra-arylhydrazines and formed by the mutual interaction of the  $NR_2$  radicles. Thus di-*p*-tolylnitrosoamine yields di-*p*-tolylamine and *p*-ditolyldihydrotolazine; di-*p*-anisylnitrosoamine yields the anisazine and di-*p*-anisylamine; *p*-nitrodiphenylnitrosoamine yields very easily *p*-nitrodiphenylamine and 5:10-di-*p*-nitrophenyldihydrophenazine,



m. p.  $183^\circ$ , reddish-brown substance; di-*p*-nitrophenylnitrosoamine yields di-*p*-nitrophenylamine and 2:4:4'-trinitrodiphenylamine; *N*-nitrosocarbazole yields carbazole and 3-nitrocarbazole. In the last two cases the expected azines have not been obtained, but nitrated amines produced by some obscure reaction.

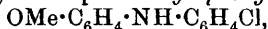
The dissociation of nitrosoamines,  $NR_2 \cdot NO$ , by heat depends on the nature of R. No dissociation occurs when R is an alkyl group, dialkylnitrosoamines volatilising without decomposition. When R is an aryl group, the dissociation proceeds the more easily the more positive is the aromatic group.

C. S.

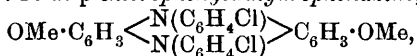
**Aromatic Hydrazines. XIII. Some New Ditary Hydrazines and Tetrazens of the Aromatic Series.** HEINRICH WIELAND and A. SÜSSER (*Annalen*, 1912, 392, 169—185).—*s*-Diphenyl-di-*p*-anisylhydrazine,  $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{NPh}\cdot\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , m. p.  $130^\circ$  (decomp.), colourless needles, and tetra-*o*-tolylhydrazine,  $\text{N}_2(\text{C}_6\text{H}_4\text{Me})_4$ , m. p.  $112^\circ$ , an unstable, amorphous powder, are obtained by oxidising *p*-methoxydiphenylamine and di-*o*-tolylamine respectively in cold acetone by powdered potassium permanganate. In accord with the generalisation that the dissociation of aromatic ditertiary hydrazines is facilitated by the presence of positive nuclei, the two preceding hydrazines dissociate very easily, the former in boiling benzene, the latter in solution at the ordinary temperature.

*s*-Diphenyldi-*p*-anisylhydrazine develops a rose coloration in cold glacial acetic acid; the colour changes to violet by warming, and the solution then contains *p*-methoxydiphenylamine and the di-methoxyperazonium acetate; the azine,  $\text{OMe}\cdot\text{C}_6\text{H}_3\cdot\left\langle\begin{smallmatrix}\text{NPh} \\ \text{NPh}\end{smallmatrix}\right\rangle\text{C}_6\text{H}_3\cdot\text{OMe}$ , corresponding with the latter, is a yellow, crystalline substance, from which, by treatment with glacial acetic and anhydrous mineral acids, azonium salts are obtained, the colours and spectra of which are very similar to those of the salts of the tetramethoxylated azine (*Abstr.* 1908, i, 1014).

*s*-Diphenyldi-*p*-anisylhydrazine, dissolved in benzene and acetone at  $15^\circ$ , is converted by ethereal hydrogen chloride mainly into *p*-methoxydiphenylamine and *p*(?)-chloro-*p*-methoxydiphenylamine,

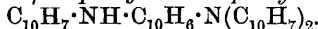


m. p.  $48\cdot5^\circ$ ; in addition, the dihydrochloride, violet needles, of 2 : 7-dimethoxy-5 : 10-di-*p*-chlorophenyldihydrophenazines,



yellow needles, decomp.  $281^\circ$ , darkening at  $244^\circ$ , is obtained.

Attempts to prepare tetranaphthylhydrazines have been unsuccessful. Doubtless the oxidation of di- $\beta$ -naphthylamine in cold acetone by potassium permanganate produces the  $\text{N}(\text{C}_{10}\text{H}_7)_2$  radicle; however, these combine with one another to produce, not the desired tetra- $\beta$ -naphthylhydrazine, but an isomeric substance,  $\text{C}_{40}\text{H}_{28}\text{N}_2$ , m. p.  $273^\circ$ , colourless crystals, which is very probably  $\alpha$ -2- $\beta$ -naphthylaminonaphthyl-di- $\beta$ -naphthylamine [*tri*- $\beta$ -naphthyl-1 : 2-naphthylenediamine],



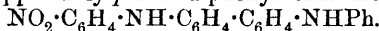
It is also produced by the dissociation of di- $\beta$ -naphthylnitrosoamine (preceding abstract), or of tetra- $\beta$ -naphthyltetrazen, or by the interaction of ethereal di- $\beta$ -naphthylamine, alcoholic sodium ethoxide, and ethereal iodine for twelve hours; in the last case, a di-iododinaphthylamine,  $\text{C}_{20}\text{H}_{13}\text{NI}_2$ , m. p.  $179^\circ$ , yellow needles, is also obtained. The trinaphthyl-naphthylenediamine forms a colourless hydrochloride with ethereal hydrogen chloride, is scarcely changed by concentrated sulphuric acid, and is not reduced by zinc dust and acetic acid.

*as*-Di- $\beta$ -naphthylhydrazine,  $\text{NH}_2\cdot\text{N}(\text{C}_{10}\text{H}_7)_2$ , m. p.  $141^\circ$ , pearly leaflets, produced by the reduction of di- $\beta$ -naphthylnitrosoamine by zinc dust and cold acetic acid and ether, is oxidised in acetone at  $-15^\circ$  to tetra- $\beta$ -naphthyltetrazen,  $\text{N}(\text{C}_{10}\text{H}_7)_2\cdot\text{N}\cdot\text{N}(\text{C}_{10}\text{H}_7)_2$ , decomp.

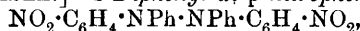
147°, unstable, yellow crystals, by saturated potassium permanganate.

[With H. FRESSEL.]—*Diphenylenehydrazine*,  $\text{C}_6\text{H}_4\text{>N}\cdot\text{NH}_2$ , m. p. 147° (decomp.), colourless needles, is obtained by treating a moist ethereal solution of *N*-nitrosocarbazole with zinc dust and glacial acetic acid in a freezing mixture. It forms a crystalline *hydrochloride* and *benzylidene* derivative,  $\text{C}_6\text{H}_4\text{>N}\cdot\text{N}:\text{CHPh}$ , m. p. 137°, yields usually carbazole by oxidation, but is converted in cold ether by *N*-hydrochloric acid and sodium hypochlorite into *bisdiphenylenetetrazen*,  $\text{C}_6\text{H}_4\text{>N}\cdot\text{N}:\text{N}\cdot\text{N}<\text{C}_6\text{H}_4$ , decomp. 216°, yellowish-green plates, which differs from all other tetrazens in its great stability towards acids. It is unchanged in boiling toluene by hydrogen chloride, and is only decomposed by concentrated sulphuric acid by warming; by prolonged boiling with copper powder in xylene, it yields nitrogen, carbazole, and a blue substance, possibly  $(\text{C}_{12}\text{H}_7\text{N})_x$ . C. S.

**Aromatic Hydrazines. XIV. Nitration of Tetraphenylhydrazine. Cyanoarylhydroxylamines.** HEINRICH WIELAND and A. ROSEEU (*Annalen*, 1912, 392, 186—195).—Nitrated tetraphenylhydrazines, the preparation of which is desirable for the comparative study of the stability of tetra-arylhydrazines, cannot be obtained by the direct action of nitric acid on account of the rapid fission of the tetraphenylhydrazine produced thereby. *p*-Nitrotetraphenylhydrazine,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NPh}\cdot\text{NPh}_2$ , m. p. 145°, orange-red plates, is obtained by warming powdered tetraphenylhydrazine with amyl nitrite. It is remarkably stable on account of the presence of the negative group (compare preceding abstracts), and is unchanged by not too prolonged boiling in solvents of high b. p., by ethereal hydrogen chloride, or by glacial acetic acid. It is reduced in alcoholic solution to diphenylamine and phenyl-*p*-phenylenediamine by stannous chloride and concentrated hydrochloric acid. *p*-Nitrotetraphenylhydrazine develops a violet coloration with concentrated sulphuric acid at 0°; after three hours, however, the substance is decomposed and yields diphenylamine, *p*-nitrodiphenylamine, and a substance,  $\text{C}_{24}\text{H}_{19}\text{O}_2\text{N}_3$ , m. p. 165°, orange prisms, which is apparently *p*-nitrodiphenylbenzidine,



[With S. GAMBARJAM.]—*s*-Diphenyl-*di-p*-nitrophenylhydrazine,

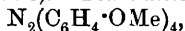


m. p. 168—169°, red, rhombic plates, is obtained by the action of pure nitrogen dioxide on a cold saturated solution of tetraphenylhydrazine in benzene. It resembles *p*-nitrotetraphenylhydrazine in its stability. It is reduced to phenyl-*p*-phenylenediamine by zinc and acetic acid. With cold concentrated sulphuric acid at 0°, it develops a violet coloration, but it decomposed after three hours, yielding *p*-nitrodiphenylamine, an orange-red substance, m. p. 211°, and mainly *di-p*-nitrophenylbenzidine,  $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ , m. p. 252°, red crystals with blue reflex.

*β-Cyano-β-phenylhydroxylamine*,  $\text{CN}\cdot\text{NPh}\cdot\text{OH}$ , obtained from *β*-phenylhydroxylamine and cyanogen bromide in the presence of sodium hydrogen carbonate (Abstr., 1904, i, 628), is extremely unstable, but can be isolated for a few minutes in crystalline leaflets. It dissolves in alkalis, but is insoluble in aqueous acids; ethereal hydrogen chloride produces after some time a crystalline *iminochloride hydrochloride*,  $\text{OH}\cdot\text{NPh}\cdot\text{CCl}\cdot\text{NH}_2\cdot\text{HCl}$ , from an aqueous solution of which at  $50^\circ$  the cyanophenylhydroxylamine is recovered. Hydrogen cyanide, aniline, and phenylcyanamide are formed by reducing a cold concentrated aqueous solution of this hydrochloride with stannous chloride and hydrochloric acid.

*β-Cyano-β-p-tolylhydroxylamine*,  $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}(\text{CN})\cdot\text{OH}$ , obtained in a similar manner, is likewise extremely unstable, and forms an *iminochloride hydrochloride*,  $\text{C}_6\text{H}_4\text{ONCl}\cdot\text{HCl}$ , decomp.  $155^\circ$ . C. S.

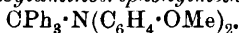
**Ditertiary Hydrazines. XV. Tetra-anisylhydrazine.** HEINRICH WIELAND and HANS LECHER (*Ber.*, 1912, 45, 2600—2605. Compare Abstr., 1908, i, 1014).—*Tetra-anisylhydrazine*,



is obtained by the oxidation of dianisylamine with lead dioxide in ethereal solution at the ordinary temperature. It forms almost colourless, stellar aggregates of prisms, m. p.  $90\cdot5^\circ$ , which slowly decompose when kept, and dissolves in concentrated sulphuric acid with a dark blue coloration. The union of the nitrogen atoms is so feeble that dissociation into the free radicle,  $\cdot\text{N}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$ , takes place in organic solvents, even at the ordinary temperature. Its solution in benzene has a light green colour, which becomes deeper on warming, owing to the greater dissociation.

With hydrochloric, sulphuric, and acetic acids, it forms dark blue quinonoid salts,  $(\text{OMe}\cdot\text{C}_6\text{H}_4)_2\text{N} > \text{NX} : \text{C}_6\text{H}_4 < \begin{smallmatrix} \text{H} \\ \text{OMe} \end{smallmatrix}$ , which, however, are very unstable and readily undergo decomposition.

The *acetate*, obtained by dissolving the hydrazine in glacial acetic acid, decomposes into dianisylamine and anisazonium acetate (Abstr., 1908, i, 1014). Further evidence of the dissociation of the hydrazine in solution is supplied by the behaviour of the compound toward nitric oxide and triphenylmethyl, with which it combines very readily in benzene solution at the ordinary temperature, yielding dianisyl-nitrosoamine and *ω*-dianisylaminotriphenylmethane,



The last-mentioned substance crystallises in colourless prisms, which melt at  $156^\circ$  to a red liquid, and dissociates much less readily than the analogously constituted compounds previously described.

In benzene or acetone solution, the hydrazine decomposes in the course of a few hours at the ordinary temperature into dianisylamine and anisazine. F. B.

**Reductions in the Glyoxaline Series. I. Reduction of Diphenylglyoxalone.** HEINRICH BILTZ (*Annalen*, 1912, 391, 169—190).—4:5-Diphenylglyoxalone is not reduced by zinc and boiling acetic and hydrochloric acids, hydriodic acid and phosphorus

at 180°, aqueous alcoholic sodium stannite, or sodium and absolute alcohol at 40°. At the b. p., however, the last reagent produces

4 : 5-diphenyl-4 : 5-dihydroglyoxalone,  $\begin{matrix} \text{CHPh}\cdot\text{NH} \\ | \\ \text{CHPh}\cdot\text{NH} \end{matrix} > \text{CO}$ , m. p. 292—293°,

together with a little of an *isomeride*, m. p. 245—246°. Diphenyldihydroglyoxalone does not react with bromine or potassium permanganate, forms a *diacetyl* derivative, m. p. 160°, yields dibenzoylcarbamide by energetic treatment with chromic acid, and is partly converted into *meso-αβ*-diphenylethylenediamine (following abstract) by hydrogen bromide in acetic acid.

The by-product, m. p. 245—246°, cannot be converted into the isomeride. It contains the glyoxaline skeleton, and in its behaviour corresponds with the formula,  $\begin{matrix} \text{CHPh}\cdot\text{NH} \\ | \\ \text{CPh}=\text{N} \end{matrix} > \text{CH}\cdot\text{OH}$ , of 2-hydroxy-4 : 5-

diphenyl-2 : 5-dihydroglyoxaline, being produced probably by the reduction of the enolic modification of the diphenylglyoxalone. It forms a *diacetyl* derivative, m. p. 190—191°, from which an *acetyl* derivative,  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2$ , m. p. 209—210°, is obtained by careful hydrolysis with aqueous alcoholic ammonia; both derivatives yield the hydroxydiphenyldihydroglyoxaline by treatment with alcoholic potassium hydroxide. Hydroxydiphenyldihydroglyoxaline is unsaturated. With bromine in chloroform, it forms an unstable orange-red *perbromide*, from which an unstable *dibromide*,  $\text{C}_{15}\text{H}_{14}\text{ON}_2\text{Br}_2$ , is produced; by warming or by treatment with alcohol, the dibromide is re-converted into the hydroxydiphenyldihydroglyoxaline. The latter is changed to 4 : 5-diphenylglyoxalone by bromine in boiling alcohol.

The action of hydrogen bromide on 2-hydroxy-4 : 5-diphenyl-2 : 5-dihydroglyoxaline in boiling chloroform yields 3-bromo-2-hydroxy-4 : 5-

diphenyltetrahydroglyoxaline,  $\begin{matrix} \text{CHPh}\cdot\text{NH} \\ | \\ \text{CHPh}\cdot\text{NBr} \end{matrix} > \text{CH}\cdot\text{OH}$ , which easily loses

hydrogen bromide by warming or treatment with alcohol. By boiling with hydrogen bromide in glacial acetic acid, the preceding bromide or hydroxydiphenyldihydroglyoxaline itself is converted into the hydrobromide of *meso-αβ*-diphenylethylenediamine.

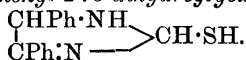
The oxidation by solid potassium permanganate of hydroxydiphenyldihydroglyoxaline in aqueous acetone yields dibenzoylcarbamide.

C. S.

**Reductions in the Glyoxaline Series. II. Reduction of Thiodiphenylglyoxalone.** HEINRICH BILTZ and PAUL KREBS (*Annalen*, 1912, 391, 191—214).—2-Thiol-4 : 5-diphenylglyoxalone is obtained very conveniently by heating benzoin and thiocarbamide at 200°. It cannot be acetylated, and is converted almost quantitatively into benzil by alcohol and bromine.

Unlike the corresponding diphenylglyoxalone (preceding abstract), thiol-4 : 5-diphenylglyoxalone yields only one product by reduction with sodium and boiling absolute alcohol. The position of the two hydrogen atoms taken up has not been ascertained beyond doubt. However, since the general behaviour of thiodiphenylglyoxalone corresponds with that of the enolic modification, the reduction product is most

probably 2-thiol-4:5-diphenyl-2:5-dihydroglyoxaline,



It has m. p. 315°, and behaves like a mercaptan. Thus it dissolves in 10% sodium hydroxide, and forms a *sodium* salt,  $\text{C}_{15}\text{H}_{13}\text{N}_2\text{SNa}$ , large leaflets. With boiling alcohol and ethyl iodide, it yields the *hydriodide*, m. p. 245°, of the *ethyl ether*,  $\text{C}_{17}\text{H}_{18}\text{N}_2\text{S}$ , m. p. 186°, colourless needles.

Attempts to replace the sulphur by oxygen and thus to produce 2-hydroxy-4:5-diphenyl-2:5-dihydroglyoxaline (preceding abstract) have not been successful. It is converted by alcohol and bromine water into benzil, and by boiling 3% nitric acid into 4:5-diphenylglyoxaline. When oxidised by alkaline potassium permanganate, it yields 4:5-diphenylglyoxaline-2-sulphonic acid.

By reduction with sodium and boiling amyl alcohol, thioldiphenyldihydroglyoxaline is converted into *meso-αβ*-diphenylethylenediamine. The *hydrochloride*, m. p. 256° (decomp.), *platinichloride*, m. p. 265° (decomp.), and *dibenzoyl* derivative, m. p. 350°, of this base, and the *hydrochloride*, m. p. 251° (decomp.), *disalicylidene* derivative, m. p. 200—201°, and *dibenzoyl* derivative, m. p. 287°, of the racemic modification, are described, since the literature of these two bases is in many points erroneous.

C. S.

**Reductions in the Glyoxaline Series. III. Reduction of Diphenylglyoxaline and Triphenylglyoxaline.** HEINRICH BILTZ and PAUL KREBS (*Annalen*, 1912, 391, 210—214).—Kohler has described (*Diss.*, Erlangen, 1887) a triphenyldihydroglyoxaline, m. p. 257°, which he obtained by the action of sodium and alcohol on lophine (2:4:5-triphenylglyoxaline). It is now shown that this substance is only impure lophine; by crystallisation from absolute alcohol, pyridine, or ether, the m. p. is raised to that of lophine, 275°. Lophine is not reduced by sodium and boiling amyl alcohol. The same is true of 4:5-diphenylglyoxaline; the product, after crystallisation from alcohol, has a constant m. p. about 216°. It is, however, only impure 4:5-diphenylglyoxaline; the impurities can be removed by purification through the hydrochloride, and the substance then has the correct m. p., 227°.

C. S.

**Reductions in the Glyoxaline Series. IV. Reduction of Thiodiphenylhydantoin.** HEINRICH BILTZ and KARL SEYDEL (*Annalen*, 1912, 391, 215—230).—5:5-Diphenylhydantoin and thio-5:5-diphenylhydantoin are extremely resistant to the attack of many reducing agents. The latter, however, is converted by sodium and boiling amyl alcohol into 5:5-diphenyltetrahydro-4-glyoxalone,  $\begin{array}{c} \text{CPh}_2\cdot\text{NH} \\ | \\ \text{CO}\text{---}\text{NH} \end{array} \text{---} \text{CH}_2$ , m. p. 185.5—186.5°, which is purified through the *hydrochloride*, decomp. 205—206°. This product is isomeric with the 4:5-diphenyldihydroglyoxalones (preceding abstracts), but differs from them in its pronounced basic character (*nitrate*, decomp. 171°; *picrate*, m. p. about 158°). By energetic oxidation it yields benzophenone, but is converted by treatment with potassium permanganate, in 2*N*-nitric acid or glacial acetic acid at 60°, or suspended in sodium

hydroxide at 70—80°, into 5:5-diphenyl-4:5-dihydro-4-glyoxalone,  $\text{CPh}_2\cdot\text{NH} \begin{array}{l} \diagup \\ \text{CO} \end{array} \text{N} \begin{array}{l} \diagdown \\ \text{CH} \end{array}$ , m. p. 166—167°. This substance, which is re-converted into its generator by zinc and boiling dilute hydrochloric acid, is amphoteric, being soluble in sodium hydroxide and forming salts with strong, inorganic acids (*hydrochloride*, m. p. 264° [decomp.]; *nitrate*, m. p. 170—171° [decomp.]). It forms an *acetyl* derivative, m. p. 138—139°, and 1-methyl derivative, m. p. 175—176°, and is converted into ammonia and *aminodiphenylacetic acid*,  $\text{NH}_2\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$ , m. p. 245—246° (decomp.), by prolonged boiling with 20% sodium hydroxide. Similarly, the 1-methyl derivative is decomposed into ammonia and *methylaminodiphenylacetic acid*,  $\text{NHMe}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$ , m. p. 211° (decomp.), by boiling alcohol and 33% potassium hydroxide. This decomposition proves that in 5:5-diphenyl-1-methyl-4:5-dihydro-glyoxal-4-one the methyl group is in position-1 and the double linking in the position 2:3.

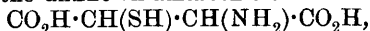
When 5:5-diphenyl-4:5-dihydro-4-glyoxalone is boiled with water, it is converted into 2-hydroxy-5:5-diphenyltetrahydro-4-glyoxalone,  $\text{CPh}_2\cdot\text{NH} \begin{array}{l} \diagup \\ \text{CO} \end{array} \text{NH} \begin{array}{l} \diagdown \\ \text{CH}\cdot\text{OH} \end{array}$ , m. p. 165° (decomp.), which is also obtained as a by-product in the action of alkaline potassium permanganate on 5:5-diphenyltetrahydro-4-glyoxalone. At 170° it loses water and is re-converted into 5:5-diphenyl-4:5-dihydro-4-glyoxalone. In a similar manner, boiling water converts 1-acetyl-5:5-diphenyl-4:5-dihydro-4-glyoxalone into 1-acetyl-2-hydroxy-5:5-diphenyltetrahydro-4-glyoxalone, m. p. 207° (decomp.). C. S.

**Reductions in the Glyoxaline Series. V. Influence of Substituents on the Acidity of Imino-groups.** HEINRICH BILTZ (*Annalen*, 1912, 391, 231—234. Compare preceding abstracts).—The influence of neighbouring substituents on the acidity of the imino-group is well illustrated by the preceding examples. 5:5-Diphenylhydantoin is strongly acidic. 5:5-Diphenyltetrahydro-4-glyoxalone is a pronounced, but not a strong, base. 2-Hydroxy-4:5-diphenyl-2:5-dihydroglyoxaline, 2-hydroxy-5:5-diphenyltetrahydro-4-glyoxalone, and 4:5-diphenyl-4:5-dihydroglyoxalone are neutral substances. 4:5-Diphenylglyoxalone has a feebly acid character; 5:5-diphenyl-3-methylhydantoin is rather more acidic, and 5:5-diphenyl-4:5-dihydro-4-glyoxalone is still more so.

Glyoxaline, 4:5-dihydroglyoxaline, and their alkyl derivatives are pronounced bases. Strongly acidic substituents in positions 4 and 5 render 4:5-dihydroglyoxaline amphoteric. Glyoxalones are neutral or very feebly amphoteric. C. S.

**Pyrimidines. LVI. Action of Hydroxylamine on 4-Methyl-1:6-dihydro-6-pyrimidone-2-thioloxalylacetic Acid.  $\alpha$ -Ox-imino- $\beta$ -thiolpropionic Acid.** TREAT B. JOHNSON and NORMAN A. SHEPARD (*Amer. Chem. J.*, 1912, 48, 279—296).—Piutti (Abstr., 1888, 677) has effected the synthesis of aspartic acid by reducing the

oxime of ethyl oxalacetate with sodium amalgam and hydrolysing the product. The present investigation was undertaken in order to ascertain whether the unknown aminothiolsuccinic acid,



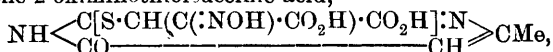
could be obtained by the action of hydroxylamine on a thiol derivative of ethyl oxalacetate.

When ethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thioloxalylacetate (Abstr., 1911, i, 925) is dissolved in strong hydrochloric acid and the solution evaporated to dryness, 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thiolpyruvic acid,  $\text{NH} \begin{array}{c} \text{C}(\text{S}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H})\cdot\text{N} \\ \text{CO} \text{---} \text{CH} \end{array} \text{CMe}$ , m. p.

210—212° (decomp.), is produced, which forms hexagonal prisms. If, however, the solution of the ethyl ester in hydrochloric acid is warmed, ethyl chloride is evolved, and, on evaporating the solution nearly to dryness, 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thioloxalacetic acid,  $\text{NH} \begin{array}{c} \text{C}[\text{S}\cdot\text{CH}(\text{CO}\cdot\text{CO}_2\text{H})\cdot\text{CO}_2\text{H}]\cdot\text{N} \\ \text{CO} \text{---} \text{CH} \end{array} \text{CMe}$ , m. p. 159—161°

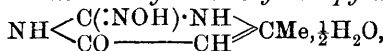
(decomp.), is obtained, which crystallises in slender prisms. When the diethyl ester is heated with potassium hydroxide solution, it is converted into ethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thiolacetate (*loc. cit.*).

By the action of hydroxylamine on 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thioloxalacetic acid, three compounds are produced. The primary product of the reaction seems to be 4-methyl-1 : 6-dihydro-6-pyrimidone-2-oximinothiolsuccinic acid,



but this could not be isolated, although its sodium salt was prepared; the acid is unstable and evolves carbon dioxide at the ordinary temperature with formation of 4-methyl-1 : 6-dihydro-6-pyrimidone-2-oximinothiolpropionic acid,  $\text{NH} \begin{array}{c} \text{C}[\text{S}\cdot\text{CH}_2\cdot\text{C}(\text{:NOH})\cdot\text{CO}_2\text{H}]\cdot\text{N} \\ \text{CO} \text{---} \text{CH} \end{array} \text{CMe}$ , m. p.

160—161° (decomp.), which crystallises in prisms. Another product of the reaction is 2-oximino-4-methyl-1 : 6-dihydro-6-pyrimidone,



m. p. 225—228° (decomp.), which forms stout blocks or prisms. The third product of the reaction is  $\alpha$ -oximino- $\beta$ -thiolpropionic acid,  $\text{HS}\cdot\text{CH}_2\cdot\text{C}(\text{:NOH})\cdot\text{CO}_2\text{H}$ , m. p. 178—180° (decomp.), which crystallises in needles.

When 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thiolpyruvic acid is treated with hydroxylamine, it is converted into 2-oximino-4-methyl-1 : 6-dihydro-6-pyrimidone.

If 4-methyl-1 : 6-dihydro-6-pyrimidone-2-oximinothiolpropionic acid is reduced with stannous chloride and hydrochloric acid, 4-methyluracil is produced. Reduction with zinc dust and formic acid results in the formation of 2-thio-4-methyluracil; on treating the filtrate from this substance with benzoyl chloride, a small quantity of benzoylalanine is obtained. Reduction with aluminium amalgam yields 4-methyluracil and 2-thio-4-methyluracil.

When 2-oximino-4-methyl-1 : 6-dihydro-6-pyrimidone is reduced with

stannous chloride and hydrochloric acid, it is converted into 4-methyluracil.

The action of hydroxylamine on ethyl 4-methyl-1:6-dihydro-6-pyrimidone-2-thioloxalacetate results in the formation of ethyl 4-methyl-1:6-dihydro-6-pyrimidone-2-thiolacetate and 2-oximino-4-methyl-1:6-dihydro-6-pyrimidone.

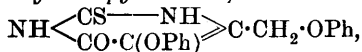
Experiments were carried out on the reduction of  $\alpha$ -oximino- $\beta$ -thiolpropionic acid, but in no case was either cysteine or cystine produced. E. G.

**Pyrimidines. LVII. Action of Potassium Thiocyanate on Primary Haloids.** TREAT B. JOHNSON and ARTHUR J. HILL (*Amer. Chem. J.*, 1912, 48, 296—306).—It has been shown previously (Abstr., 1908, i, 837) that by the action of potassium thiocyanate on pyrimidine imide chlorides, corresponding with the formula  $\text{N} \cdot \text{C} \cdot \text{N} \cdot \text{C} \cdot \text{C} \cdot \text{CCl}$ ,

the final product is a thiocarbimide. In some cases, however, it was found that the primary thiocyanates could be isolated and purified. The haloid derivatives of 4- and 5-methyldiketotetrahydropyrimidines,  $\text{NH} \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \text{CO} \text{---} \text{C} \end{smallmatrix} \text{C} \cdot \text{CH}_2\text{R}$  and  $\text{NH} \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \text{CO} \text{---} \text{C}(\text{CH}_2\text{R}) \end{smallmatrix} \text{C} \cdot$ , should theo-

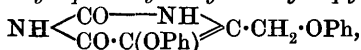
retically react with potassium thiocyanate to form thiocarbimides, and the present work was undertaken to test this assumption.

When the sodium salt of ethyl  $\alpha$ -diphenoxycetoacetate,  $\text{OPh} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CNa}(\text{OPh}) \cdot \text{CO}_2\text{Et}$ , is heated with an alcoholic solution of thiocarbamide, 2-thio-5-phenoxy-4-phenoxy-methyltetrahydro-6-pyrimidone,

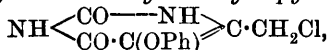


m. p. 218°, is produced, which crystallises in slender prisms. On treating this compound with ethyl iodide and sodium ethoxide, it is converted into 2-ethylthiol-5-phenoxy-4-phenoxy-methyl-1:6-dihydro-6-pyrimidone,  $\text{NH} \begin{smallmatrix} \text{C}(\text{SEt}) \text{---} \text{N} \\ \text{CO} \cdot \text{C}(\text{OPh}) \end{smallmatrix} \text{C} \cdot \text{CH}_2 \cdot \text{OPh}$ , m. p. 170°, which forms hexagonal prisms.

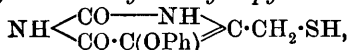
2:6-Diketo-5-phenoxy-4-phenoxy-methyltetrahydropyrimidine,



m. p. 200°, obtained by the action of chloroacetic acid on 2-thio-5-phenoxy-4-phenoxy-methyltetrahydro-6-pyrimidone, crystallises in needles, and when heated with hydrochloric acid is converted into 2:6-diketo-5-phenoxy-4-chloromethyl-tetrahydropyrimidine,



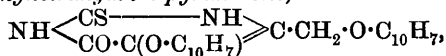
m. p. 248°, which forms square plates. If the latter substance is heated with an alcoholic solution of potassium thiocyanate, it yields 2:6-diketo-5-phenoxy-4-thiolmethyltetrahydropyrimidine,



which crystallises in needles, and decomposes at 182°. The thiocyanate seems to be the primary product of the reaction, but instead

of becoming transformed into a thiocarbimide, it loses its cyanogen radicle and yields the mercaptan.

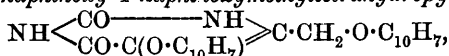
When the sodium salt of ethyl *aa*-dinaphthoxyacetoacetate is heated with an alcoholic solution of thiocarbamide, 2-thio-5-naphthoxy-4-naphthoxymethyltetrahydro-6-pyrimidone,



m. p. 224—226°, is produced, which crystallises in rhombic plates, and when treated with ethyl bromide and sodium ethoxide is converted into 5-naphthoxy-2-ethylthiol-4-naphthoxymethyl-1:6-dihydro-6-pyrimidone,

$\text{NH} \begin{array}{c} \text{C}(\text{SEt}) \text{---} \text{N} \\ \text{CO} \cdot \text{C}(\text{OC}_{10}\text{H}_7) \end{array} \text{C} \cdot \text{CH}_2 \cdot \text{OC}_{10}\text{H}_7$ , m. p. 198°, which crystallises in needles.

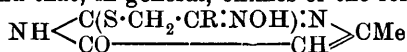
2:6-Diketo-5-naphthoxy-4-naphthoxymethyltetrahydropyrimidine,



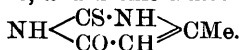
m. p. 256—258°, prepared by the action of chloroacetic acid on 2-thio-5-naphthoxy-4-naphthoxymethyltetrahydro-6-pyrimidone, forms minute needles. Attempts to convert this compound into 2:6-diketo-5-naphthoxy-4-chloromethyltetrahydropyrimidine were not successful.

E. G.

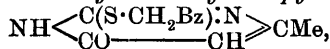
**Pyrimidines. LVIII. Oximes of Some Thioglycollide Compounds and their Behaviour on Reduction.** TREAT B. JOHNSON and ROBERT C. MORAN (*Amer. Chem. J.*, 1912, 42, 307—320).—Johnson and Shepard (this vol., i, 911) have described  $\alpha$ -oximino- $\beta$ -thiolpropionic acid and 4-methyl-1:6-dihydro-6-pyrimidone-2-oximino-thiolpropionic acid. Attempts to reduce these substances to the corresponding amino-compounds were not successful, and the results rendered it desirable to examine another series of oximes containing the complex  $\text{HON}:\text{C} \cdot \text{CH}_2 \cdot \text{S} \cdot$  in order to ascertain whether the unexpected behaviour on reduction was due to the presence of the carboxyl group. An investigation has therefore been made of certain oximes containing an alkyl group in place of the carboxyl group, and it has been found that, in general, oximes of the formula



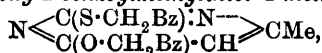
(where  $\text{R} = \text{CH}_3$ ,  $\text{C}_6\text{H}_5$ , or  $\text{CO}_2\text{H}$ ) are converted by reducing agents into amines,  $\text{NH}_2 \cdot \text{CHRMe}$ , and 2-thio-4-methyluracil,



2-Benzoylmethylthiol-4-methyl-1:6-dihydro-6-pyrimidone,

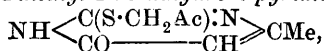


m. p. 175°, obtained by the action of bromoacetophenone on the sodium salt of 2-thio-4-methyluracil, crystallises in prisms; its sodium salt decomposes at 206°. The mother liquor from this substance yields 6-benzoylmethoxy-2-benzoylmethylthiol-4-methylpyrimidine,



m. p. 118—119°, which forms prismatic crystals, and on hydrolysis with concentrated hydrochloric acid is converted into 2-benzoylmethylthiol-4-methyl-1:6-dihydro-6-pyrimidone. The latter compound on prolonged hydrolysis yields 4-methyluracil, and on reduction with aluminium amalgam gives 2-thio-4-methyluracil.

2-Acetylmethylthiol-4-methyl-1:6-dihydro-6-pyrimidone,



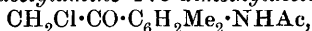
m. p. 152°, prepared by the action of chloroacetone on the sodium salt of 2-thio-4-methyluracil, crystallises in slender needles.

The *oxime* of 3-benzoylmethylthiol-4-methyl-1:6-dihydro-6-pyrimidone,  $\text{NH} \begin{array}{c} \text{C}(\text{S} \cdot \text{CH}_2 \cdot \text{CPh} : \text{NOH}) : \text{N} \\ \text{CO} \text{---} \text{CH} \end{array} \text{CMe}$ , m. p. 183°, forms pale yellow crystals; its *hydrochloride* was prepared. On reducing this oxime with ferrous sulphate and ammonia, formic acid and zinc dust, or sodium amalgam, 2-thio-4-methyluracil is invariably produced. In the experiment in which sodium amalgam was used, phenylethylamine was also obtained.

The *phenylhydrazone* of 2-benzoylmethylthiol-4-methyl-1:6-dihydro-6-pyrimidone,  $\text{NH} \begin{array}{c} \text{C}(\text{S} \cdot \text{CH}_2 \cdot \text{CPh} : \text{N} \cdot \text{NHPh}) : \text{N} \\ \text{CO} \text{---} \text{CH} \end{array} \text{CMe}$ , m. p. 295°, crystallises in needles, and on reduction with sodium amalgam or aluminium amalgam yields 2-thio-4-methyluracil. E. G.

**Ring Containing a Triple Linking.** PAUL RUGGLI (*Annalen*, 1912, 392, 92—100).—*oo'*-Dicarbimidotolane,  $\text{NCO} \cdot \text{C}_6\text{H}_4 \cdot \text{C} : \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NCO}$ , m. p. 149—150·5°, almost colourless needles, obtained by passing carbonyl chloride into a suspension of dry, finely divided *oo'*-diaminotolane dihydrochloride in hot xylene, is converted by boiling alcohol into *oo'*-dicarbethoxyaminotolane,  $\text{CO}_2\text{Et} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{C} : \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$ , m. p. 134·5—135·5°, white leaflets. The action of oxalyl, malonyl, or sulphuryl chloride on *oo'*-diaminotolane does not yield crystalline products, but the interaction of *oo'*-diaminotolane and succinyl chloride in very dilute benzene solution yields, in addition to amorphous products, cyclosuccinylldiaminotolane,  $\text{NH} \begin{array}{c} \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \\ \text{C}_6\text{H}_4 \cdot \text{C} : \text{C} \cdot \text{C}_6\text{H}_4 \end{array} \text{NH}$ , m. p. 237—238°, colourless, felted needles. The substance cannot be diazotised, and does not respond to Lauth's test for an amino-group. It cannot be methylated by methyl sulphate, and is remarkably stable to acids and alkalis; by prolonged boiling with 33% methyl-alcoholic potassium hydroxide, it yields *oo'*-diaminotolane and succinic acid (identified by the fluorescein test). C. S.

**4:5:4':5'-Tetramethylindigotin.** FRANZ KUNCKELL and HANNS SCHNEIDER (*J. pr. Chem.*, 1912, [ii], 86, 429—432. Compare this vol., i, 268).—*ω*-Chloro-2-acetyl-amino-4:5-dimethylacetophenone,

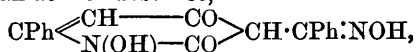


prepared by the interaction of chloroacetyl chloride and aceto-4-*o*-xylylide in carbon disulphide solution in the presence of aluminium chloride, forms yellowish-red, golden needles, m. p. 166—167°, and is hydrolysed by hydrochloric acid to *ω*-chloro-2-amino-4:5-dimethylaceto-

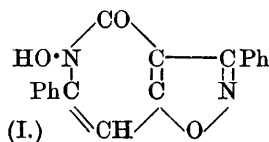
*phenone hydrochloride*, lustrous, green, silky needles (decomp. above  $300^{\circ}$ ), from which the free *base*, having m. p.  $124^{\circ}$ , is liberated by the action of ammonium carbonate. It yields a *nitro*-derivative, crystallising in almost white needles m. p.  $180^{\circ}$ , and is converted by boiling with aqueous sodium hydroxide into 4 : 5 : 4' : 5'-*tetramethylindigotin*.

It is also mentioned that bromopropionyl bromide reacts with aceto-4-*o*-xylidide to form a substance crystallising in greenish-yellow needles, and that *p*-acetotoluidide has been converted into 5 : 5'-*dibromo*-6 : 6'-*diacetylamino*-3 : 3'-*dimethylindigotin*.  
F. B.

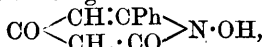
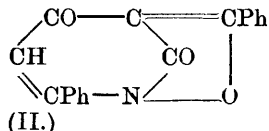
The Action of Hydroxylamine and Phenylhydrazine on Benzoyldehydracetic Acid. JOH. SCHÖTTLE (*Ber.*, 1912, 45, 2340—2347. Compare Petrenko-Kritschenko and Schöttle, *Abstr.*, 1911, i, 1020 ; also this vol., i, 128).—When a mixture of benzoyldehydracetic acid or its phenyl-lactam with excess of hydroxylamine hydrochloride and potassium hydroxide is kept at room temperature for a week, an acidic substance,



m. p.  $151\text{--}152^{\circ}$  (decomp.), is obtained ; the *silver* salt was isolated. If, however, an aqueous alcoholic solution of the same substances without the potassium hydroxide is warmed on the water-bath for three to four hours, three molecules of water are eliminated, with the formation of a crystalline acidic substance, m. p.  $193^{\circ}$  (decomp.), to which is

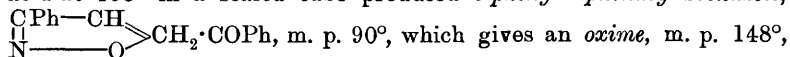


attributed the annexed formula (I) ; this gives a deep blue coloration with ferric chloride ; the *potassium* salt, m. p.  $232\text{--}233^{\circ}$  (decomp.), and *silver* salts were prepared, also the *acetyl* derivative, m. p.  $178^{\circ}$ . In the preparation of the above substance (I.) there is obtained a small quantity of a substance (formula II), needles, m. p.  $218^{\circ}$ . The structure given in formula (I) is confirmed by the action of alcoholic potassium hydroxide, which gives rise to a substance,



needles, m. p.  $182\text{--}183^{\circ}$  ; the *silver* salt and unstable *acetyl* derivative were isolated.

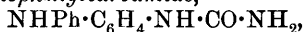
Hydrolysis of substance (I) with hydrochloric acid at  $193^{\circ}$  in a sealed tube produced 3-*phenyl*-5-*phenacetyl*isooxazole,



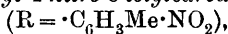
and can be oxidised in alkaline acetone solution by permanganate to 3-*phenylisooxazole*-5-*carboxylic acid*,  $\begin{array}{c} \text{CPh} \text{---} \text{CH} \\ \parallel \quad \diagup \\ \text{N} \text{---} \text{O} \end{array} \text{C} \cdot \text{CO}_2\text{H}, \text{ m. p. } 177\text{--}178^{\circ}, \text{ and benzoic acid.}$

The action of phenylhydrazine hydrochloride on benzoyldehydracetic acid or its phenyl-lactam in alcoholic solution gives as product a very stable substance, m. p.  $268^{\circ}$ , of which the constitution is uncertain.  
D. F. T.

**Aromatic Carbamides.** A. KRAMMER (*J. pr Chem.*, 1912, [ii], 86, 359—366).—*p*-Anilinophenylcarbamide,

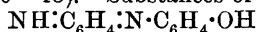


prepared by the interaction of *p*-aminodiphenylamine and potassium cyanate in aqueous solution, has m. p. 201°, and yields a reddish-violet bromo-derivative,  $\text{C}_{13}\text{H}_{12}\text{ON}_3\text{Br}$ , m. p. 163°. When heated with aromatic amines it forms substituted carbamides of the general formula  $\text{NHPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{NHR}$ . The following compounds were prepared in this manner: *p*-anilinodiphenylcarbamide, a reddish-violet, microcrystalline substance, m. p. 213·5°; *p*-anilino-*o*-tolylcarbamide ( $\text{R} = \cdot\text{C}_6\text{H}_4\text{Me}$ ), m. p. 234°; *p*-anilino-*m*-tolylcarbamide, m. p. 226°; *p*-anilino-*p*-tolylcarbamide, m. p. 231°, which forms a greenish-yellow nitroso-derivative,  $\text{NHPh} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CO} \cdot \text{N}(\text{NO}) \cdot \text{C}_6\text{H}_4\text{Me}$ , m. p. 190°; *p*-anilinophenyl-*o*-nitrophenylcarbamide ( $\text{R} = \cdot\text{C}_6\text{H}_4 \cdot \text{NO}_2$ ) has m. p. 178°, and is also obtained by nitrating *p*-anilinodiphenylcarbamide; *p*-anilinophenyl-4-nitro-*o*-tolylcarbamide



m. p. 184°; *p*-anilinophenyl-3-nitro-*p*-tolylcarbamide, m. p. 181°. The nitro-compounds have a brown colour, whilst the unsubstituted tolyl compounds are reddish-violet to bluish-violet. F. B.

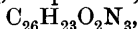
**Simplest Indophenols and Indamines.** GUSTAV HELLER (*Annalen*, 1912, 392, 16—48).—Substances of the type



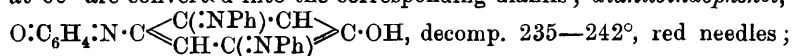
are usually classified as indophenols. The author classifies all dyes containing  $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot$  as indophenols and all dyes containing  $\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot$  as indamines.

In 33% sodium hydroxide at  $-10^\circ$ , phenol and *p*-aminophenol are oxidised by sodium hypochlorite (D.R.-P. 157288), yielding the sodium salt, blue leaflets, of the indophenol,  $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , m. p. 160° (decomp.), which crystallises from benzene in red needles and from petroleum in brown leaflets. The acetyl derivative, m. p. 115—116°, forms clusters of red needles. The indophenol is remarkably stable to sulphuric acid stronger than 70%; it yields *p*-benzoquinone by treatment with warm dilute hydrochloric acid, but is converted by concentrated hydrochloric acid into quinol and *p*-benzoquinoneimine; the latter, however, reacts with some unchanged indophenol to form a complex substance, m. p. above 310°, violet leaflets.

By treatment with primary aromatic amines in cold alcohol and acetic acid, the sodium derivative of indophenol yields dianilino-derivatives of the type  $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{C} \begin{smallmatrix} \text{C}(\text{NHA}r) \cdot \text{CH} \\ \text{CH} \cdot \text{C}(\text{NHA}r) \end{smallmatrix} \text{C} \cdot \text{OH}$ . Thus aniline yields  $\text{C}_{24}\text{H}_{19}\text{O}_2\text{N}_3$ , m. p. 210°, brown needles (acetyl derivative, m. p. 197°); *p*-toluidine yields  $\text{C}_{26}\text{H}_{23}\text{O}_2\text{N}_3$ , m. p. 250°; *o*-toluidine yields

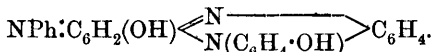


m. p. 227—240° (decomp.), green needles; 2-*m*-xyldine yields  $\text{C}_{28}\text{H}_{27}\text{O}_2\text{N}_3$ , m. p. 280°, dark brown needles; acetyl-*p*-phenylenediamine yields  $\text{C}_{28}\text{H}_{25}\text{O}_4\text{N}_5$ , m. p. 285°, violet-brown needles. By oxidation with chromic acid, these dianilino-derivatives in alcohol and acetic acid at 60° are converted into the corresponding dianils; dianilindophenol,



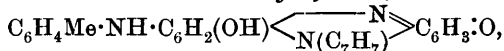
*di-o-toluidindophenol*,  $C_{26}H_{21}O_2N_3$ , decomp.  $245^\circ$ , red needles; *di-p-acetylaminosaniindophenol*, m. p. above  $300^\circ$ ; *di-2-m-xyliindophenol*,  $C_{28}H_{25}O_2N_3$ , darkening at  $225^\circ$ , flat plates.

These dianilo-derivatives are stable to acids, but are converted by boiling alcoholic potassium hydroxide into arylated safranols. The conversion might occur in two ways; for example, dianilindophenol can be transformed into  $NHPh \cdot C_6H_2(OH) \langle \begin{smallmatrix} N \\ NPh \end{smallmatrix} \rangle C_6H_3 \cdot O$  or

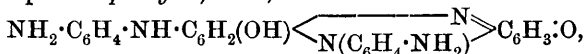


The former constitution is accepted; the transformation represented by the latter formula should be impossible with the *di-m-xyliindophenol*, whereas, actually, a safranols is obtained in this case.

The substances are characterised as safranols by their great stability, resistance to reduction, and the green coloration with concentrated sulphuric or hydrochloric acid. 7-Anilinosafraanol, m. p. above  $285^\circ$ , red needles, is identical with Fischer and Hepp's anilinosafraanol (Abstr., 1895, i, 608; 1896, i, 323), and is converted into their dihydroxyaposafranols (7-hydroxysafraanol) by 30% sulphuric acid at  $180-185^\circ$ . 7-o-Toluidino-10-o-tolylsafranols,

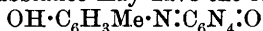


decomp.  $265^\circ$ , separates from alcohol in dark red, flattened, triclinic crystals containing 2EtOH, and is converted by 25% sulphuric acid at  $170-175^\circ$  into 7-hydroxy-10-o-tolylsafranols,  $C_{19}H_{14}O_3N_2$ , reddish-brown crystals, m. p. above  $280^\circ$ . 7-m-Xyliidino-10-m-xylylsafranols,  $C_{28}H_{25}O_2N_3$ , m. p. above  $300^\circ$ , microscopic, red plates, and 7-p-aminosaniindino-10-p-aminophenylsafranols,



are described; the latter is the only one of these safranols of which the hydrochloride,  $C_{24}H_{19}O_2N_5 \cdot 3HCl$ , has been isolated. (In the formulæ of these safranols, the hydroxylic hydrogen atom may be attached to either of the oxygen atoms.)

The oxidation by sodium hypochlorite of a mixture of *p*-aminophenol and *m*-cresol in alkaline solution at  $-10^\circ$  yields the sodium salt, olive-green needles, of methylindophenol, m. p.  $124^\circ$ , metallic green crystals. This substance may have the formula



or  $O \cdot C_6H_3Me \cdot N \cdot C_6H_4 \cdot OH$ . However, it is not tautomeric, and receives the former constitution because it yields toluquinol, m. p.  $124^\circ$ , by decomposition by dilute hydrochloric acid. By reduction with alkaline sodium hyposulphite, it yields *pp'*-dihydroxyphenyl-o-tolylamine, the dibenzoyl derivative of which has m. p.  $132-133^\circ$ . This methylindophenol yields dianilino- and dianilo-derivatives and a safranols by methods similar to those described above; *di-p-toluidinomethylindophenol*,  $C_{27}H_{25}O_2N_3$ , m. p.  $203^\circ$ , brownish-black needles, *di-p-toluidinomethylindophenol*,  $C_{27}H_{25}O_2N_3$ , m. p.  $251^\circ$ , orange needles, and 7-p-toluidino-10-p-tolyl-1-methylsafranols,  $C_{27}H_{23}O_2N_2$ , m. p. above  $300^\circ$ , are described.

The alternative constitution,  $O \cdot C_6H_3Me \cdot N \cdot C_6H_4 \cdot OH$ , is ascribed to

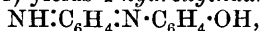
the *methylindophenol*, m. p. 178—179°, reddish-brown needles, which is obtained by the oxidation of phenol and 6-amino-*m*-cresol by cold alkaline sodium hypochlorite.

By similar processes of oxidation, *p*-aminophenol and *o*-cresol yield a *methylindophenol*, which forms an *anilino*-derivative,  $C_{19}H_{16}O_2N_2$ , m. p. 223—224°, crystalline powder, and phenol and 5-amino-*o*-cresol yield an isomeric *methylindophenol*, which forms a *dianilino*-derivative,  $C_{25}H_{21}O_2N_3$ , m. p. 167—168°, blackish-brown leaflets.

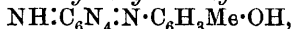
Phenol-blue is most conveniently prepared by oxidising a mixture of phenol and *as*-dimethyl-*p*-phenylenediamine by alkaline sodium hypochlorite at 0° (Gnehm, Abstr., 1904, i, 451). It has m. p. 167° (not 160°), is decomposed by dilute hydrochloric acid, yielding quinol at the ordinary temperature and *p*-benzoquinone at higher temperatures, and reacts with alcoholic aniline, best at 50—60°, to form *dianilinophenol-blue*,  $C_{26}H_{24}ON_4$ , m. p. 226°, brown needles.  $\alpha$ -Naphthol-blue is prepared in a similar manner.

Interaction with primary aromatic amines at the ordinary temperature is characteristic of indophenols; indamines do not exhibit such behaviour.

The oxidation of *p*-phenylenediamine and phenol in aqueous sodium hydrogen phosphate and sodium hydrogen carbonate by lead peroxide at 7° (D.R.-P. 179294) yields 4-*hydroxyindamine*,



m. p. 105—106°, blue needles; in a similar manner, *p*-phenylenediamine and *m*-cresol yield 4-*hydroxy-2-methylindamine*,



m. p. 143—144°, blue needles. These two dyes receive the constitutions depicted, because they are soluble in alkalis and yield quinol by decomposition with dilute hydrochloric acid. 4'-*Amino-3-methylindophenol* (?), m. p. 154—155°, obtained from *p*-phenylenediamine and *o*-cresol, receives the constitution  $NH_2 \cdot C_6N_4 \cdot N : C_6H_3Me \cdot O$ , because of its insolubility in alkalis.

By reduction with zinc and acetic acid or with alkaline sodium hyposulphite, the three dyes are respectively converted into colourless leuco-compounds, which are re-oxidised by atmospheric oxygen.

C. S.

**Constitution of the Compound Derived from Benzoylchloro-carbamide and Alkali.** OTTO DIELS and HARUKICHI OKADA (*Ber.*, 1912, 45, 2437—2441).—As shown by Diels and Wagner (this vol., i, 511), benzoylchloro-carbamide when acted on by dilute alkali loses a molecule of hydrogen chloride, and is converted into a substance to

which the structure  $\begin{array}{c} \text{COPh} \cdot \text{N} \\ | \\ \text{HN} \end{array} > \text{CO}$  is assigned. The compound has now been further studied.

It is converted by aqueous hydrogen chloride or by hydrogen bromide in acetic acid into benzoic acid, and the corresponding salt of hydrazine. When heated with aniline, diphenylcarbamide, and benzhydrazide are obtained.

On heating with hydrazine hydrate, the 3-membered ring is broken, *benzoylcarbohydrazide*,  $\text{COPh} \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH}_2$ , being formed,

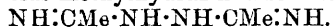
which on further heating breaks down into benzoic acid and carbonylhydrazide.

Mild reducing agents eliminate carbon dioxide and reduce it to benzylhydrazine.

*Benzoylcarbonylhydrazide* crystallises in colourless plates with a fatty lustre, m. p.  $186^{\circ}$ , which reduce Fehling's solution. E. F. A.

**Action of Hydrazine on Dicyanodiamide.** KARL A. HOFMANN and OSKAR EHRHARD (*Ber.*, 1912, 45, 2731—2740).—The authors have re-examined the action of hydrazine on dicyanodiamide, and assign to melamazine the formula  $C_6N_{12}H_6 \cdot H_2O$  in place of  $C_6N_{12}H_8 \cdot H_2O$ , that previously adopted (*Abstr.*, 1911, i, 843). They now adopt the name trisdeamidoguanazole, or, more shortly, pyroguanazole.

If a mixture of dicyanodiamide and hydrazine hydrate is exposed to air at the ordinary temperature, an intensely red coloration appears. Probably the  $-C \equiv N$  group of the dicyanodiamide reacts with hydrazine hydrate to form a readily oxidisable hydrotetrazine. This is the more probable, since benzonitrile in alcoholic solution under the action of hydrazine hydrate and air deposits diphenyltetrazine (compare Pinner, *Abstr.*, 1898, i, 94). Acetonitrile, however, under similar conditions, yields methylhydrazinecarbinolamine,



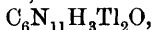
When dicyanodiamide and hydrazine hydrate are heated on the water-bath, a good yield of guanazole is obtained (compare Pellizzari, *Abstr.*, 1892, i, 356; 1894, i, 517), which, when heated at  $275^{\circ}$  during thirty minutes, is transformed into pyroguanazole, one molecule of ammonia being evolved from each molecule of guanazole. *Pyroguanazole hydrochloride* separates from solution in concentrated hydrochloric acid +  $2HCl$ ; from dilute hydrochloric acid, on the other hand, +  $HCl$ . The *platinichloride*,  $(C_6N_{12}H_6 \cdot H_2O)_4H_2PtCl_6$ , was analysed. A *penta-acetyl* derivative was obtained by the prolonged action of acetic anhydride or pyroguanazole at  $125^{\circ}$ .

Pyroguanazole, when oxidised by hot acid potassium permanganate, evolves six atoms of nitrogen from each molecule of substance. In alkaline solution, however, only four atoms of nitrogen are eliminated, cyanuric acid together with a yellow *product*,  $C_4H_4O_2N_6$ , being formed. The latter evolves ammonia when heated with potassium hydroxide, and yields a *silver* salt,  $C_4H_2O_2N_6Ag_2$ . It probably has the constitution  $HN < \begin{smallmatrix} CO-NH \\ C(:NH) \cdot N \end{smallmatrix} > C \begin{smallmatrix} N \\ \parallel \\ N \end{smallmatrix} > C \cdot OH$ .

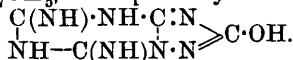
Towards acids, pyroguanazole exhibits extraordinary stability. Concentrated sulphuric acid does not decompose it at  $170^{\circ}$ , but, after twenty-four hours' heating with hydrochloric acid (20%), it is resolved into carbon dioxide, ammonium chloride, and hydrazine chloride. Prolonged treatment with Caro's acid yields a yellow *product*, which, on treatment with ammonia, gives a yellow *powder* of the approximate constitution  $C_6H_2O_3N_9 \cdot 2NH_3$ , and, when acted on by ammoniacal silver nitrate, a brown *silver* salt,  $C_6O_3N_9Ag_3 \cdot 3NH_3$ . Thus, the hydrazine portion of the molecule appears to be oxidised by Caro's acid.

In the absence of oxygen, pyroguanazole is soluble in alkali with the formation of a colourless solution, which, however, readily absorbs

oxygen with simultaneous elimination of nitrogen and formation of an intensely bluish-violet solution, from which a *thallium* salt,



may be obtained. At a higher temperature, an additional quantity of nitrogen is evolved, and the previously-described thallium salt (Abstr., 1911, i, 843) is obtained. At the same time, the number of acetyl groups which can be introduced into the molecule by means of acetic anhydride sinks from five to about two. The composition of the bluish-violet substance remains somewhat uncertain, since it is readily acted on by air. If the alkaline solution is evaporated in the presence of air, it becomes deep brown in colour, and yields a *silver* salt,  $\text{C}_4\text{H}_3\text{ON}_7\text{Ag}_2\text{NH}_3$ , when treated with ammoniacal silver nitrate solution. The same oxidation product is more readily obtained by oxidation of an alkaline solution of pyroguanazole by hydrogen peroxide, and then yields an *ammonium* salt,  $(\text{C}_4\text{N}_7\text{OH}_5)_2\text{NH}_3$ , which when boiled with acid potassium permanganate, evolves one molecule of nitrogen from each molecule,  $\text{C}_4\text{N}_7\text{OH}_5$ , and probably has the constitution represented by the formula



H. W.

*p*-Dimethylaminobenzenediazonium Chloride. ROBERT STOLLÉ (Ber., 1912, 45, 2680—2685).—In addition to dibenzoylhydrazide and tetramethyl-di-*p*-aminodiphenylmethane (compare this vol., i, 225), the interaction of azodibenzoyl and dimethylaniline yields a small amount of an additive compound which is considered to be *dibenzoyl-p*-dimethylaminophenylhydrazide,  $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{NBz}\cdot\text{NHBz}$ . This has m. p.  $199^\circ$ , and on hydrolysis yields *p*-aminodimethylaniline and benzoic acid. With the object of confirming the above formula by the direct synthesis of the dibenzoyl derivative from *p*-dimethylaminophenylhydrazine, the authors have attempted to prepare the latter compound (1) by the reduction of *p*-dimethylaminobenzenediazonium chloride with stannous chloride, and (2) by the successive action of sodium hydrogen sulphite and hydrochloric acid on sodium *p*-dimethylaminobenzeneazosulphonate in aqueous solution. It was found, however, that the reduction of the diazonium chloride gave rise to *p*-aminodimethylaniline and ammonia, whilst in the second case the action of hydrochloric acid on the intermediately formed *p*-dimethylaminophenylhydrazinesulphonic acid resulted in the removal of both the sulphonic acid and *p*-dimethylaminophenyl groups with the formation of hydrazine.

*p*-Dimethylaminobenzenediazonium chloride is obtained in pale yellow crystals exploding at  $130^\circ$  by the action of amyl nitrite on *p*-aminodimethylaniline in alcoholic solution (compare Hantzsch, Abstr., 1902, i, 325). It combines with stannous chloride in the presence of hydrochloric acid, yielding a crystalline *stannichloride*,  $\text{C}_8\text{H}_{10}\text{N}_3\text{Cl}\cdot\text{SnCl}_2\cdot\text{HCl}$ , and with mercuric chloride in alcoholic solution to form the compound,  $\text{C}_8\text{H}_{10}\text{N}_3\text{Cl}\cdot\text{HgCl}_2$ , which crystallises in needles, m. p.  $150^\circ$  (decomp.).

*p*-Dimethylaminobenzenediazonium sulphate, prepared in a similar manner, crystallises in pale green leaflets, m. p.  $158^\circ$  (decomp.).

*p*-Dimethylaminobenzeneazosulphonic acid,  $C_8H_{11}O_3N_3S$ , obtained in the form of its sodium salt (orange-yellow needles) by the interaction of *p*-dimethylaminobenzenediazonium chloride and sodium hydrogen sulphite in aqueous solution, crystallises in violet-red prisms, m. p.  $144^\circ$ ; the potassium salt, brick-red needles, and silver salt, violet-red needles, are also described. Its alcoholic solution is reduced by stannous chloride and hydrogen chloride in ethereal solution to *p*-dimethylaminophenylhydrazinesulphonic acid, which forms pale green leaflets, m. p.  $189^\circ$ , and is hydrolysed by water or hydrochloric acid to *p*-aminodimethylaniline. The dibenzoyl derivative of the last-mentioned compound crystallises in prisms, m. p.  $240^\circ$ . F. B.

*o*-Aminoazobenzene. FELIX H. WITT (*Ber.*, 1912, 45, 2380—2384).—*o*-Nitroaniline is most conveniently benzoylated by treatment with benzoyl chloride and diethylaniline on the water-bath; the yield is 96–98% of the theoretical.

Benzoyl-*p*-phenylenediamine and nitrosobenzene condense in a cold mixture of glacial acetic acid and alcohol (10 : 4) to form *o*-benzoyl-aminoazobenzene,  $NHBz \cdot C_6H_4 \cdot N_2Ph$ , m. p.  $122^\circ$ , reddish-yellow needles, the hydrolysis of which by boiling alcoholic sodium ethoxide yields *o*-aminoazobenzene, m. p.  $59^\circ$ , garnet-red, monoclinic prisms. The orange-yellow sulphate,  $C_{12}H_{13}N_3 \cdot H_2SO_4$ , hydrochloride, yellow needles, and acetyl derivative, m. p.  $126^\circ$ , reddish-yellow needles, are described. The substance yields aniline and *o*-phenylenediamine by fissive reduction, and phenylaziminobenzene by oxidation by chromic and acetic acids. C. S.

The Change in Hydrogen Ion Concentration during Heat Coagulation of Proteins. G. QUAGLIARIELLO (*Biochem. Zeitsch.*, 1912, 44, 157—161).—A solution of coagulated albumin is always electrically negative towards the corresponding solution of uncoagulated protein, owing to diminution of the hydrogen ion concentration. This change in concentration can also be detected when the coagulation has only proceeded so far that there is no macroscopic alteration in the liquid. It is then only small, but becomes larger with progressive coagulative change, reaching its maximum with the agglutination of the protein. The magnitude of the change also depends on the acid used in the solution, being less for acetic than for hydrochloric and nitric acids. The concentration necessary for flocculation is independent of the nature of the acid. In normal sodium chloride or nitrate solutions, the protein separates in a flocculent form at room temperature on addition of acids. This happened in the cases of hydrochloric and nitric acids at a concentration of 0.05*N*, and in acetic acid at the concentration 0.5*N*. Subsequent warming causes no further change in the hydrogen ion concentration. The changes in this concentration on heat coagulation cannot therefore be due to elimination of carbon dioxide. In solutions in which the protein separated on heat coagulation, the hydrogen ion concentration diminished by about 50% of the original value; when no flocculation occurred, the diminution was only 5—7%. S. B. S.

**Heat Coagulation of Proteins. IV. The Conditions Controlling the Agglutination of Proteins Already Acted Upon by Hot Water.** HARRIETTE CHICK and CHARLES J. MARTIN (*J. Physiol.*, 1912, 45, 261—295. Compare this vol., i, 734).—Previous papers have dealt more specially with the first phase in heat coagulation, namely, denaturation of the protein. The present research relates to the second phase, agglutination which follows it. Dispersion of denaturated protein by acid and alkali is due to the electric charge given to the particles. If this is neutralised and the proteins become isoelectric with the solution, agglutination occurs. The optimum acidity for precipitation in the absence of electrolytes is equal to a concentration of hydrogen ions of about  $3 \times 10^6 N$ . Agglutination is influenced by neutral salts by (a) alterations in the concentration of hydrogen ions, or by (b) neutralisation or increase of the electric charge carried by the protein particles. Dispersion by salts is due to the adsorption of ions by the denaturated particles. For every solution containing denaturated protein there is a critical temperature depending on the reaction and on the concentration of protein and electrolytes, below which agglutination does not take place. The supposed conversion of albumin into globulin by heating the former in an alkaline solution (Starke, Moll) is simply explained by differences in the state of aggregation. The substance supposed to be globulin is merely heat-denaturated protein in a loose state of aggregation. W. D. H.

**Hydrogen Peroxide as a Hydrolysing Agent.** NADINE SIEBER (*Zeitsch. physiol. Chem.*, 1912, 81, 185—199).—Experiments in which various proteins (keratin, casein, hæmoglobin, etc.), and also tubercle bacilli were heated under pressure with hydrogen peroxide, show that cleavage takes place, so supporting the view that this reagent is not only an oxidising, but also a hydrolysing, agent. W. D. H.

**The Xanthoproteic Reaction.** KATSUJI INOUE (*Zeitsch. physiol. Chem.*, 1912, 81, 80—85).—The exact meaning of the protein colour reactions is still far from clear, although it is certain that the majority are reactions of certain cleavage products of the protein molecule. The xanthoproteic reaction is given by a number of protein "Bausteine." In the present research, silk fibroin was used, and from the coloured product due to the action of nitric acid, a mononitro-tyrosine was separated. Whether a similar compound with phenyl-alanine occurs is not yet ascertained. W. H. D.

**The Polarimetric Estimation of the Glucosamine Content of Ovomuroid and Pseudomucin.** CARL NEUBERG and OMER SCHEWKET (*Biochem. Zeitsch.*, 1912, 44, 491—494).—The proteins were hydrolysed with hydrochloric acid, and the amino-acids, etc., were precipitated according to the method of Neuberg and Ishida, first by mercuric acetate and then by phosphotungstic acid. The glucosamine was then estimated in the colourless filtrate polarimetrically. By this method ovomucoid was found to contain 24%, and pseudomucin 36.6%, of glucosamine. S. B. S.

**Action of Hydroxylamine on the Blood Colouring Matter. Methæmoglobin.** EUGEN LETSCHE (*Zeitsch. physiol. Chem.*, 1912, 80, 412—429).—By the action of hydroxylamine, oxyhæmoglobin is converted quantitatively into methæmoglobin having the spectrophotometric quotient  $1.186^\circ$ . Nitrogen is liberated at the same time, produced from hydroxylamine by the oxidising action of the oxyhæmoglobin. This is in agreement with Küster's suggestion that methæmoglobin contains less oxygen than oxyhæmoglobin.

The absorption ratio for methæmoglobin in the region  $556.1$ — $564.6 \mu\mu$  is  $2.103 \times 10^{-3}$ . Hydroxylamine acts as an oxidising agent towards reduced hæmoglobin. E. F. A.

**Preparation and Recrystallisation of Hæmin.** ANT. HANSIK (*Zeitsch. physiol. Chem.*, 1912, 80, 35—44).—Hæmatin has been split off from oxyhæmoglobin by continued boiling with sufficiently concentrated aqueous potassium hydroxide, and the preparation of hæmin from this material studied in acetone, glacial acetic acid, and ethyl-alcoholic solutions. Characteristic hæmin crystals having the composition  $C_{34}H_{32}O_4N_4ClFe$  were obtained in each case. Unsatisfactory results were obtained in attempting to prepare hæmin from the hæmatin prepared originally from hæmin. E. F. A.

**Molecular Size of Hæmin and Hæmoglobin.** OSCAR PILOTY and H. FINK (*Ber.*, 1912, 45, 2495—2498).—The molecular weight of hæmatoporphyrin has been shown by Piloty and Dorn (this vol., i, 519) to be about 1200. No simple derivatives of hæmin are available to test whether a doubling of the molecule does not take place in the formation of hæmatoporphyrin from hæmin. Mesoporphyrin obtained by the action of hydrogen iodide has a molecular weight not above 600, corresponding with about half that of hæmatoporphyrin. During its formation losses may arise due to incomplete action on hæmatoporphyrin or due to the formation of more simple substances, such as hæmopyrrole. The maximum yield obtained is 39.2%, which makes it probable that it is derived from only one-half of the hæmin molecule. Accordingly, the molecular weight of hæmin is about 1303, and that of hæmoglobin about 30,000. The coloured portion of hæmoglobin consists of eight and not of four pyrrole nuclei, as previously supposed. E. F. A.

**Oxidation of Dimethylhæmin.** WILLIAM KÜSTER and ALFRED GREINER (*Ber.*, 1912, 45, 2503—2504. Compare this vol., i, 670).—On oxidation of dimethylhæmin with chromium trioxide in acetic acid, some 42% of the theoretical yield of methylhæmatinic acid is obtained. This on hydrolysis yields pure hæmatinic acid. This behaviour indicates that the hæmin molecule contains two carbonyl groups.

E. F. A.

**Pigment of the Blood. IV. Hæmopyrrole.** OSCAR PILOTY and JOSEF STOCK (*Annalen*, 1912, 392, 215—244).—"Hæmopyrrole," obtained from the blood or from chlorophyll derivatives, is a mixture (Piloty and Quitmann, *Abstr.*, 1910, i, 133). In addition to the

hæmopyrrole, *isohæmopyrrole*, and *phyllopyrrole* isolated by Willstätter and Asahina (this vol., i, 41), the authors have succeeded in obtaining new constituents. Since the name hæmopyrrole is now used in the literature to denote four different substances, some system of nomenclature is very necessary. The authors retain the name hæmopyrrole to denote the whole mixture, the constituents of which are then denoted by hæmopyrrole-*a*, -*b*, -*c*, etc., in the order of their b. p.'s.

A large quantity, 320 grams, of crude hæmopyrrole, obtained from 1400 grams of hæmin by Nencki and Zaleski's method, has been submitted in succession to fractional distillation, fractional precipitation with ethereal picric acid, and fractional crystallisation of the picrates. The following substances of definite constitution have thereby been isolated: (1) Hæmopyrrole-*a*,  $C_7H_{11}N$ , b. p.  $81^\circ/18$  mm., which does not form a crystalline picrate, yields methylethylmaleimide by oxidation with chromic acid, and is therefore 3-methyl-4-ethylpyrrole. (2) Hæmopyrrole-*b* (2:3-dimethyl-4-ethylpyrrole), m. p. about  $16^\circ$ , b. p.  $87-88.5^\circ/12.5$  mm. (picrate, m. p.  $122.5^\circ$ ), which is Willstätter and Asahina's *isohæmopyrrole* (*loc. cit.*). (3) Hæmopyrrole-*c* (3:5-dimethyl-4-ethylpyrrole), b. p.  $84-85^\circ/13$  mm. (picrate, m. p.  $137.5^\circ$ ), which is identical with Knorr and Hess's synthetic compound (Abstr., 1911, i, 1019). (4) Hæmopyrrole-*d* (2:3:5-trimethyl-4-ethylpyrrole) is identical with Willstätter and Asahina's *phyllopyrrole* (*loc. cit.*) synthesised by Fischer and Bartholomäus (this vol., i, 297). (5) *Bishæmopyrrole-e* (*bis*-2:3-dimethyl-1-ethylpyrrole,  $CM_e \begin{array}{c} \diagup CM_e \cdot CH \cdot CH \cdot CM_e \\ \diagdown NEt \cdot CH \cdot CH \cdot NEt \end{array} CM_e$  [?]), an oil, which forms a *picrate*,  $C_{22}H_{29}O_7N_5$ , m. p.  $148^\circ$ , small, red needles. Willstätter and Asahina's hæmopyrrole (*loc. cit.*) is shown to be a mixture of hæmopyrroles-*b* and -*c*.

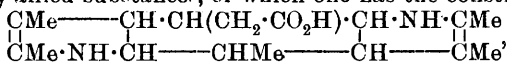
Hæmopyrroles-*a*, -*b*, -*c* each yield methylethylmaleimide by oxidation. At least two of them should yield the same oxime. The fact that they form different oximes, m. p.  $197-198^\circ$ ,  $221.5^\circ$ , and  $215^\circ$  respectively, apparently renders necessary the introduction of stereochemical constitutions. C. S.

**Phonopyrrolecarboxylic Acid and its Companions.** OSCAR PILOTY and E. DORMANN (*Ber.*, 1912, 45, 2592-2595).—It has recently been shown (this vol., i, 519) that the reduction of hæmin by hydriodic acid and phosphonium iodide gives rise to phono- and xantho-pyrrolecarboxylic acids, which very closely resemble the *isophonopyrrolecarboxylic acid* obtained by Piloty and Thannhauser (this vol., i, 736) by the action of hydriodic acid on bilirubin.

In view of the great similarity of the acids and the difficulty of separating and characterising them, the authors have subjected the phonopyrrolecarboxylic acid, obtained from hæmin, to fractional precipitation with picric acid in order to determine whether it is accompanied by *isophonopyrrolecarboxylic acid*. It is found that the crude phonopyrrolecarboxylic acid yields two picrates, m. p.  $138.5$  and  $146^\circ$ , of which the less fusible one is apparently identical with the picrate of *isophonopyrrolecarboxylic acid*, and yields an acid m. p.  $118-122^\circ$ . On treatment with nitrous acid, this gives rise to two oximes, one of

which is identical with the oxime previously obtained from phonopyrrolecarboxylic acid, whilst the other sinters at  $202^{\circ}$ , becomes brown at  $212^{\circ}$ , and has m. p.  $227^{\circ}$  (decomp.) It is also found that the picrate of m. p.  $138.5^{\circ}$  is not a single chemical individual, but is derived from a mixture of acids. From these results the conclusion is drawn that phonopyrrolecarboxylic acid is accompanied by several closely related acids. When boiled with methyl alcohol the yellow picrate of the acid mixture is converted into a brown picrate,  $C_{15}H_{16}O_9N_4$ , crystallising in prismatic needles, m. p.  $122^{\circ}$ . On decomposition with aqueous potassium hydroxide, the brown picrate yields phonopyrrolecarboxylic acid (yellow picrate, m. p.  $158-159^{\circ}$ ), together with an acid which crystallises in long, flat, radiating needles, m. p.  $58^{\circ}$ , and forms a brown picrate,  $C_{16}H_{18}O_9N_4$  (?), m. p.  $120^{\circ}$ . F. B.

**Hæmatopyrrolidinic Acid.** OSCAR PILOTY and P. HIRSCH (*Ber.*, 1912, 45, 2595—2600).—From the amorphous character of the acid itself and also of its picrate, it would appear that hæmatopyrrolidinic acid is not a single chemical individual, but consists of a mixture of substances of very similar structure and composition. It is suggested that the picrate, which has a constant composition, is a double picrate of two closely allied substances, of which one has the constitution :



whilst the other consists of a compound of similar structure, but in a lower state of reduction, or is derived from a hæmopyrrole, isomeric with that which forms the basis of the above formula. This suggestion receives support from the results obtained in a re-examination of the pyrrole mixture obtained by Piloty and Merzbacher (*Abstr.*, 1909, i, 857) by fusing zinc hæmatopyrrolidinate with potassium hydroxide.

The following substances were isolated from the pyrrole mixture by fractional distillation and fractional precipitation with picric acid : (1) 2:3-Dimethylpyrrole (this vol., i, 736). (2) A hæmopyrrole, b. p.  $84-86^{\circ}/12$  mm., which forms a picrate, m. p.  $109-112^{\circ}$ , and on treatment with nitrous acid yields an oxime (decomp.  $201^{\circ}$ ). (3) A pyrroline, which forms a picrate,  $C_{14}H_{18}O_7N_4$ , m. p.  $144^{\circ}$ , and is probably identical with the pyrroline isolated in the form of its picrate by Piloty and Quitmann (*Abstr.*, 1910, i, 133) from the product obtained by the action of hydriodic acid on hæmatoporphyrin. (4) An oil, b. p.  $73-76^{\circ}/10.5$  mm., which has the composition  $C_7H_{11}N$ , and consists of a mixture of pyrroles. On treatment with nitrous acid it does not yield an oxime, but is oxidised to citraconimide and a mixture of maleimides. The isolation of the pyrroline furnishes strong evidence in favour of the above formula. F. B.

**Dehydrobilic Acid, a Coloured Oxidation Product of Bilic Acid.** OSCAR PILOTY and J. S. THANNHAUSER (*Ber.*, 1912, 45, 2393—2395).—By oxidation with aqueous potassium permanganate below  $7^{\circ}$ , sodium bilate (this vol., i, 736) yields, after acidification of the filtered solution, *dehydrobilic acid*,  $C_{17}H_{22}O_3N_2$ , decomp. above  $260^{\circ}$ , citron-yellow prisms, which does not respond to the pine-shaving test or react with *p*-dimethylaminobenzaldehyde, and forms a sodium

salt, yellow needles. Accepting the authors' formula of bilic acid (*loc. cit.*), the colour of dehydrobilic acid may be accounted for by the presence of a system of conjugated double linkings. C. S.

**Behaviour of the True Nucleic Acids to Dyes. I.** R. FEULGEN (*Zeitsch. physiol. Chem.*, 1912, 80, 73—78).—When sodium nucleate and the chloride of malachite-green are brought together, a double interaction takes place with the formation of sodium chloride and the nucleate of malachite-green. This compound is a black, porous mass with a red surface reflex; the absence of chlorine from it is against the assumption that it is an adsorption compound. E. F. A.

**Guanine Hexoside Obtained on Hydrolysis of Thymus-nucleic Acid.** PHÆBUS A. LEVENE and WALTER A. JACOBS (*J. Biol. Chem.*, 1912, 12, 377—380).—Previous investigations by the authors have shown that plant nucleic acid yields various pentosides. Direct proof that the purine bases have the same glycosidic union in thymus-nucleic acid is, however, wanting. Repeated attempts to obtain the nucleosides from thymus-nucleic acid by the same methods failed; but by the employment of an enzyme, the source and nature of which are not given, a guanine hexoside,  $C_{11}N_{15}O_6N_5$ , was separated. It is semi-crystalline, soluble in hot alcohol, does not reduce Fehling's solution, and only gave the orcinol test in the presence of copper. From the products of hydrolysis, an osazone melting at  $198^\circ$  and guanine sulphate were obtained. W. D. H.

**Structure of Thymus-nucleic Acid.** PHÆBUS A. LEVENE and WALTER A. JACOBS (*J. Biol. Chem.*, 1912, 12, 411—420).—The separation of yeast-nucleic acid into its constituent nucleotides is due to the stability of the carbohydrate ribose which they contain. The instability of the hexose in thymus-nucleic acid leads to difficulties in decomposing this by the same methods, a part being at once cleaved into lævulinic acid. As the nature of the hexose is still uncertain, the structural formulæ given in the paper are regarded as provisional only. The crystalline brucine and barium salt of a dinucleotide containing thymine and cytosine was examined, and the conclusion drawn that each phosphoric acid group contains a secondary and a tertiary hydroxyl, and that the linking between the nucleotides occurs between the sugar groups. W. D. H.

**Guanylic Acid.** PHÆBUS A. LEVENE and WALTER A. JACOBS (*J. Biol. Chem.*, 1912, 12, 421—426).—Although Bang does not accept the view that guanylic acid is a simple mono-nucleotide, recently-ascertained facts support the idea. It is now possible to obtain the substance in the form of a pure crystalline brucine salt, and analysis of this confirms the authors' hypothesis. There is, however, more basis for the assumption that the structure of guanylic acid is not identical with that of inosinic acid. Both guanylic and yeast-nucleic acids permit the detaching of phosphoric acid quite easily, whereas in inosinic and thymus-nucleic acids the same is accomplished with difficulty. This is probably due to a difference in the position of the

phosphoric acid on the sugar, but definite evidence of the position has not yet been forthcoming.  
W. D. H.

**Action of Saliva, Tissue Fluids, Bacteria, and Bacterial Extracts on Polypeptides.** J. W. TAYLOR and I. WALKER HALL (*J. Path. Bact.*, 1912, 17, 121—123).—Saliva, blood, exudations, and transudations from the blood, certain bacteria, and bacterial extracts were found capable of splitting glycyl-*l*-tryptophan. The liberation of tryptophan, and the ease with which this substance can be detected, render this test an easy one for the demonstration of peptolytic enzymes.  
W. D. H.

**The Thermostability of Trypsin and Pepsin.** KOHSHI OHTA (*Biochem. Zeitsch.*, 1912, 44, 472—480).—It has been claimed by E. W. Schmidt that trypsin still retains its activity when heated to 100° in water in the presence of various colloids, such as peptone, gelatin, or agar-agar. The author has repeated these experiments, using various methods to detect proteoclastic activity, and has failed to confirm Schmidt's observations. He has also tried the same experiments with pepsin, and has failed to obtain an active preparation after heating various ferment solutions in water at 100° in the presence of colloids.  
S. B. S.

**Diastase. II. The Preparation of Pure Diastase and its Properties.** ERNST PRIBRAM (*Biochem. Zeitsch.*, 1912, 44, 293—302. Compare Fränkel and Hamburg, *Abstr.*, 1906, i, 917).—In order to prepare diastase from malt extract, it is not necessary to use pure yeast cultures to destroy the sugars if the ferment mixture is not allowed to get too acid by the formation of lactic acid. The preparation was made therefore from Pilzen malt, the mash being prevented from becoming acid by the addition of calcium carbonate. The sugar-free filtrate of the fermentation mixture is then evaporated to a syrup, and filtered from the calcium lactate which separates. Although the diastase does not dialyse through parchment, it can be filtered through gelatin filters under pressure, and the author describes (with figures) the apparatus employed for this purpose. Most experiments were carried out with the dialysed preparation. The dried preparation purified in this way contains 7.7% nitrogen and 1.5% ash. Fifteen % of the nitrogenous matter separates as a coagulum on heating, which gives a strong reaction with Millon's reagent, but a very weak biuret reaction. The filtrate on hydrolysis with sulphuric acid yields a reducing substance, which does not form an osazone, but forms a barium salt, and is probably a polycarbohydrate acid; it exists in the ferment in combination with a somewhat simple polypeptide. The purified diastase is inactive, but is activated by the addition of traces of lactic acid.  
S. B. S.

**The Influence of Antiseptics on the Action of Maltase.** W. KOPACZEWSKI (*Biochem. Zeitsch.*, 1912, 44, 349—352).—The best antiseptics for employment in investigating the action of maltase on sugars are toluene and chloroform. Mustard oil is inconvenient, as its

reducing action interferes with the estimation of sugars. If sodium fluoride is used, the optimal concentration is 0.4—0.5%. In this concentration the action of the ferment is accelerated. Formaldehyde has an inhibitory action, which can be detected in a concentration of 0.1%. The hydrogen ions exert a deleterious action even in relatively low concentrations.

S. B. S.

**The Reversibility of Ferment Actions. Influence of the Dilution of Ethyl Alcohol on the Synthesising Action of Emulsin in this Medium.** EMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1912, 155, 319—322. Compare this vol., i, 592, 593, 672; Bertrand and Compton, this vol., i, 592).—Numerous attempts have been made, without success, to synthesise disaccharides by means of enzymes from the products of their hydrolysis by the same enzymes (compare Croft Hill, *Trans.*, 1898, 73, 634; 1903, 80, 578). The authors have set up experiments with mixtures of  $\beta$ -ethyl glucoside and alcohol (85%), and dextrose and alcohol (85%), in separate flasks, the amounts of glucoside and dextrose used being equivalent. To each mixture was added the same amount of emulsin, and they were left at the ordinary temperature with occasional shaking for sixteen to twenty-one days, when the two liquids were found to have exactly the same rotation. By varying the strength of the alcohol, the actual final rotation, whilst being the same for the two mixtures, was found to vary with the strength of the alcohol used. The more dilute the alcohol, the greater is the hydrolysis and the less the synthesis, and vice versa.

W. G.

**Action of Enzymes on Hexose Phosphate.** VICTOR J. HARDING (*Proc. Roy. Soc.*, 1912, B, 85, 418—422).—Hexose phosphate is slowly hydrolysed by Ricinus lipase and by emulsin from almonds, whilst the autolysed pancreas of the ox is almost without action. An aqueous extract of zymine hydrolyses hexose sulphate slowly. Autolysed yeast-juice possesses a very marked hydrolytic action, and the enzyme effecting this hydrolysis may be precipitated from the juice with a mixture of alcohol and ether.

W. J. Y.

**New Properties of Peroxydases and their Behaviour in the Absence of Peroxides.** JULES WOLFF (*Compt. rend.*, 1912, 155, 618—620).—Péroxydase, from young barley shoots, produces a marked catalytic effect on the rate of oxidation of orcinol, in the presence of alkali hydroxides or carbonates, by atmospheric oxygen without any peroxides being present. The same relative increase in oxidation is noticed if the alkalis are replaced by sodium phosphate.

W. G.

**1:4-Dichloroarsinobenzoyl Chloride. Esters of Benzarsinious and Benzarsinic Acids.** ERNEST FOURNEAU and OCHSLIN (*Bull. Soc. chim.*, 1912, [iv], 11, 909—914).—The preparation of 1:4-dichloroarsinobenzoyl chloride and of a number of its derivatives are described.

Benzarsinic acid,  $\text{AsO}(\text{OH})_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$  (*p*-carboxyphenylarsinic

acid, Abstr., 1908, i, 591), on treatment with phosphorus trichloride in chloroform yields benzarsinious dichloride (*p*-carboxyphenylarsinious chloride),  $\text{AsCl}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , already obtained by La Coste (Abstr., 1881, 903), and this by the further action of phosphorus pentachloride is converted into *dichloroarsinobenzoyl chloride*,  $\text{AsCl}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{COCl}$ , b. p. 189—190°/19 mm., a mobile liquid, which fumes in moist air, is soluble in chloroform or benzene, and on keeping passes into a crystalline mass. It reacts like an acid chloride with hydroxy-compounds. When it is dissolved in alcohol and the mixture treated with water, *ethyl arsino benzoate oxide*,  $\text{AsO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}$ , m. p. 277°, is precipitated as an amorphous powder, from which sodium hydroxide solution liberates the corresponding *acid*,  $\text{AsO} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$ , brilliant flat needles, which does not melt up to 280°.

On oxidation with hydrogen peroxide in alkalis, the oxide is converted into *ethyl benzarsinate* (*p*-carbethoxyphenylarsinic acid),  $\text{AsO}(\text{OH})_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}$ , m. p. 260° (decomp.), crystallising in small brilliant spangles. The *quinine* salt, similarly prepared, in two stages, forms small, brilliant cubes, m. p. 200° (approx.), is sparingly soluble in organic solvents, but is readily dissolved by acids or alkalis. A sodium carbonate solution of the salt on treatment with sodium hyposulphite yields *benzarsenoquinine*,  $\text{As}_2(\text{C}_6\text{H}_4 \cdot \text{CO}_2 \cdot \text{C}_{20}\text{H}_{23}\text{O}_2\text{N}_2)_2$ , as a bright yellow powder.

Stovaine,  $\text{C}_2\text{H}_5 \cdot \text{CMe}(\text{OBz}) \cdot \text{CH}_2 \cdot \text{NMe}_2 \cdot \text{HCl}$ , has a special affinity for nerve substance, and its arsenical analogue has been prepared by treating dimethylaninodimethylethylcarbinol with dichloroarsinobenzoyl chloride. The resulting *dichloroarsinobenzoate hydrochloride*,  $\text{C}_{14}\text{H}_{20}\text{O}_2\text{N} \cdot \text{HCl}$ , m. p. 194°, crystallises in small, colourless needles from alcohol, but has not been obtained free from the corresponding *oxide*,  $\text{C}_2\text{H}_5 \cdot \text{CMe}(\text{O} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}) \cdot \text{CH}_2 \cdot \text{NMe}_2$ , which can be prepared by treating the compound just described with sodium carbonate solution in presence of ether to remove it as formed; it is a viscous oil, as is also its *hydrochloride*; the latter produces on the tongue an intense and persistent tingling. On reduction with sodium hyposulphite, the oxide yields *arsenostovaine*,  $\text{C}_{28}\text{H}_{40}\text{O}_4\text{N}_2\text{As}_2$ , as a golden-yellow powder, soluble in acids.

*Guaicacyl arsino benzoate oxide*, m. p. 191°, obtained by the action of dichloroarsinobenzoyl chloride on guaiacol dissolved in benzene in presence of pyridine, crystallises in tufts of colourless needles, and on oxidation with hydrogen peroxide in acetone yields *guaicacyl benzarsinate*, which crystallises in brilliant, slender needles, and does not melt on heating.

T. A. H.

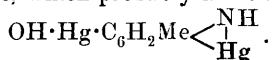
**Aromatic Arsenic Compounds. II. Azo-dyes Containing Arsenic.** P. KARRER (*Ber.*, 1912, 45, 2359—2363. Compare this vol., i, 740).—The reaction of *p*-nitrosophenylarsinic acid, hydroxylamine hydrochloride, and *m*-tolylenediamine in aqueous sodium carbonate at 0° yields, after acidifying the solution, the red azo-dye,  $\text{C}_6\text{H}_2\text{Me}(\text{NH}_2)_2 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}(\text{OH})_2$ , which is produced by condensing diazotised arsanilic acid with *m*-tolylenediamine. *Azobenzene-p*-arsinic acid,  $\text{NPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}(\text{OH})_2$ , is an amorphous, brown powder obtained by the action of *p*-nitrosophenylarsinic acid on aniline

in boiling glacial acetic acid. *Azobenzene-pp'-diarsinic acid*,  $\text{AsO}(\text{OH})_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}:\text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}(\text{OH})_2$ , obtained in a similar manner from arsanic acid and *p*-nitrosophenylarsinic acid, is a dark brown powder, which develops a purple-red coloration with concentrated mineral acids. *Bisazobenzene-4:3':4''-triarsinic acid*,

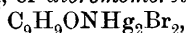
$\text{AsO}(\text{OH})_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2 \cdot \text{C}_6\text{H}_3(\text{AsO}_3\text{H}_2) \cdot \text{N}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{AsO}(\text{OH})_2$ , a black powder with green reflex, is similarly obtained from *p*-phenylenediaminearsinic acid. C. S.

**Influence of Nuclear Alkyl Groups on the Mercuriation of Aniline and its Nitrogen Substitution Products.** WALTER SCHRAUTH and WALTER SCHOELLER (*Ber.*, 1912, 45, 2808—2818).—In extension of previous work (*Abstr.*, 1911, i, 699), the results of an investigation of the action of mercuric acetate on toluidines and their acyl derivatives are given.

[With JULIUS ROTHER.]—Molecular proportions of *o*-toluidine and mercuric acetate in methylalcohol give rise to 15% of mercuri-*o*-toluidine, the chief product being a *diacetoxymercuri*-derivative,  $\text{C}_{11}\text{H}_{13}\text{O}_4\text{NHg}_2$ , m. p. 228° (corr. decomp.), which crystallises in microscopic needles, is insoluble in most organic solvents, slightly soluble in methyl alcohol, but readily in ammonia or amines. On treatment with sodium hydroxide in water, it yields *dihydroxymercuri-o-toluidine*, long, colourless needles; this on warming at 100° loses  $\text{H}_2\text{O}$ , giving an infusible canary-yellow substance, which probably has the constitution



The *diacetoxymercuri-o-toluidine* on acetylation in ethyl acetate solution gives *diacetoxymercuriaceto-o-toluidide*,  $\text{C}_{13}\text{H}_{15}\text{O}_5\text{NHg}_2$ , m. p. 240° (corr.), from which by double decomposition with sodium chloride or bromide in water, the corresponding *dichloromercuri*-derivative,  $\text{C}_9\text{H}_9\text{ONHg}_2\text{Cl}_2$ , or *dibromomercuri*-compound,



may be obtained, crystallising in microscopic needles. *Di-iodomercuriaceto-o-toluidide* is precipitated in flocks, but passes into a crystalline modification on keeping.

Mercury-*o*-toluidine was obtained as *chloromercuri-o-toluidine*,  $\text{C}_7\text{H}_8\text{NHgCl}$ , m. p. 178°, by adding sodium chloride to the mother liquor from which the *diacetoxymercuri*-compound had separated; it crystallises from dry alcohol in glancing needles, and on acetylation yields *chloromercuriaceto-o-toluidide*,  $\text{C}_{11}\text{H}_{12}\text{O}_2\text{NHgCl}$ , m. p. 170° (corr.), in colourless leaflets.

*Diacetoxymercuri-m-toluidine* is more soluble in dilute alcohol than the ortho-isomeride, has no definite melting point, and yields an *acetyl* derivative. The corresponding *dihydroxy*-compound could not be obtained. *Triacetoxymercuri-m-toluidine*,  $\text{C}_{13}\text{H}_{15}\text{O}_6\text{NHg}_3$ , obtained by the action of mercuric acetate in excess on *m*-toluidine, forms bright yellow, microscopic crystals; the *acetyl* derivative is a colourless, heavy powder.

The *acetyl* derivatives of all three toluidines react with mercuric acetate in water, giving mono-substitution products. *Acetoxymercuri*-

*aceto-o-toluidide*,  $C_{11}H_{13}O_3NHg$ , m. p.  $233^\circ$  (corr.), forms needles. The *meta-isomeride*, m. p.  $99^\circ$  (corr.), crystallises from 30% alcohol, and the *para-compound*, m. p.  $229^\circ$  (corr.), crystallises in leaflets.

Ethyl *o*-toluidinoacetate gives a mono- or di-substitution product according to the concentration of mercuric acetate used. *Ethyl acetoxymercuritolidinoacetate*,  $OAc \cdot Hg \cdot C_6H_3Me \cdot NH \cdot CH_2 \cdot CO_2Et$ , m. p.  $122.5^\circ$  (corr.), crystallises in needles, and on hydrolysis by alkalis gives *hydroxymercuri-o-toluidinoacetic anhydride*,  $C_6H_3Me \cdot \begin{smallmatrix} NH-CH_2 \\ | \\ Hg \cdot O \cdot CO \end{smallmatrix}$ , as a flocculent, colourless precipitate. *Ethyl diacetoxymercuri-o-toluidinoacetate*,  $C_6H_2Me(Hg \cdot O \cdot Ac)_2 \cdot NH \cdot CH_2 \cdot CO_2Et$ , m. p.  $167^\circ$  (corr.), forms small, slender needles.

Ethyl *m*-toluidinoacetate forms *mono-* or *tri-*substitution products, depending on the concentration of mercuric acetate used. The first of these has m. p.  $127.5^\circ$  (corr.), and on hydrolysis gives *hydroxymercuri-m-toluidinoacetic anhydride*, which is yellow. *Ethyl triacetoxymercuri-m-toluidinoacetate*, m. p.  $185^\circ$  (corr.), is crystalline, and dissolves with difficulty in alcohol.

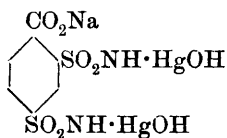
Ethyl *p*-toluidinoacetate gives only a mono-substitution product, m. p.  $140^\circ$  (corr.), which crystallises in small needles, and on hydrolysis yields *hydroxymercuri-p-toluidinoacetic anhydride* as a colourless, amorphous substance.

The position of the entering mercuric acetate was determined in certain cases by Dimroth's method (Abstr., 1902, i, 656); thus acetoxymercuriaceto-*o*-toluidide gives 5-iodoaceto-*o*-toluidide with iodine, whilst the diacetoxym-*o*-compound gives 4:6-di-iodoaceto-*m*-toluidide; the former must therefore have its groups in the positions  $CH_3 \cdot NH_2 \cdot Hg = 1 : 2 : 5$ , whilst the second has its substituents arranged thus:  $CH_3 \cdot NH_2 \cdot Hg : Hg = 1 : 3 : 4 : 6$ . According to Pesci (Abstr., 1898, i, 648), *p*-toluidine takes up mercury in the *ortho*-position with respect to the amino-group. The *iodo-compound*, m. p.  $222.5^\circ$  (corr.), obtained from diacetoxymercuriacetyl-*o*-toluidine crystallises in long, silky needles. According to Holleman's rule the mercuric acetate residue should enter in the following positions with respect to the amino-group in the ethyl toluidinoacetates: *ortho*-ester, 4 and 6; *meta*-ester, 2, 6, and 4; *para*-ester, 2 (compare Abstr., 1911, i, 699). T. A. H.

**Colloidal Acetate of Penta-mercuriacetanilide.** M. RAFFO and G. ROSSI (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 120—121).—By heating together mercuric acetate and acetanilide in the molecular ratio 5:1, the authors have prepared the acetate of penta-mercuriacetanilide, having the composition  $C_6(HgOAc)_5 \cdot NHAc, 2H_2O$ . The mixture, impregnated with a little mercury, is heated for an hour at  $115^\circ$ , the temperature being then raised slowly to  $145^\circ$ , at which it is maintained for about half an hour. The resulting pasty mass is cooled, treated with a small quantity of boiling water, filtered, and the residue left for some hours in contact with cold water. The substance dissolves, giving a viscous solution which resembles egg-albumin. This solution coagulates at  $80^\circ$ , but the coagulum redissolves on cooling. If the solution is boiled for some time, the coagulum is no longer soluble in water. On addition of acetic acid to the viscous solution, needle-

shaped crystals of the above composition are slowly deposited. The colloidal character of the solutions which this substance yields is supposed to be connected with its high molecular weight. H. M. D.

**Preparation of Readily Soluble Compounds of Oxymercurisalicyl Anhydride (Salicylic Acid Mercury Oxides).**



JOHANNES KERB (D.R.-P. 247625).—A description of complex soluble double salts of mercury with organic acids.

The compounds obtained from sodium *o*-hydroxymercurisulphaminobenzoate (1 mol.) and mercury salicylate (2 mols.), and from sodium 2:4-dihydroxymercurisulphaminobenzoate (a feebly basic powder) with mercury salicylate (4 mols.), are pale yellow powders, soluble in water, and decomposed by ammonium sulphide with separation of mercury. F. M. G. M.

**Aluminium Triphenyl.** SIEGFRIED HILPERT and GERHARD GRÜTTNER (*Ber.*, 1912, 45, 2828—2832).—The preparation and properties of aluminium triphenyl are described. The substance was obtained by mixing mercury diphenyl with aluminium foil and heating to 140° in an atmosphere of dry hydrogen or nitrogen. The yellow, viscous mass thus obtained was boiled with ether and the solution evaporated in absence of air and moisture, when it deposited colourless needles, m. p. 112—113°, containing ether of crystallisation, which could only be removed by melting the product under reduced pressure. The ether-free *aluminium triphenyl* thus obtained forms masses of radiating needles, m. p. 196—200°, and cannot be distilled, even under reduced pressure. It explodes when heated in contact with cupric oxide, so that its carbon content could only be determined by a wet method. The compound is fairly stable when kept in compact masses in dry air, but when dry air is passed through a solution in ether, a colourless, amorphous precipitate,  $\text{AlOC}_6\text{H}_5$  (?), is formed, along with some diphenyl.

With water, aluminium triphenyl reacts vigorously and the mixture is apt to take fire. The products are benzene, diphenyl, and alumina. With alcohol an infusible *product* is formed, which is decomposed by water, liberating phenol. Chloroform reacts with aluminium triphenyl, giving a yellow, semi-crystalline *product*, which is slowly decomposed by water with the separation of alumina and the liberation of some chloroform, but no triphenylmethane or the substances likely to accompany it could be detected. Carbon tetrachloride reacts similarly to chloroform. With iodine in ether, aluminium triphenyl reacts in the proportions necessary to give aluminium iodide and phenyl iodide, and a crystalline intermediate product separates. T. A. H.

## Organic Chemistry.

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**Kachler's Ethylene-Ferrous Chloride.** WILHELM MANCHOT and JULIUS HAAS (*Ber.*, 1912, 45, 3052—3055).—Kachler (*Ber.*, 1869, 2, 510) has described the compound  $C_2H_4FeCl_2 \cdot 2H_2O$ , prepared by heating ferric chloride in ethereal solution with the addition of phosphorus in carbon disulphide in sealed tubes at 140—150°. The existence of this compound is improbable on theoretical grounds, and it is now shown to be an additive product of ferrous chloride and ether which has already largely decomposed before it can be analysed. Apparently the ferric chloride is reduced by the phosphorus, and the insoluble ferrous chloride at the moment of formation combines with ether and crystallises.

E. F. A.

**Bromine Absorptive Capacity of Organic Compounds.** ISIDOR KLIMONT [in part, with WILHELM NEUMANN and E. SCHWENK] (*Arch. Pharm.*, 1912, 250, 561—589).—A critical résumé is first given of the methods that have been proposed or used for determining the bromine absorption of organic compounds. The method adopted is that already described (this vol., i, 37; compare Mossler, *Zeitsch. allg. Österr. Apoth.-Ver.*, 1907, p. 225, and Gaebel, this vol., ii, 497). It has been applied to aliphatic, hydroaromatic, and aromatic substances, and the experimental results are given in the original. From these the following conclusions are drawn. The method gives erroneous results if hydrogen bromide is liberated, since this produces hydriodic acid when potassium iodide is added, which may act as a reducing agent and give rise to high bromine numbers. The high bromine numbers given by old turpentine oils are probably due to this cause. In presence of too much water, bromine may produce hydrobromic acid, and for this reason 50% sulphuric acid is used to liberate the bromine.

Aliphatic compounds containing a single ethylene linking and either one  $-OH$  or  $-CO \cdot OH$  group give normal results. In presence of two carboxyl groups the results are abnormal; thus, maleic acid combines easily with bromine, but the results are not quantitative, because part of the maleic acid is converted into fumaric acid, which takes up bromine much less easily in the cold. Similar trouble is experienced with citraconic, mesaconic, and aconitic acids.

The open-chain terpenes and their derivatives give abnormal results, because they readily undergo ring formation under these conditions or in some cases take up water, forming saturated compounds. Cyclic terpenes in which the ethylenic linking is not present in a "bridge," for example, dipentene and camphene, give normal results. A "bridge" between atoms in the para-position is unaffected, but one in the meta-position behaves as an ethylenic linking; thus, pinene absorbs four atoms of bromine, but the results are not quite quantitative, probably owing to partial displacement of the "bridge" to the para-position.

Phenol absorbs six atoms of bromine, three of which are liberated as

hydrogen bromide, and abnormal results are given by the phenol ethers and polyhydric phenols. Benzene derivatives with an ethylenic linking in the side-chain give normal results, but these are sometimes interfered with in the case of stereoisomerides.

Results are quoted showing that the method gives different but constant results for turpentine oils of different origins, and is capable of detecting sophistication in turpentine oil. T. A. H.

**Acetylenic Compounds.** ROBERT LESPIEAU (*Ann. Chim. Phys.*, 1912, [viii]. 27, 137—189).—A résumé of work already published. Compare especially the following papers: Abstr., 1899, i, 184; 1905, i, 401, 566; 1907, i, 580; 1908, i, 125, 496; 1909, i, 205, 282, 691; 1910, i, 149; 1911, i, 347; this vol., i, 7, 331. T. A. H.

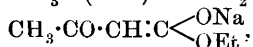
**Theory of Racemisation, Substitution, and the Walden Inversion.** JOHANNES GADAMER (*Chem. Zeit.*, 1912, 36, 1327—1329).—The author gives a brief re-statement of his theory of racemisation (*Chem. Zeit.*, 1910, 34, 1004).

With reference to the different behaviour of metallic hydroxides, some giving a normal hydrolysis, whilst others cause a Walden inversion, it is suggested that the effect in the first case is primarily due to the anion (with rapid action), and that in the second case the cation (with a relatively slow action) is the agent. In an inversion of a molecule  $\text{CabcCl}$  by treatment with silver hydroxide, it is supposed that the chlorine atom is first removed, when the remaining groups tend to distribute themselves evenly around the central carbon atom; on account of the acquired momentum, however, they overswing themselves and pass into the relatively opposite configuration to the original, when the hydroxyl group attaches itself.

In the additive reactions assumed by the theory to participate in the processes, the author's views differ from those of previous workers, in that the addition is supposed to occur, not directly at the asymmetric atom, but at the halogen atom, the groups of the molecule thus formed undergoing subsequent rearrangement. D. F. T.

**Products of the Action of Sodium Alkylloxides on Acid Esters.** ANASTASE DAMBERGIS and TELEM. KOMNENOS (*Ber. Deut. Pharm. Ges.*, 1912, 22, 417—424).—When ethyl acetate is treated with a methyl-alcoholic solution of sodium methoxide, partial transformation into methyl acetate occurs without formation of ethyl acetoacetate. The latter substance is also not produced when ethyl-alcoholic sodium ethoxide reacts with ethyl acetate. Sodium acetate is the main product of the latter change.

The solid product of the action of sodium on ethyl acetate consists solely of ethyl sodioacetoacetate unmixed with sodium ethoxide. It is found to require considerably less acid for neutralisation than is expected. The difference is ascribed to the probable presence of the two isomeric compounds  $\text{CH}_3\cdot\text{C}(\text{ONa})\cdot\text{CH}\cdot\text{CO}_2\text{Et}$  and



to the latter of which no alkaline action is attributed.

H. W.

**Bromoacetic Anhydride.** WILHELM STEINKOPF (*Ber.*, 1912, 45, 3136—3139. Compare Gal, *Compt. rend.*, 1870, 71, 272).—*Bromoacetic anhydride* may be prepared by distilling bromoacetyl bromide with sodium bromoacetate, sodium acetate, or phosphoric oxide under diminished pressure. It is a colourless liquid, b. p. 133—135°/12.5 mm., which solidifies to a white, crystalline mass, m. p. 41—42°, and reacts with ethylene glycol, yielding the dibromoacetate, b. p. 176.5—177.5°/14 mm. (compare Vorländer, *Abstr.*, 1895, i, 19).

F. B.

**Action of Oxychlorides of Silicon on Sodium Salts of Fatty Acids.** JOAQUIN E. ZANETTI (*J. Amer. Chem. Soc.*, 1912, 34, 1598—1600).—Experiments are described which show that silicon oxychlorides react with sodium acetate, propionate, and butyrate, with the production of the corresponding anhydrides, together with sodium chloride and silica. The action of the silicon oxychlorides is therefore analogous to that of the oxychlorides of phosphorus, sulphur, and carbon.

E. G.

**Direct Synthesis of the Glycerides.** ITALO BELLUCCI (*Gazzetta*, 1912, 42, ii, 283—305. Compare *Abstr.*, 1911, i, 259, 416, 515).—[With D. BACHILLI and E. GARRONI.]—The author has investigated the formation of glycerides when glycerol is heated at 215—220° and 30—40 mm. with the equimolecular quantity of palmitic, stearic, or oleic acid. The progress of the esterification as heating is continued is represented in curves, and is similar in all three cases. Mixtures of mono-, di- and tri-glycerides are formed, and if the heating is continued after all the acid is combined, the quantity of monoglyceride tends to increase.

R. V. S.

**Basicity of Acids Containing Alcoholic Hydroxyl Groups.** II. GENNARO CALCAGNI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 343—349, 445—449).—In a former paper the author has recorded the variation of conductivity of solutions of these acids during neutralisation with ammonia (compare Calcagni and Bernardini, *Abstr.*, 1911, ii, 1078). In the present paper similar experiments are described, the neutralisation being effected with glucinum hydroxide, which the author has already used for this purpose in the case of lactic acid (*Abstr.*, 1910, i, 708). The conductivity curves show that glycollic, lactic, and hydroxyisobutyric acids form in each case two types of salts, the ratios between acid and base being  $1:\frac{1}{2}$  and  $1:1$  respectively, so that they act as dibasic acids. Malic acid is a tribasic acid, forming three salts in the proportions  $1:\frac{1}{2}$ ,  $1:1$ , and  $1:1\frac{1}{2}$ . Tartaric acid forms three salts ( $1:\frac{1}{2}$ ,  $1:1$ , and  $1:2$ ), and is, therefore, tetrabasic. Citric acid forms four salts ( $1:\frac{1}{2}$ ,  $1:1$ ,  $1:1\frac{1}{2}$ ,  $1:2$ ), and is consequently tetrabasic. Hence the alcoholic hydroxyl groups of the fatty acids behave like carboxylic hydroxyl groups. It also appears that these acids give only normal salts with  $\text{Gl}(\text{OH})_3$ , so that the complex salts of which the existence has been asserted are not formed in reality.

R. V. S.

**Cerebronic Acid.** PHÆBUS A. LEVENE and WALTER A. JACOBS (*J. Biol. Chem.*, 1912, 12, 381—388).—This acid was discovered by Thudichum, who considered it to be an isomeride of stearic acid. Thierfelder, however, found that its formula is  $C_{25}H_{50}O_8$ , and that it contained one hydroxyl group. In the present research it was found to be normal  $\alpha$ -hydroxypentacosic acid, and in the hydrolysis mixture it occurs in the form of two isomerides, one dextrorotatory ( $[\alpha]_D^{30} = +4.16^\circ$ ), and the other optically inactive. The two can be separated by fractional precipitation with lithium acetate.

W. D. H.

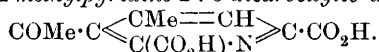
**Free Acetoneoxalic [Acetylpyruvic] Acid and its Derivatives.** OTTO MUMM and CLEMENS BERGELL (*Ber.*, 1912, 45, 3040—3051).—Ethylacetylpyruvate is readily obtained on condensing acetone with ethyl oxalate by means of sodium ethoxide (Claisen and Styles, *Abstr.*, 1887, 917), but it has not been hydrolysed to the acid. It was sought to obtain this in a manner analogous to that followed with benzoylpyruvic acid (Mumm and Münchmeyer, *Abstr.*, 1911, i, 79) by condensing 5-methylisooxazole with methyl sulphate to the  $\alpha$ -methylimide of acetylpyruvonitrile,  $CH_3 \cdot CO \cdot CH_2 \cdot C(:NMe) \cdot CN$ , but the only degradation product obtained was acetylpyruvamide,  $CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CO \cdot NH_2$ . This is more conveniently prepared by the action of aqueous ammonia on ethyl sodioacetylpyruvate. The action of phenylhydrazine on this amide leads to phenylmethylpyrazolecarboxylamide,  $CMe \begin{array}{c} \text{CH} - \text{C} \cdot \text{CO} \cdot \text{NH}_2 \\ \diagdown \quad \diagup \\ \text{NPh} \quad \text{N} \end{array}$ . The ammonium salt

of ethyl acetylpyruvate loses water at room temperature to form the  $\alpha$ -imide of *ethyl acetylpyruvate*,  $CH_3 \cdot CO \cdot CH_2 \cdot C(:NH) \cdot CO_2Et$ .

*Acetylpyruvic acid* is obtained without difficulty by hydrolysing ethyl sodioacetylpyruvate with 4*N*-sodium hydroxide for one and a-half hours and extraction of the acid with ether. It forms colourless prisms, m. p.  $98^\circ$ , and can be partly sublimed in a vacuum without decomposition. It gives a red coloration with ferric chloride in alcoholic solution. It is monobasic to methyl-orange, and dibasic to phenolphthalein. It reacts with hydroxylamine, forming 5-methylisooxazole-3-carboxylic acid,  $CMe \begin{array}{c} \text{CH} - \text{C} \cdot \text{CO}_2H \\ \diagdown \quad \diagup \\ \text{O} \quad \text{N} \end{array}$ . With benzaldehyde a

*monobenzylidene* compound,  $CH_3 \cdot CO \cdot C(:CHPh) \cdot CO \cdot CO_2H$ , is obtained; with aniline hydrochloride in aqueous solution, *acetylpyruvanilide*,  $CH_3 \cdot CO \cdot CH_2 \cdot CO \cdot CO \cdot NHPh$ , is obtained, whereas with aniline in alcohol the product is a *phenylimide*,  $CH_3 \cdot CO \cdot CH_2 \cdot C(:NPh) \cdot CO_2H$ . When excess of aniline is used, three molecules react and two molecules of water are eliminated.

Acetylpyruvic acid in ethereal solution reacts with dry ammonia to form the *ammonium* salt. When this is kept, water is eliminated and the ammonium salt of a pyridinedicarboxylic acid obtained, namely, 3-acetyl-4-methylpyridine-2:6-dicarboxylic acid,



This gives an intense, orange-red coloration with ferrous sulphate.

When boiled with acetic acid or heated above its melting point, a carboxyl group is eliminated, forming 3-acetyl-4-methylpyridine-2(or 6)-carboxylic acid.

*Benzylideneacetylpyruvic acid* has m. p. 165—166°. The  $\alpha$ -phenyl-imide crystallises in orange-yellow plates, m. p. 139°; it only gives a coloration with ferric chloride after a time. The isomeric *anilide* crystallises in large, pale yellow plates, m. p. 140—141°. It immediately gives a coloration with ferric chloride. A mixture of the two isomerides has m. p. 20—30° lower. The compound,  $C_{23}H_{23}O_2N_3$ , produced by interaction with 3 mols. of aniline, crystallises in pale yellow, long rods, m. p. 170° (decomp.). It gives a reddish-violet solution with concentrated hydrochloric acid.

3-Acetyl-4-methylpyridine-2:6-dicarboxylic acid crystallises in colourless prisms + Aq, m. p. 133°, or anhydrous, m. p. 175°. The monocarboxylic acid has m. p. 260°.

The  $\alpha$ -methylimide of acetylpyruvonitrile has m. p. 68°, and has both acid and basic properties. It gives a red coloration with ferric chloride.

*Acetylpyruvamide* has m. p. 131—132° (decomp.). *Ethyl acetylpyruvate  $\alpha$ -imide* crystallises in thin prisms, m. p. 36—38°.

E. F. A.

## Physico-chemical Studies of Photographic Developers. II. Oxidation of Ferrous Ion in Presence of Oxalate Ion.

NIKOLAI SCHILOFF and BORIS BERKENHEIM (*Zeitsch. Elektrochem.*, 1912, 18, 939—943).—Although potassium oxalate and ferrous sulphate in acidified aqueous solution are both unacted on by free oxygen, the gas is rapidly absorbed by solutions containing the two substances. When the oxalate is present in excess, the total amount of oxygen absorbed by a given solution is practically identical with that required for the complete oxidation of the ferrous salt. The quantity of oxalate present remains almost unchanged, the slight diminution actually observed corresponding with the small amount of oxygen absorbed in excess of that required by the ferrous salt.

From observations on the quantity of oxygen absorbed by solutions in which the ratio of oxalate to ferrous salt was continuously varied, it is found that the molar ratio of oxalate to ferrous salt must be at least equal to three before complete oxidation of the ferrous salt is attained.

The facts can be explained on the assumption that the oxidisable substance is the complex ferro-oxalate ion,  $Fe(C_2O_4)_2^{2-}$ . On oxidation, this gives rise to the more stable ferri-oxalate ion, in which the ratio of oxalate to iron is as 3 : 1. Provided the solution contains oxalate in excess of this ratio, complete oxidation of the iron occurs, but if the proportion of oxalate is smaller, the oxidation of the ferro-oxalate ion will become impossible when a certain stage is reached, and the oxygen absorbed by such a solution will be less than that corresponding with the oxidation of the ferrous iron present. In accordance with this view, it is found that the addition of ferric sulphate to a given solution causes a large diminution in the quantity of absorbed oxygen. Furthermore, for a given ratio of oxalate to ferrous salt (this ratio being less

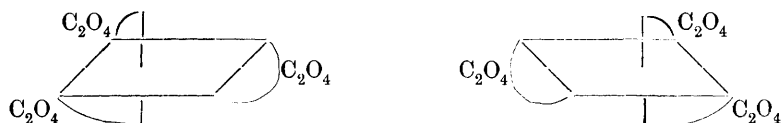
than 3) it is found that the quantity of oxygen absorbed increases with the dilution, which effect is probably due to the increasing dissociation of the complex ferri-oxalate ion.

H. M. D.

### Mirror Image Isomerism with Chromium Compounds. III.

ALFRED WERNER (*Ber.*, 1912, 45, 3061—3070).—The optically active compounds hitherto obtained by the author (*Abstr.*, 1911, i, 613, 838, 960; this vol., i, 10, 96, 298, 417) owe their activity to the presence of an optically active cation; they also contain nitrogen as one of the components of the cation. In the present paper optically active compounds are described containing an optically active anion, which does not contain nitrogen.

The blue trioxalochromiates (chromic oxalates) have the general formula  $[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{R}_3$ , and contain trivalent chromium. Each oxalic acid residue is combined with the central chromium atom by means of a principal and a subsidiary valency, so that the compounds should show molecular asymmetry II, in accordance with the scheme:



When potassium barium trioxalochromiate,  $[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{BaK}$ , is treated with the calculated quantity of dilute sulphuric acid, a solution of the potassium dihydrogen salt,  $[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{KH}_2$ , is obtained. When a hot alcoholic solution of strychnine, in quantity sufficient to give the di-strychnine salt, is added to this solution, a light greyish-violet precipitate of potassium di-strychnine trioxalochromiate separates after a short time. This salt is readily recrystallised from 80% alcohol, and its aqueous solution is optically active, having  $[\alpha]_D + 430^\circ$ . It shows a very pronounced rotation dispersion. The aqueous solution rapidly undergoes auto-racemisation, becoming inactive after one and a-quarter hours. The salt is soluble in aqueous acetone, and the solution is more stable than the one in pure water as solvent, and has  $[\alpha]_D + 450^\circ$ .

When the potassium di-strychnine salt is recrystallised from hot water, the dilute hot solution deposits greyish-violet to slate-grey, leaf-like crystals of a totally different habit from those obtained from alcoholic solution. The aqueous solution of this salt, which is found to be tri-strychnine trioxalochromiate, is laevorotatory,  $[\alpha]_D - 300^\circ$ ; in aqueous acetone,  $[\alpha]_D - 320^\circ$ . To account for this result it was supposed that the potassium di-strychnine salt first obtained was a mixture containing excess of the dextro-salt, but fractional recrystallisation disproved this. Further investigation showed that the mother liquors from which the salts separated were optically inactive, or practically so, but that on concentration further crops of the active salts were obtained.

The observed results can be explained on the assumption that the active salts are produced during the actual process of crystallisation, and that no partial racemates are formed in solution, bearing in mind the fact that auto-racemisation takes place very rapidly. In solutions

which have been warmed, or kept for some time, there are equal quantities of the potassium di-strychnine salt (*d*-acid) and potassium di-strychnine salt (*l*-acid), so that the solution is inactive. The former salt is sparingly soluble in alcohol, and crystallises out; auto-racemisation takes place rapidly in solution, giving fresh quantities of the *d*-salt, which crystallise out, and so on. The result is that an active salt is obtained, leaving an inactive mother liquor. In the case of aqueous solutions it is the *l*-salt which is least soluble, and consequently separates.

The auto-racemisation can be accounted for by assuming that one of the oxalic acid residues is only loosely combined with the chromium atom, and that in solution the linking is partly broken, so that rearrangement can take place. This is supported by the fact that the blue trioxalochromiates readily lose one oxalic acid residue.

That the anion is really optically active in the above salts is shown by the fact that when a paste of the potassium di-strychnine salt is triturated with solid potassium iodide, strychnine iodide is precipitated, leaving a bluish-violet solution from which alcohol precipitates potassium trioxalochromiate. The aqueous solution of this salt gives  $[\alpha]_D^{25} + 1300^\circ$ , which is the highest specific rotation hitherto observed for a compound which has been isolated in the solid state, and is specially remarkable because of the comparative simplicity of the chromium-oxalic acid complex.

*Potassium barium trioxalochromiate*,  $[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{KBa}_2\cdot 2\text{H}_2\text{O}$ , is obtained as a greyish-lilac precipitate when a solution of 20 grams of blue potassium trioxalochromiate in 100 c.c. of cold water is treated with 15 grams of finely powdered barium chloride. It forms strongly dichroic, greyish-lilac needles. *Potassium distrychnine trioxalochromiate* (*d*-acid),  $[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{K}(\text{C}_{21}\text{H}_{23}\text{O}_2\text{N}_2)_2\cdot 4\text{H}_2\text{O}$ , prepared in the way indicated above, forms small, lilac-grey leaflets, with a pearly lustre. For recrystallisation the proportion of  $1\frac{1}{2}$  grams of salt to 100 c.c. of alcohol (8 alcohol : 2 water) must not be exceeded, otherwise the active salt is mixed with racemate. In a three-field polarimeter the aqueous solution gives a greyish-violet middle field, the outer fields being orange in colour. In aqueous solution,  $[\alpha]_D^{25} + 430^\circ$  and  $[\text{M}]_D^{25} + 4719\cdot 25^\circ$ , whilst in acetone solution (7 acetone : 3 water),  $[\alpha]_D^{25} + 450^\circ$ ,  $[\text{M}]_D^{25} + 4937\cdot 75^\circ$ .

*Tristrychnine trioxalochromiate* (*l*-acid),  $[\text{Cr}(\text{C}_2\text{O}_4)_3](\text{C}_{21}\text{H}_{23}\text{O}_2\text{N}_2)_3\cdot 4\text{H}_2\text{O}$ , prepared as indicated above, forms long, glistening leaflets, with a greyish-lilac shimmer. In aqueous solution, as also in aqueous acetone,  $[\alpha]_D^{25} - 330^\circ$  and  $[\text{M}]_D^{25} - 5016^\circ$ .

*d*-Potassium trioxalochromiate,  $[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{K}_3\cdot \text{H}_2\text{O}$ , forms a bluish-green, crystalline precipitate; in aqueous solution,  $[\alpha]_D^{25} + 1300^\circ$  and  $[\text{M}]_D^{25} + 5637^\circ$ ; in aqueous acetone,  $[\alpha]_D^{25} + 1360^\circ$  and  $[\text{M}]_D^{25} + 5897^\circ$ . The *l*-potassium trioxalochromiate,  $[\text{Cr}(\text{C}_2\text{O}_4)_3]\text{K}_3\cdot \text{H}_2\text{O}$ , is obtained from the tri-strychnine salt by a method similar to that used for obtaining the *d*-potassium salt from the *d*-di-strychnine salt. In aqueous solution,  $[\alpha]_D^{25} - 900^\circ$ ,  $[\text{M}]_D^{25} - 4336^\circ$ , and in aqueous acetone,  $[\alpha]_D^{25} - 1000^\circ$ ,  $[\text{M}]_D^{25} - 4903^\circ$ . The rotation is less than that of the *d*-salt, because the preparation takes longer and auto-racemisation occurs to some extent.

T. S. P

**Keto-enolic Tautomerism. VI. Relation between the Constitution and the Equilibrium of Keto-enolic Desmotropic Compounds.** KURT H. MEYER (*Ber.*, 1912, 45, 2843—2864).—The author gives a résumé of the various chemical and physical methods of estimating the proportion of keto- and enolic modifications in a desmotropic compound, and is of opinion that his improved alcoholic bromine- $\beta$ -naphthol process (*Abstr.*, 1911, i, 832) is the best on account of its simplicity and convenience. A large number of desmotropic substances have been examined by this method, with the following important results. Any desmotropic substance which forms individual crystals is an individual compound; keto-enolic tautomerism is not exhibited by the crystallised substance. The modification in which a desmotropic substance exists in the crystalline state is not a criterion of its condition in the liquid or gaseous state; dibenzoylacetylmethane, which is ketonic in the solid state, is enolised to the extent of 98% in benzene, and methyl oxalacetate, enolic in the crystalline form, is present as the keto-form to the extent of 77% in alcohol.

In 3—5% solutions, an approximate proportionality has been observed between the equilibrium constants (that is, ratio of the concentration of the enolic to that of the ketonic modification) of desmotropic substances of allied constitutions and similar solubilities, in any given solvent. Thus the equilibrium constant of methyl benzoylacetate is about 2.2 times, and that of acetylacetone about 30—50 times, as great as that of ethyl acetoacetate in a given solvent.

Substances, such as acetaldehyde, acetone, acetophenone, or pyruvic acid, containing one  $\cdot\text{COR}$  group, do not contain an appreciable amount of the enolic modification, even in alcoholic solution in the presence of sodium ethoxide.

A comparison of substances containing a methylene group attached to two  $\cdot\text{COR}$  groups (where R may be H, Me, Ph, OH, OMe, OEt,  $\text{NH}_2$ ,  $\text{CO}_2\text{Me}$ , or  $\text{CO}_2\text{Et}$ ) shows that the percentage of the enolic modification, in a series of substances (in the liquid state or in alcohol) containing  $\cdot\text{CH}_2\cdot\text{COR}$  in common, increases when the R's in the other  $\cdot\text{COR}$  group are arranged in the order OMe, OEt, OH,  $\text{NHPh}$ , Me, Ph, and  $\text{CO}_2\text{Et}$  (or Me); in other words, to give a specific example, a substance containing a benzoyl group has a greater tendency to enolise than a similarly constituted substance containing an acetyl group.

A similar regularity is not observed in compounds containing three substituents. The tendency to enolise of a substance,  $\text{CH}_2(\text{COR})_2$ , is diminished when a methylene hydrogen atom is replaced by methyl, ethyl, or benzyl, and is, in general, increased when the hydrogen is replaced by another  $\cdot\text{COR}$  group. However, benzoylacetone is entirely enolic, whilst dibenzoylacetylmethane is entirely ketonic, in the crystalline states.

The author's bromine process confirms Wislicenus' statements regarding the isomeric modifications of ethyl formylphenylacetate (this vol., i, 623). The crystalline  $\gamma$ - and  $\beta$ -esters are entirely enolic; the liquid  $\alpha$ -ester consists of 76% of enolic modification (or modifications) and 24% of the keto-form.

C. S.

**Keto-enolic Tautomerism. VII. Desmotropy of Malonic and Methanetricarboxylic Esters.** KURT H. MEYER (*Ber.*, 1912, 45, 2864—2869).—By the alcoholic bromine process, the authors show that (i) ethyl malonate does not contain the enolic modification; (ii) a few units % of the enolic modification are present when a solution of ethyl malonate in alcoholic sodium ethoxide is acidified, but do not persist for more than a minute; (iii) when a solution of ethyl malonate in methyl alcoholic sodium methoxide is added to a cold methyl alcoholic solution of bromine and hydrochloric acid, about 50% of the enolic modification is present. This proves that ethyl sodiomalonate has the constitution  $\text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{C}(\text{ONa})\cdot\text{OEt}$ , and that the free enol changes extremely rapidly to the keto-form.

Similar behaviour is shown by ethyl methanetricarboxylate. The crystalline substance is entirely the ketonic modification. Fused or in alcoholic solution, it contains about 0.2% of the enol. Its solution in methyl alcoholic sodium methoxide contains about 10% of the enol when acidified and treated immediately with alcoholic bromine, and about 80% of the enol when treated simultaneously with hydrochloric acid and the bromine solution.

The author shows that the bromination of malonic acid at  $0^\circ$  by aqueous bromine is independent of the concentration of the bromine. The reaction, therefore, as in the cases of acetone and ethyl acetoacetate, occurs in two stages, a slow change to the enolic form, followed by an immeasurably rapid addition of bromine. C. S.

**Reaction between Maleic Acid and Sodium Thiosulphate.** SEBASTIAN M. TANATAR and I. VOLJANSKY (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1320—1324. Compare this vol., i, 160).—The addition of sodium thiosulphate (1 mol.) solution to a solution of maleic acid (1 mol.) containing sulphuric acid (1 mol.) yields sodium sulphate and the ester,  $\text{CO}_2\text{Et}\cdot\text{CH}(\text{SH})\cdot\text{CH}(\text{SO}_2\cdot\text{OH})\cdot\text{CO}_2\text{Et}$ , which forms a viscous, yellow liquid and, on hydrolysis with hydrochloric acid, gives a mixture of the two acids: (1)  $\text{CO}_2\text{H}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{SO}_2\cdot\text{OH})\cdot\text{CO}_2\text{H}$  and (2)  $\text{CO}_2\text{H}\cdot\text{CH}(\text{SH})\cdot\text{CH}(\text{SO}_2\cdot\text{OH})\cdot\text{OO}_2\text{H}$ ,

the latter being converted into the former, with evolution of hydrogen sulphide, when heated in acid solution. In the pure state, acid (1) decomposes at  $105^\circ$ ; its *silver*,  $\text{C}_4\text{H}_3\text{O}_8\text{SAg}_3$ , *barium*, and *calcium* salts were prepared.

Similar compounds were prepared by the action of potassium sulphite on fumaric and maleic acids by Credner (*Zeitsch. Chem.*, 1870, 77) and Messel (this Journ., 1871, 131) respectively, the latter author obtaining the acid,  $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}(\text{SO}_2\cdot\text{OH})\cdot\text{CO}_2\text{H}$ . T. H. P.

**Condensation of Mercaptans with Formic Acid to Esters of Orthotrithioformic Acid.** JOSEF HOUBEN (*Ber.*, 1912, 45, 2942—2946. Compare Houben and Schultze, this vol., i, 5; Holmberg, *Abstr.*, 1907, i, 474; this vol., i, 161).—The author has shown that methenyltrithiolacetic acid is formed by the action of formic acid on thioglycollic acid in the absence of condensing agents. He has also re-investigated the b. p. of ethyl orthotrithioformate, and, contrary to the experiments of Holmberg (*loc. cit.*), has confirmed the value previously found. H. W.

**Thiolcamphoric Acid.** M. M. RICHTER (*Ber.*, 1912, 45, 3155—3156).—*Monothiolcamphoric acid*,  $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}\cdot\text{SH}$ , prepared by warming a mixture of sulphur and sodium sulphide with camphoric anhydride, forms a viscous oil which readily decomposes, giving off hydrogen sulphide. The anhydride could not be obtained, camphoric anhydride resulting in its place. This was also formed instead of the expected disulphide on oxidation with iodine and potassium iodide in sodium carbonate solution. E. F. A.

***r*-Dilactylic Acid and *i*-Dilactylic Acid.** ÉMILE JUNGFLEISCH (*Compt. rend.*, 1912, 155, 799—804).—The crude dilactylic acid obtained by the action of the sodium derivative of ethyl lactate on ethyl  $\alpha$ -chloropropionate (compare Abstr., 1907, i, 471) consists, for the most part, of the *r*- and *i*-acids, which are separated by means of their magnesium salts, that of the *i*-acid being the less soluble in cold water. After repeated crystallisation, *magnesium *r*-dilactylate*,  $\text{C}_6\text{H}_8\text{O}_5\text{Mg}\cdot 6\text{H}_2\text{O}$ , was obtained in colourless, voluminous prisms. The crystals exhibit marked birefracton, but inappreciable dispersion. The salt is soluble to the extent of 7—8 parts in 100 parts of cold water.

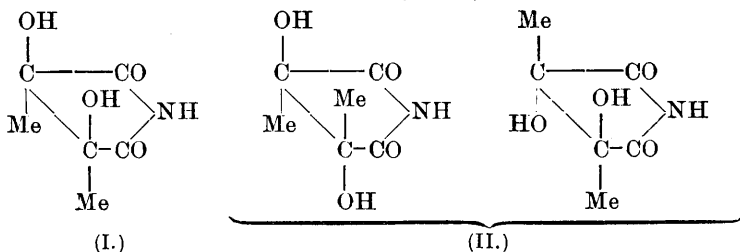
*Magnesium i-dilactylate*,  $\text{C}_6\text{H}_8\text{O}_5\text{Mg}\cdot 3\text{H}_2\text{O}$ , separates in small, grained crystals, with medium birefracton and high dispersive power. At 15°, 100 parts of water dissolve 2.28 parts of the salt. The optical characters of both these salts are given. The acids can be obtained from the salts by solution in dilute sulphuric acid, concentration in a vacuum, and extraction with ether, from which after evaporation the acids separate. The *r*-acid crystallises in large plates, m. p. 142°, and exhibits marked dispersion and strong birefracton. It can be resolved through its brucine salt. The *i*-acid separates in slender needles, m. p. 69—70°, which are hygroscopic. W. G.

**Isomeric Diacetylcyanohydrins and their Transformation into the Imides of Dimethylmesotartaric Acid and Dimethyl-racemic Acid.** OTTO DIELS and PAUL STRAUMER (*Ber.*, 1912, 45, 2946—2953).—According to Fittig, Keller, and Daimler (Abstr., 1889, 490), diacetyl combines with hydrogen cyanide to yield a dicyanohydrin, m. p. 110°. The authors find that this substance is transformed by warm nitric acid or hydrochloric acid into an isomeric cyanohydrin, m. p. 162°. Acetyl chloride transforms each into the same acetyl derivative, obviously on account of the transformation of the cyanohydrin of lower m. p. into that of higher m. p. by the liberated hydrogen chloride. Attempts to hydrolyse the two cyanohydrins are rendered difficult for a similar reason, but, under definite conditions, the authors have succeeded in obtaining different products of hydrolysis of the two substances, which they regard, however, as cyclic imides of the formulæ I and II (next page).

Saponification by alkali in the cold converts these substances into solutions which show differences similar to those observed with the two inactive modifications of tartaric acid.

Diacetylcyanohydrin, m. p. 110°, after softening at 108°, was obtained by the action of an anhydrous ethereal solution of hydro-

cyanic acid on diacetyl in the presence of potassium carbonate. When boiled with concentrated nitric acid (D 1·4) during one and a-half



minutes, it was transformed into the *isomeride*, m. p. about 162°, after softening at 155°. The latter, when heated above its m. p., evolved hydrogen cyanide and diacetyl, which, on cooling, partly recombined to form the cyanohydrin, m. p. 110°. The latter was also obtained when a solution of the former in hot water was allowed to cool. Either cyanohydrin, on treatment with acetyl chloride and a trace of sulphuric acid, yielded the same *diacetyl* derivative, m. p. 172°.

The cyanohydrin, m. p. 110°, was hydrolysed by prolonged treatment with fuming hydrochloric acid at 40—42°. Among the products were ammonium chloride, the cyanohydrin, m. p. 162°, a *substance*, m. p. about 245° (decomp.) after previous softening, and the well-crystallised *imide*, m. p. 171°. When the latter was treated with zinc dust, unpleasant, basic vapours were evolved, which imparted a deep cherry-red colour to a pine shaving moistened with hydrochloric acid. The cyanohydrin, m. p. 162°, was hydrolysed under similar conditions, and an *imide*, m. p. 160°, obtained, which behaved similarly to the above imide on treatment with zinc dust.

Both imides were saponified by potassium hydroxide (33%). The product obtained from the imide, m. p. 171°, gave no precipitate with calcium chloride in weak acetic acid solution, and did not deposit crystals of an acid potassium salt when strongly acidified with the same reagent. In the same circumstances, the solution obtained from the imide, m. p. 160°, gave an immediate white precipitate with calcium chloride, and, after a short time, a crystalline precipitate when strongly acidified with acetic acid.

H. W.

**Hydrolysis of *l*-Acetylmalic Acid.** BROR HOLMBERG (*Ber.*, 1912, 45, 2997—3008).—In connexion with his views on the Walden inversion (this vol., i, 603), the author has submitted to careful examination the hydrolysis of *l*-acetylmalic acid.

*l*-Acetylmalic acid obtained by the method of Anschütz and Bennert (*Abstr.*, 1890, 363) has m. p. 134—135°,  $[\alpha]_D -10\cdot71^\circ$  (in water), whilst conductivity determinations give  $k$  0·00237. The sodium salt in water has  $[\alpha]_D -1\cdot46^\circ$ .

Hydrolysis of this substance by alkalis or acids gives malic acid of practically the rotation expected for the pure acid. It is therefore surmised that in the hydrolysis by either method, scission occurs at the valency attaching the Ac-group to the malic acid nucleus; if

scission occurred at the AcO-linking, racemisation or inversion would be expected.

From a kinetic consideration of the reactions it is deduced that the alkali hydrolysis should be bimolecular, but the acid hydrolysis unimolecular; experiment confirms this view, but wholly different velocity constants are observed for different concentrations or different alkalis in the first case, whilst in the second case the velocity constants are not directly proportional to the concentration of the hydron. These discrepancies are explained by the effect of the cation in the first case, and in the second case by the suggestion that the acetylmalic ion undergoes hydrolysis much more rapidly than the undissociated acid.

In an addendum, the author replies to Senter's criticism (this vol., i, 828).  
D. F. T.

**Mechanism of Oxidation Processes.** HEINRICH WIELAND (*Ber.*, 1912, 45, 2606—2615).—It has been shown previously (this vol., i, 248) that the catalytic oxidation of primary alcohols to aldehydes by finely divided metals of the platinum group is due to the activation of the hydrogen, which probably combines with the metal to form a hydride.

The further oxidation of aldehydes to acid appears to be due to a similar dehydrogenation of the aldehyde-hydrate, and not to the direct introduction of oxygen in the molecule, as is usually imagined:  $\text{CHR}(\text{OH})_2 \rightarrow \text{R} \cdot \text{CO}_2\text{H} + \text{H}_2$ .

This view is supported by the following facts: when moist acetaldehyde or benzaldehyde is shaken with palladium-black in the absence of air, acetic and benzoic acids are produced, together with hydrogen, which remains combined with the palladium. Admission of air to the reaction mixture causes the oxidation of the hydrogen to water. The oxidation of the hydrogen may also be effected by means of *p*-benzoquinone, methylene-blue, and other quinonoid compounds; thus moist acetaldehyde, when shaken with palladium and *p*-benzoquinone in the absence of air, is oxidised to acetaldehyde, the quinone being reduced first to quinhydrone and finally to quinol.

That the oxidation of aldehydes to acids by other oxidising agents really consists in the dehydrogenation of the aldehyde-hydrate is rendered very probable by the behaviour of acetaldehyde towards silver oxide. When perfectly dry these two substances do not react, although oxidation at once ensues if moist silver oxide is used. Further, chloral in benzene solution is oxidised only very slowly by silver oxide, whilst the hydrate suffers almost instantaneous oxidation.

The dehydrogenation of formaldehyde proceeds in a manner somewhat different from that of the aldehydes already mentioned. Formaldehyde at once reduces silver oxide with the formation of carbon monoxide and not of formic acid, as was to be expected from the behaviour of acetaldehyde and benzaldehyde; when passed over palladium-black, it is decomposed into carbon monoxide and hydrogen.

Although it is probable that the oxidation of aldehydes usually takes place by the dehydrogenation of an aldehyde-hydrate, the author agrees with Baeyer and Villiger (*Abstr.*, 1900, i, 437) that the first phase in the autoxidation of aldehydes consists in the addition of

oxygen to the carbonyl group with the formation of a per-acid, which then reacts with a second molecule of aldehyde to form the corresponding acid.

The autoxidation of acetaldehyde and benzaldehyde is greatly accelerated by the presence of palladium, a result, no doubt, due to the adsorption of the oxygen by the finely divided metal, whereby the concentration of the oxygen is enormously increased. Quantitative experiments on the rate of oxidation of benzaldehyde by oxygen, both in the presence and absence of palladium, show that water has little effect on the velocity of oxidation; this is referred to the slow rate at which the dehydrogenation of the aldehyde-hydrate proceeds, as compared with the formation of acid by direct autoxidation. With acetaldehyde, on the other hand, the catalytic oxidation by palladium is retarded by the presence of water. The authors explain this result on the assumption that the concentration of the aldehyde is diminished, owing to the formation of the aldehyde-hydrate, which does not undergo autoxidation.

It is also mentioned that the first phase in the catalytic autoxidation of acetaldehyde by dry palladium consists in the formation of acetic anhydride.

It has been shown previously (this vol., i, 347) that the initial product of the combustion of carbon monoxide is formic acid, which then decomposes into carbon dioxide and hydrogen. Since carbon monoxide is an intermediate product in the combustion of coal gas in the bunsen flame, the author has examined the products for formic acid; cold water, on which a flame was allowed to impinge, was found to contain a small amount of formic acid. The acid was also identified in the air of rooms in which flames were burning and in the products of combustion of methane.

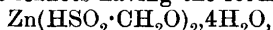
Under the influence of dry palladium at 250°, methane breaks down into carbon and hydrogen. When passed in a moist condition through a hot tube, it yields carbon dioxide and hydrogen.

The author also finds that carbon burns slowly in dry oxygen at 730°, thus confirming the observation of Baker (Abstr., 1889, 465).

F. B.

**Preparation of Crystalline Zinc Formaldehydesulphoxylate.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 248253. Compare Abstr., 1910, i, 40, and ii, 291).—The di-zinc salt of formaldehydesulphoxylic acid has been previously prepared, and the anhydride ("Decrolin") finds technical employment.

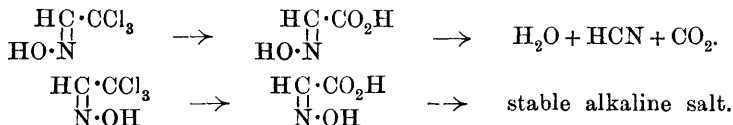
When a solution containing zinc formaldehydesulphite and zinc formaldehydesulphoxylate after concentration under reduced pressure is treated with alcohol, the former salt remains in solution, whilst zinc formaldehydesulphoxylate,  $\text{Zn}(\text{HSO}_2 \cdot \text{CH}_2\text{O})_2$ , separates in crystalline form; a 70% aqueous solution of this salt at 20° slowly deposits small, rhombic leaflets having the formula



whilst a 100% aqueous solution at 60° furnishes the compound  $\text{Zn}(\text{HSO}_2 \cdot \text{CH}_2\text{O})_2 \cdot 3\text{H}_2\text{O}$  in glistening mother-of-pearl-like scales.

F. M. G. M.

**Stereoisomerism of Trichloroacetaldoxime.** F. CARLO PALAZZO (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 530—535. Compare Palazzo and Fazio, *Abstr.*, 1911, i, 421).—As a result of experiments [with Egidi] shortly to be published, the author finds an explanation of the anomalies previously observed in regard to Meyer's chloraloxime in the fact that it is not an individual substance, but a mixture of two stereoisomerides. The decomposition with alkali is to be regarded as occurring as follows:



R. V. S.

**Synthesis of Alkyl Glucosides by the Action of Emulsin.**  
 *$\beta$ -isoPropyl Glucoside and  $\beta$ -isoAmyl Glucoside.* ÉMILE BOURQUELOT and MARC BRIDEL (*Compt. rend.*, 1912, 155, 854—857; *J. Pharm. Chim.*, [vii], 6, 442—445. Compare this vol., i, 790).—The glucosides were prepared by the general method already described (this vol., i, 672).  *$\beta$ -isoPropyl glucoside*, m. p. 123—125° (corr.), crystallises in colourless, odourless, hygroscopic needles, having a bitter taste. It is soluble in water, alcohol, and ethyl acetate, and has  $[\alpha]_D - 36.3^\circ$  in water. It has a very feeble reducing power, probably due to the presence of a small amount of dextrose. The synthesis is not so complete as in the case of its isomeride,  *$\beta$ -propyl glucoside*, thus showing an analogy with the esterification of the alcohols.  *$\beta$ -isoAmyl glucoside*, m. p. 99—100° (corr.), crystallises in colourless needles, having a disagreeable bitter taste; it is not hygroscopic, and does not reduce Fehling's solution; it has  $[\alpha]_D - 36.4^\circ$  in water. Both these glucosides are readily hydrolysed by emulsin in aqueous solution. W. G.

**Synthesis of Alkyl Galactosides by means of Emulsin.**  
 *$\beta$ -Ethyl Galactoside.* ÉMILE BOURQUELOT and HENRI HÉRISSEY (*Compt. rend.*, 1912, 155, 731—733; *J. Pharm. Chim.*, 1912, [vii], 6, 385—390. Compare Bourquelot and Bridel, this vol., i, 592, 672, 790).— *$\beta$ -Ethyl galactoside* can be synthesised by the action of emulsin, obtained from almonds, on a 0.5% solution of galactose in alcohol (79—80%), kept at the room temperature for eighty-three days. So prepared, it crystallises in fine needles, m. p. 123—125°, and agrees in all respects, save its melting point, with the  *$\beta$ -ethyl galactoside* prepared by Fischer and Armstrong from  *$\beta$ -acetylchlorogalactose* (compare *Abstr.*, 1902, i, 746). It is readily hydrolysed by sulphuric acid, or slowly by the same emulsin. Hydrochloric acid in alcoholic solution converts it into its  *$\alpha$ -isomeride*. W. G.

**The Preparation of Glucosides.** WALTER A. JACOBS (*J. Biol. Chem.*, 1912, 12, 427—428).—Two methods for the preparation of glucosides were devised by Fischer; in the first, the alcoholic solution of the sugar is saturated with hydrochloric acid; this is neutralised with barium carbonate and removed as barium chloride. The large

expenditure of time required for repeated concentrations and extractions with alcohol led him to devise a second method, in which the sugar and alcohol are heated with a small amount of dry hydrochloric acid for thirty to fifty hours, and the acid removed by silver oxide, but the reaction occupies several days and is not complete. The following method is simple and gives a good yield in a day. The sugar and alcohol are treated with acid as in Fischer's first method. After an hour all reducing power disappears; the mixture is then concentrated to a quarter of its volume in a vacuum at 20°, and then poured into ordinary alcohol containing a little acetic acid. The excess of hydrochloric acid is removed by lead carbonate, and the filtrate after treatment with hydrogen sulphide is then concentrated in a vacuum and the glucosides isolated as usual. W. D. H.

**The Behaviour of Starch under the Influence of the Silent Electric Discharge.** WALTHER LÖB (*Biochem. Zeitsch.*, 1912, 46, 121—123).—One c.c. of 1% starch solution after the action of the discharge for two and a-quarter hours gives only a faint yellow colour with iodine solution, osazones can be formed, and the solution readily reduces Fehling's reagent. 0.5 Gram dissolved in 3 c.c. of water still yields a blue colour with iodine solution after four hours' action of the discharge; in this case the solution also yields osazones. Ten c.c. of 1% starch solution gives no reaction with iodine after three and a-quarter hours' treatment. S. B. S.

**Influence of Temperature on Hydration of and Absorption of Alkali by Regenerated Cellulose.** CLAYTON BEADLE and HENRY P. STEVENS (*8th Intern. Congr. Appl. Chem.*, 1912, 13, 25—38).—An investigation on the influence of temperature on the absorption of water and sodium hydroxide from aqueous sodium hydroxide solutions containing 1—25% sodium hydroxide by regenerated cellulose, the particular form of regenerated cellulose employed being a monofil of 360 denier made by the cuprammonium process.

It is found that, for any given temperature between 5° and 40°, a maximum hydration takes place, these maxima being greater the lower the temperature; the maximum for 0°, however, falls below that for 5°; at 5°, 12°, 20°, 30°, and 40°, maximum hydration takes place in about 9%, 10%, 10—11%, 11—12%, and 11—12% sodium hydroxide solution respectively, the amounts of water absorbed per 100 parts of regenerated cellulose at these maxima being roughly 2700, 1560, 920, 620, and 480 parts.

Similarly with regard to the absorption of sodium hydroxide, in which case maximum absorption at 5°, 12°, 20°, 30°, and 40° takes place in 9%, 10%, 11—12%, 12—14%, and 14% sodium hydroxide solution respectively, the maximum amounts of sodium hydroxide absorbed being 256, 162, 112, 82, and 78 parts respectively per 100 parts of regenerated cellulose.

The solution absorbed by the cellulose from dilute sodium hydroxide solutions between 0° and 40° is more concentrated than the unabsorbed or surrounding liquid, but for every given temperature there exists a certain concentration at which the absorbed solution has the same

composition as the surrounding solution; this point is somewhere about 6% for 0°, 8–9% for 20°, and 9–10% for 30°.

The effect of the addition of sodium chloride to the sodium hydroxide solution has also been investigated. It is found that the hydration of the cellulose varies but very slightly, increasing between 4% and 13% sodium hydroxide content, above which strength it slightly diminishes; at its maximum hydration (at 5°) it is never more than about one-tenth of the hydration observed in the absence of sodium chloride. The proportion of sodium hydroxide absorbed by the cellulose, however, becomes greater owing to the presence of the sodium chloride.

The addition of other soluble salts also alters the hydration and sodium hydroxide absorption in a marked degree. W. H. G.

**Methylethylpropylisobutylammonium *d*-Camphorsulphonate.** EDGAR WEDEKIND (*Ber.*, 1912, 45, 2940–2942. Compare Pope and Read, *Trans.*, 1912, 101, 519).—The author has made unsuccessful attempts to resolve methylethylpropylisobutylammonium hydroxide by means of *d*-camphorsulphonic acid and *d*-bromocamphorsulphonic acid.

H. W.

**Action of Metals on Alkyldichloroamines.** ERWIN OTT (*Ber.*, 1912, 45, 2922–2923).—According to Willstätter and Kahn, the action of finely-divided silver on dimethylchloroamine results in the formation of tetramethylmethylenediamine,  $\text{CH}_2(\text{NMe}_2)_2$ , and dimethylamine hydrochloride. The author shows that silver, zinc or magnesium have very little action on solutions of alkyldichloroamines in neutral solvents. Baeyer's "activated" magnesium reacts readily with ethereal solutions of dichloroamines, and yields the amines themselves after addition of water. Sodium reacts vigorously with a solution of ethyldichloroamine in xylene at 80–100°, with evolution of nitrogen, saturated hydrocarbons, and acetylene, and formation of sodium chloride and sodium acetylides. Methyldichloroamine behaves somewhat similarly, without, however, evolving acetylene.

$\beta$ -Alkylhydroxylamines may be readily isolated as intermediate products in the reduction of alkyldichloroamines to amines in aqueous alkaline suspension by means of metals, alkali sulphides, etc.

H. W.

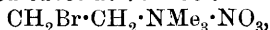
**Preparation of a Therapeutically Valuable Derivative of Hexamethylenetetramine.** EMANUEL MERCK and W. EICHHOLZ (D.R.-P. 247990).—When an alcoholic solution of hexamethylenetetramine is treated with an equimolecular proportion of glycocholic acid, the solution evaporated in a vacuum, and the syrupy product left in a desiccator, it hardens to a mass which can be pulverised and sinters at about 78°, decomposing without fusion at 100–103°.

F. M. G. M.

**Some Derivatives of Choline. II.** ROEMER R. RENSCHAW (*J. Amer. Chem. Soc.*, 1912, 34, 1615–1619).—[With F. G. FLOOD].—Iodocholeline iodide, m. p. 237.5° (corr.), can be obtained in 70% yield by leaving a solution of trimethylamine (1 mol.) and ethylene iodide

(1 mol.) in toluene for 6—8 days in sealed tubes. The *periodide*,  $\text{CH}_2\text{I}\cdot\text{CH}_2\cdot\text{NMe}_3\text{I}_2$ , forms long, dark reddish-brown, lustrous needles. Iodocholine *nitrate*, m. p.  $183\cdot5^\circ$  (corr.), prepared by the interaction of iodocholine iodide and silver nitrate, crystallises in thin, lustrous plates, and when heated for twelve hours with an aqueous solution of silver glycerophosphate yields silver iodide, choline phosphate, glycerol, and some silver phosphate.

[With B. M. MACBRIDE.]—Bromocholine bromide, m. p.  $235\cdot5^\circ$  (corr.), can be obtained in 90% yield by heating ethylene bromide with trimethylamine in sealed tubes at  $70\text{--}80^\circ$ . The *nitrate*,



m. p.  $200^\circ$  (corr.), crystallises in large plates.

E. G.

**New Compounds of the Choline Type. II. Acetyl Derivatives of  $\alpha$ -Methylcholine, " $\beta$ -Homocholine," and " $\gamma$ -Homocholine."** G. A. MENGE (*J. Biol. Chem.*, 1912, 13, 97—109).—The compounds described are prepared by heating the choline compound with a considerable excess of the acyl chlorides generally in a sealed tube at  $100^\circ$ . The reaction product is poured into dry ether, and the acyl derivative separated as an oily solid.

*Acetyl- $\alpha$ -methylcholine* is a slightly oily, crystalline, hygroscopic, white solid; the *platinichloride* forms a dense yellow, crystalline precipitate, m. p.  $222\text{--}223^\circ$  (corr.); the *aurichloride* is a pale yellow, crystalline solid, m. p.  $124\text{--}125\cdot5^\circ$  (corr.).

*Benzoyl- $\alpha$ -methylcholine* forms a crystalline, hygroscopic solid; the *platinichloride* darkens above  $233^\circ$ , decomp.  $236\cdot5\text{--}237\cdot5^\circ$  (corr.); the *aurichloride* forms a pale yellow, very viscous oil.

*Phenylacetyl- $\alpha$ -methylcholine* is likewise an oil. The *platinichloride* has decomp.  $245\cdot7\text{--}246\cdot7^\circ$  (corr.).

*Phenylacetyl- $\beta$ -methylcholine* is precipitated as an oily semi-solid product; the *platinichloride* has m. p.  $216\text{--}217^\circ$  (corr.). The *aurichloride* sinters above  $60^\circ$ , m. p.  $74\cdot5\text{--}76^\circ$ , becoming limpid and clear at  $85^\circ$ .

*Phenylacetyl- $\gamma$ -homocholine* separates as a colourless, flaky solid. The *platinichloride* crystallises in clusters of prisms, m. p.  $193\text{--}194^\circ$  (corr.); the *aurichloride* forms flaky crystals, m. p.  $129\text{--}131^\circ$  (corr.).

*Propionyl- $\alpha$ -methylcholine* forms a *platinichloride*, m. p.  $231\text{--}232^\circ$  (corr.).

*Valeryl- $\alpha$ -methylcholine* *platinichloride* sinters above  $219^\circ$ , decomp. with effervescence  $228\text{--}229^\circ$  (corr.); the *aurichloride* forms prisms, which sinter at  $72^\circ$ , m. p.  $75^\circ$ .

*Monobromoisoheptyl- $\alpha$ -methylcholine* *platinichloride* crystallises in clusters of very fine needles, decomp.  $226\text{--}227^\circ$  (corr.).

The *platinichloride* of *palmityl- $\alpha$ -methylcholine* decomp.  $240\text{--}241^\circ$ ; the *aurichloride* has m. p.  $72\text{--}75^\circ$ .

E. F. A.

**Behaviour of the Amino-acids and Polypeptides to Neutral Salts. I.** PAUL PFEIFFER and J. VON MODELSKI (*Zeitsch. physiol. Chem.*, 1912, 81, 329—354).—The amino-acids and polypeptides form well characterised, crystalline compounds with neutral salts, which exist also in aqueous solution. They are obtained either by allowing an aqueous solution of the components to evaporate, or by adding alcohol and effecting crystallisation in closed vessels.

Glycine forms additive compounds with the chlorides and bromides of calcium, strontium, and barium of the type  $\text{CaCl}_2 \cdot 2\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , which are stable in the air. Calcium chloride also forms compounds with 1 and with 3 mols. of glycine; barium chloride, however, yields only one type of compound. Lithium chloride and bromide yield compounds with 1 and 2 mols. of glycine; lanthanum chloride combines with 3 mols. Alanine, glycylglycine, and diglycylglycine form similar additive compounds with calcium and lithium chlorides.

These compounds are considered to have the constitution of salts both of the carboxyl and amine group, namely,  $\text{R} \begin{smallmatrix} \text{CO}_2\text{M} \\ \text{NH}_3\text{X} \end{smallmatrix}$ , and are accordingly termed amphi-salts.

Glycine is more soluble in water in presence of neutral salts. The negative residues of the alkaline earth salts arranged in decreasing order of activity are as follows:  $\text{ClO}_4 \rightarrow \text{NO}_3 \rightarrow \text{Br} \rightarrow \text{Cl} \rightarrow \text{CO}_2\text{Me}$ . Calcium is more active than strontium or barium in increasing solubility.

It is considered that most of the protein salt complexes known are true chemical compounds.

*Diglycine barium chloride*,  $\text{H}_2\text{O}$ , forms large, transparent crystals with rhombic faces. It has not melted at  $250^\circ$ . The corresponding *bromide* forms characteristic, transparent plates, m. p.  $180^\circ$ .

*Diglycine strontium chloride*,  $3\text{H}_2\text{O}$ , separates in colourless, transparent, radially grouped crystals, which sinter at  $75\text{--}80^\circ$ . The *bromide* forms similar prismatic crystals, m. p.  $94^\circ$ , to a clear, viscid mass.

*Diglycine calcium chloride*,  $4\text{H}_2\text{O}$ , yields transparent, prismatic needles, m. p.  $68^\circ$ . The corresponding *bromide* forms colourless, flat needles without any definite melting point.

*Diglycine magnesium chloride*,  $2\text{H}_2\text{O}$ , forms tiny, colourless, intergrown crystals, which sinter at  $215\text{--}220^\circ$ .

*Diglycylglycine calcium chloride* gives anhydrous, transparent crystals of varying habit, which are not melted at  $250^\circ$ .

*Glycylglycine lithium chloride* crystallises in small, transparent needles.

*Dialanine calcium chloride*,  $3\text{H}_2\text{O}$ , forms colourless needles. E. F. A.

Losses in the Isolation of the Monoamino-acids by the Ester Method. III. Liberation of the Esters by means of Lead Hydroxide. EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1912, 81, 226—227).—Zelinsky, Annenkoff, and Kulikoff (Abstr., 1911, i, 773) have described the preparation of the free amino-acid esters from their hydrochlorides by heating with excess of lead hydroxide. The method has been tested with alanine and glycine or with mixtures of both acids, but the yields obtained are very unsatisfactory. E. F. A.

The Possible Isomeric Tripeptides from the Three Mono-aminocarboxylic Acids: Glycine, *d*-Alanine, and *l*-Leucine. EMIL ABDERHALDEN and ANDOR FODOR (*Zeitsch. physiol. Chem.*, 1912, 81, 1—52).—The six possible tripeptides from glycine, *d*-alanine, and *l*-leucine have been synthesised by the ordinary methods. They differ only slightly in physical properties; this emphasises the difficulty of the identification of proteins. Mixtures of all six cannot be separated into the components.

The cell ferments (press juice from liver or pancreas, etc.) behave alike as regards the order in which they attack the tripeptides. Activated pancreatic extract behaves quite differently, attacking the compounds from the other end.

*Chloroacetyl-d-alanyl-l-leucine*, prepared from *d*-alanyl-*l*-leucine,  $[\alpha]_D^{20} - 16.96^\circ$ , crystallises in macroscopic needles in feather-like aggregates, m. p.  $175^\circ$ ,  $[\alpha]_D^{20} - 51.58^\circ$ .

*Glycyl-d-alanyl-l-leucine* separates in macroscopic, slender, colourless needles, m. p.  $239-240^\circ$  (decomp.),  $[\alpha]_D^{20} - 89.85^\circ$ . The *copper* derivative is a bright blue, amorphous, glassy mass.

*Chloroacetyl-l-leucyl-d-alanine* forms colourless crystals, m. p.  $136-137^\circ$ ,  $[\alpha]_D^{20} - 41.5^\circ$ .

*Glycyl-l-leucyl-d-alanine* crystallises in concentrically arranged needles of silky lustre, m. p.  $235-236^\circ$ ,  $[\alpha]_D - 59.04^\circ$ . The *copper* derivative is reddish-violet in aqueous solution.

*Chloroacetyl-l-leucine* has m. p.  $132-133^\circ$ ,  $[\alpha]_D^{20} - 13.82^\circ$ ; the corresponding dipeptide has  $[\alpha]_D - 35.23^\circ$ .

*d-a-Bromopropionylglycyl-l-leucine* forms macroscopic, concentrically grouped needles or prisms, m. p.  $152^\circ$ ,  $[\alpha]_D^{20} + 14.7^\circ$ .

*d-Alanylglycyl-l-leucine* separates in lustrous, silky needles, m. p.  $243^\circ$  (decomp.),  $[\alpha]_D^{20} - 11.2^\circ$ . The copper compound forms a vitreous blue mass, dissolving in water with an ultramarine-blue coloration. *l*-Leucylglycine has  $[\alpha]_D^{20} - 84.5^\circ$ .

*a-d-Propionyl-l-leucylglycine* crystallises in slender, intergrown needles, m. p.  $154-155^\circ$ ,  $[\alpha]_D^{20} - 24.8^\circ$ .

*d-Alanyl-l-leucylglycine* forms needles, m. p.  $246-247^\circ$  (decomp.),  $[\alpha]_D^{20} - 30.43^\circ$ . The *copper* salt is greyish-blue and violet-red in aqueous solution.

*d-Alanylglycine* has  $[\alpha]_D^{20} + 48.33^\circ$ .

*a-d-Bromoisohexoyl-d-alanylglycine* yields stellate aggregates of needles, m. p.  $129^\circ$ ,  $[\alpha]_D^{20} - 2.52^\circ$ .

*l-Leucyl-d-alanylglycine* crystallises in slender needles, which become brown at  $244^\circ$ , m. p.  $252-253^\circ$ . The copper compound is unique in being very soluble in absolute alcohol.

*Glycyl-d-alanyl-l-leucine* is hydrolysed by yeast juice to glycine and *d*-alanyl-*l*-leucine.

*Glycyl-l-leucyl-d-alanine* is hydrolysed in a similar manner to glycine and *l*-leucyl-*d*-alanine. The precise character of the products of hydrolysis of these two tripeptides by other ferment solutions could not be established.

*d-Alanylglycyl-l-leucine* is hydrolysed by activated pancreas extract to *d*-alanylglycine and *l*-leucine; all other enzymes convert it into *d*-alanine and glycyl-*l*-leucine.

*d-Alanyl-l-leucylglycine* is hydrolysed by all enzymes to *d*-alanine and *l*-leucylglycine.

*l-Leucyl-d-alanylglycine* gives *l*-leucyl-*d*-alanine with activated pancreas enzyme, and *d*-alanylglycine and *l*-leucine in all other cases.

Lastly, *l*-leucylglycyl-*d*-alanine gives glycyl-*d*-alanine and *l*-leucine with yeast extract, and *l*-leucylglycine and *d*-alanine with pancreas extract.

E. F. A.

**Separation of Amino-acids by means of the Carbamino-reaction.** MAX SIEGFRIED and E. SCHUTT (*Zeitsch. physiol. Chem.*, 1912, 81, 260—273).—The carbamino-reaction for the separation of amino-acids has been tested under a variety of conditions (compare Siegfried and Schmitz, Abstr., 1910, i, 448). It is found that glutamic and aspartic acids are completely precipitated, glycine almost completely, and about four-fifths of the total leucine and asparagine. Glucosamine is also precipitated to the extent of 80%. Some 20—35% of the other monoamino-acids are precipitated as carbamino-derivatives; phenylalanine, however, which is very resistant to the carbamino-reagent (Siegfried and Neumann, Abstr., 1908, i, 379), only gives about 8% of precipitate.  
E. F. A.

**Putrefaction Researches with *d*-Glutamic Acid and Studies on  $\gamma$ -Aminobutyric Acid.** EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1912, 81, 294—314).—Ackermann stated that in the putrefaction of glutamic acid mixed with sodium chloride, dextrose and Witte's peptone,  $\gamma$ -aminobutyric acid was found in small quantity. It is very doubtful if this originates from the glutamic acid, for in the present research no trace of it was found either when glutamic or pyrrolidonecarboxylic acid was employed. The question whether by biological (bacterial) agents, pyrrolidonecarboxylic can be converted into pyrrolidinecarboxylic acid was also investigated, but without decisive results.  
W. D. H.

**Decomposition of Salts of Glutamic Acid on Heating their Aqueous Solutions and a New Optically Active Non-sugar.** VLADIMIR STANĚK (*Zeitsch. Zuckerind. Böhm.*, 1912, 37, 1—17).—When aqueous solutions of glutamic acid are heated, two isomeric acids are formed, namely, *l*-glutimic acid, which predominates at lower temperatures, such as those customary in sap-boiling in the industry, and *dl*-glutimic acid, which is almost the sole product at temperatures above 200°. *l*-Glutimic acid forms colourless crystals, m. p. 162—163°,  $[\alpha]_D - 9.9^\circ$ ; when hydrolysed with hydrochloric acid the levorotatory hydrochloride of glutamic acid is obtained. In similar conditions inactive glutimic acid yields the hydrochloride of *dl*-glutamic acid. *l*-Glutimic acid has been identified in molasses, where it is present to the extent of at least 3%. This causes an error of 1.23% in the determination of the sugar present by polarimetric methods.  
E. F. A.

**The Copper Complexes of Amino-acids, Peptides, and Peptones.** I. PHILIP A. KOBER and K. SUGIURA (*J. Biol. Chem.*, 1912, 13, 1—14).—A quantitative method is described for preparing copper salts of soluble amino-acids and peptides, of insoluble amino-acids having soluble copper salts, and insoluble amino-acids having insoluble copper salts. Some fifty of these compounds are described, and contain 1 atom of copper to one mol. of peptide. On an average, 99% of the copper of all amino-acid salts is precipitated as oxide when treated with a certain excess of alkali. In the case of peptide salts, the figure varies from 6.3 to 7.3%.  
W. D. H.

**Copper Complexes of Amino-acids, Peptides, and Peptones.**  
**II. Their Configurations and Relation to the Biuret Reaction.** PHILIP A. KOBER and K. SUGIURA (*Amer. Chem. J.*, 1912, 48, 383—411).—In an earlier paper (preceding abstract) it has been shown that monobasic  $\alpha$ -amino-acids invariably form complex copper salts,  $\text{CuA}_2$ , and that the same is true of  $\beta$ -amino-acids except in cases, such as *isoserine*, in which there is an OH-group in the  $\alpha$ -position. With dibasic amino-acids, such as glutamic and aspartic acids, compounds of the formula  $\text{CuA}$  are produced. Fischer has found that amino-acids with the  $\text{NH}_2$ -group in the  $\gamma$ -,  $\delta$ -, or  $\epsilon$ -position do not form complex copper salts whether there is an OH-group in the  $\alpha$ -position or not.

The results of the examination of fifty polypeptides have now shown that 1 mol. of polypeptide combines with only 1 mol. of copper hydroxide. The imino-group alone does not seem sufficient to form a copper salt; thus bromo- or chloro-derivatives of dipeptides, as well as hippuric acid and formyl derivatives of amino-acids, all having an imino-group but no amino-group, do not form complex salts with copper hydroxide. On the basis of these facts and a consideration of the valency of protein nitrogen, a discussion is given of the possible configurations of the copper complexes.

A study has been made of the behaviour of the various classes of amino-acids towards the biuret reaction. It has been found that all simple dipeptides from monoamino-acids (excluding their amides) and their carboxyl derivatives give a deep blue colour with copper in alkaline solution. The neutral copper salts of all tripeptides from monoamino-acids and their carboxyl derivatives (amide derivatives excepted) and of all amides of dipeptides change colour on addition of excess of alkali and give "semi-biuret" colours, of shades varying with the constituent amino-acids and the temperature. The colour of the neutral copper salts of all tetrapeptides of monoamino-acids and of amides of tripeptides change on addition of excess of alkali from the deep blue of the neutral copper complex to the purple-red biuret colour. It seems that a true biuret reaction can only take place when four nitrogen atoms are so arranged that they can combine "co-ordinately" (in the sense in which the word is used by Werner) with the copper in an alkaline solution. A semi-biuret reaction can only occur when three nitrogen atoms are so arranged that they can combine co-ordinately with the copper in an alkaline solution. E. G.

**Preparation of  $\alpha$ -Bromo- $\alpha$ -ethylbutyrylcarbamide.** FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 249906).—It is found that  $\alpha$ -bromo- $\alpha$ -ethylbutyrylcarbamide (Abstr., 1911, i, 118), m. p. 116—118°, can be more satisfactorily prepared as follows: (1)  $\alpha$ -bromo- $\alpha$ -ethylbutyrylamide (100 parts) is dissolved in 500 parts of carbon tetrachloride, and treated with the requisite amount of cyanic acid and the mixture heated at 100° during five hours, or (2) from  $\alpha$ -bromo- $\alpha$ -ethylbutyrylcarbamyl chloride, a colourless liquid, b. p. 90—98°/20 mm. (obtained by the action of phosphorus pentachloride on  $\alpha$ -bromo- $\alpha$ -ethylbutyrylurethane), by the action of 10% ammonium hydroxide solution (3 parts) at a low temperature. F. M. G. M.

**Preparation of Amides and Carbamides of Higher Bromo- or Iodo-fatty Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 248993).—The amides and carbamides of halogenated acids containing an eleven-carbon complex are found to be of therapeutic value, and to be readily prepared by ordinary methods.

*Di-iodobrassidyl chloride* crystallises from methyl alcohol; the *amide*, colourless aggregates, has m. p.  $93^{\circ}$ , and can also be prepared by treating *behenolamide* (m. p.  $92^{\circ}$ ) at  $60^{\circ}$  during three hours with an acetic acid solution of iodine.

The *carbamide* of dibromobehenic acid forms colourless crystals, m. p.  $149^{\circ}$ , and the *amide*, a crystalline, colourless product, m. p.  $78^{\circ}$ . *Iodobehenamide* has m. p.  $78^{\circ}$ . F. M. G. M.

**Thiocarbimides: Ethyl Allyliminothiolcarbonate.** WILHELM SCHNEIDER (*Ber.*, 1912, 45, 2961—2965).—The thiocarbimide of glucosides, for example, sinigrin, can be regarded as derived from a hypothetical alkyliminothiolcarbonic acid,  $\text{NR}:\text{C}(\text{SH})\cdot\text{OH}$  (Gadamer, *Abstr.*, 1897, i, 360; 1898, i, 38). A derivative of this acid, namely, ethyl methyl phenyliminothiolcarbonate,  $\text{NPh}:\text{C}(\text{SMe})\cdot\text{OEt}$ , has already been prepared (Liebermann, *Abstr.*, 1881, 44; 1882, 296); but as aromatic thiocarbimides apparently do not occur naturally, the author by a similar process has prepared the corresponding allylimino-compound.

[With GUSTAV HÜLLWECK.]—Allylthiourethane (Hofmann, *Ber.*, 1869, 2, 117) treated in alcoholic solution with an equimolecular quantity of ammoniacal silver solution gives a yellow *silver salt*,  $\text{C}_3\text{H}_5\cdot\text{N}:\text{C}(\text{SAg})\cdot\text{OEt}$ , m. p.  $112^{\circ}$ — $118^{\circ}$ , which reacts with ethyl iodide in ethereal solution at  $100^{\circ}$ , producing *ethyl allyliminothiolcarbonate*, an oil, b. p.  $88$ — $92^{\circ}/14$  mm., of characteristic odour, which gradually decomposes when exposed to air and light. On boiling with an alkaline solution of lead oxide, no formation of lead sulphide occurs.

D. F. T.

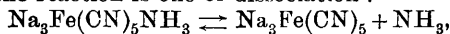
**Preparation and Properties of Pure Thiocyanic Acid.** U. RÜCK and H. STEINMETZ (*Zeitsch. anorg. Chem.*, 1912, 77, 51—89).—The method of Rosenheim and Levy (*Abstr.*, 1907, i, 489) has been improved in detail, and an apparatus is described, but much decomposition of the product by the sulphuric acid occurs. Better results are obtained by using potassium hydrogen sulphate in place of sulphuric acid. For the preparation of pure gaseous thiocyanic acid, an apparatus is described in which purified and dried hydrogen enters a flask containing glass and porcelain balls, which can be agitated by means of a glass stirrer, together with potassium thiocyanate (1 mol.). Potassium hydrogen sulphate ( $1\frac{1}{4}$  mol.) is added gradually through a side-tube. A vacuum of about 40 mm. is maintained. The gas evolved is free from sulphur dioxide, formic acid, or hydrogen sulphide. The yield, as determined by conversion into the white silver salt, is 20%. The method of Rosenheim and Levy always yields a coloured silver salt.

It is not possible to dry the materials so thoroughly that the product is quite anhydrous, the best result being a 97% acid. It is, therefore, necessary to dry the gas. Commercial phosphoric oxide

introduces impurities, but the pure compound is chemically indifferent, and Merck's preparation proves to be sufficiently free from impurities. The drying tubes are packed with this phosphoric oxide, arranged in about 20 layers in each tube, supported on glass wool. Condensation takes place in U-tubes cooled by solid carbon dioxide and alcohol. The solid product usually shows a very faint yellow tint. A special closed apparatus is described in which the solid thiocyanic acid may be weighed, dissolved in water, and precipitated by silver nitrate. The product proves to be pure.

The gas is stable, and only slightly poisonous. The solid is stable in dry hydrogen at  $-15^{\circ}$ , and dissolves readily in water, alcohol, ether, or benzene. The yellow decomposition product is insoluble in benzene, but dissolves readily in alcohol. Cryoscopic measurements in benzene, nitrobenzene, and glacial acetic acid give results indicating a mixture of single and double molecules. C. H. D.

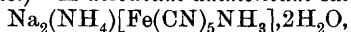
**Iron Salts which Combine with Carbon Monoxide.** WILHELM MANCHOT [with ERNEST MERRY and PIERRE WORINGER] (*Ber.*, 1912, 45, 2869—2879).—Little is known of the absorption of gases by iron compounds other than that present in the blood. Manchot and Friend (*Abstr.*, 1908, ii, 375) have shown that cuprous chloride as such does not absorb carbon monoxide, but only in the form of a complex. The same is true of iron compounds. Hofmann's ferropentacyano-amminosodium,  $[\text{Fe}(\text{CN})_5\text{NH}_3]\text{Na}_3\cdot 6\text{H}_2\text{O}$ , absorbs carbon monoxide in aqueous solution, the ammonia being replaced by carbon monoxide. The reaction is dependent on the temperature and concentration; thus a solution containing 0.022 mol. of the iron salt absorbs only about 12.5 litres of carbon monoxide after many hours at  $0^{\circ}$ , whilst a solution containing 0.0037 mol. absorbs 22.4 litres (per gram-atom of iron) at  $21.2^{\circ}$  in fifteen minutes. Since absorption of carbon monoxide does not occur in aqueous ammonia, but proceeds rapidly in acid solution, it seems that the reaction is one of dissociation:



the absorption of carbon monoxide being rapid under conditions favourable to the removal of ammonia.

Similar results have been obtained in experiments on the absorption of nitric oxide by the same iron compound. The iron compound does not absorb ethylene or acetylene, but slowly combines with one equivalent of oxygen, the iron being simultaneously oxidised to the ferric state.

Hofmann obtained the iron compound of the constitution given above by saturating a cold 25% aqueous solution of sodium nitroprusside with ammonia, and filtering the crystalline precipitate before the whole of the nitroprusside had disappeared. (The author finds the substance has the composition  $\text{Na}_3[\text{Fe}(\text{CN})_5\text{NH}_3]\cdot 3\text{H}_2\text{O}$ , after drying over calcium chloride.) A *disodium ammonium salt*,



is obtained when the mixture is kept for twenty-four hours, so that the whole of the nitroprusside enters into the reaction. The reaction between sodium nitroprusside and aqueous ammonia, therefore, is accompanied by reduction of the iron to the ferrous state and

proceeds according to the equation,  $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] + 3\text{NH}_3 + \text{H}_2\text{O} = \text{Na}_2(\text{NH}_4)[\text{Fe}(\text{CN})_5\cdot\text{NH}_3] + \text{NH}_4\cdot\text{NO}_2$ ; ammonium nitrite has been detected in the solution. C. S.

*cyclopentadiene*. KARL VON AUWERS (*Ber.*, 1912, 45, 3077—3080).—The refraction of a very pure specimen of *cyclopentadiene* obtained by distillation at a low temperature under diminished pressure has been determined with the following results:  $n_a$  1.45031,  $n_D$  1.45418,  $n_B$  1.46355,  $n_\gamma$  1.47172,  $D_4^{+1}$  0.8190, at 4.1°.

A comparison of the dispersivity of this specimen with the values obtained by Stobbe and Reuss (this vol., i, 842), shows that *cyclopentadiene* distilled under ordinary pressure is not so strongly polymerised, as has hitherto been supposed, and, consequently, the previously observed depression of the molecular refraction cannot be due to polymerisation (compare Auwers and Eisenlohr, *Abstr.*, 1910, ii, 367, 561).

Thiophen, furfuran, and pyrrole resemble *cyclopentadiene* in exhibiting a depression in their molecular refraction, and it would thus appear that this depression is characteristic of both iso- and hetero-cyclic ring-systems of the type  $\begin{matrix} \text{CH}:\text{CH} \\ \text{CH}:\text{CH} \end{matrix} > \text{X}$  (where  $\text{X} = \text{CH}_2, \text{S}, \text{O}, \text{NH}$ ).

According to the author, the depression is to be referred not to a specific influence of the supplementary or subsidiary valencies, but to the group  $\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}$ , the position of which, in the five-membered ring, becomes fixed in such a manner as to lead to the neutralisation of the main and partial valencies. F. B.

**Benzene Structure Reviewed from Thermochemical Standpoint.** II. WILLEBRORD TOMBROCK (*Chem. News*, 1912, 106, 201—202. Compare this vol., i, 842).—The heat of combustion of benzene may be accounted for by Kekulé's formula on the assumption that the thermal influence of the aromatic character is considerable, or by the centric formula on the assumption that the thermal influence of the aromatic character is negligible. G. S.

**Thermochemistry of Benzene.** H. STANLEY REDGROVE (*Chem. News*, 1912, 106, 224—225).—In connexion with Tombrock's last communication (this vol., i, 842), the author gives further thermochemical calculations which show the untenability of Kekulé's formula for benzene, and are in favour of Baeyer and Armstrong's centric formula. T. S. P.

**Observations on the Hydrogenation of Aromatic Compounds.** HEINRICH WIELAND (*Ber.*, 1912, 45, 2615—2617).—From his experiments on the catalytic hydrogenation of olefinic and aromatic compounds (this vol., i, 247) in the presence of colloidal palladium, the author has drawn the conclusion that unsaturated compounds which decolorise potassium permanganate may be catalytically hydrogenised. In reply to Willstätter and Hatt (this vol., i, 545), who maintain that no such relationship exists, the author points out that the difference in the rate of reduction of aromatic and olefinic compounds is so great

that under the conditions employed by him the former remain practically unchanged, whereas the olefines are more or less rapidly hydrogenised. Further, the permanganate reaction must be carried out under definite conditions in order that the above-mentioned relationship may be maintained.

Benzene is readily oxidised by a permanganate solution acidified with sulphuric acid, and may be catalytically reduced by palladium-black and hydrogen under the conditions employed by Willstätter and Hatt.

Palladium is less sensitive to retarding influences than platinum; the reduction of benzene by palladium and hydrogen still takes place, although with somewhat diminished velocity, in the presence of thiophen, which completely inhibits the hydrogenation by means of platinum.

F. B.

**Autoxidation of Benzenoid Hydrocarbons when Exposed to Light.** HERMANN SUIDA (*Ber.*, 1912, 45, 2909—2910).—The author has shown that considerable quantities of peroxides of hydrocarbons are formed during the autoxidation of homologues of benzene. He considers that in the case of the autoxidation of phenanthraquinone in the presence of aromatic hydrocarbons (Benrath and von Meyer, this vol., i, 876), the former plays the role of a suitable "acceptor" by disturbing the equilibrium usually attained in the autoxidation of hydrocarbons,  $R + O_2 \rightleftharpoons RO_2$ , by the removal of oxygen.

H. W.

**Isomeric Changes of Haloids Containing a Tertiary Radicle in the Molecule.** A. I. LEPIN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1165—1189).—After discussing the literature of the subject (compare Michael and Leupold, *Abstr.*, 1911, i, 250, and others), the author describes his own experiments on  $\alpha$ -bromo- $\alpha$ -phenyl- $\beta\beta$ -dimethylpropane,  $CM_3 \cdot CHPhBr$ . From the results obtained he draws the conclusion that haloids, the molecule of which contains a tertiary radicle and in which the halogen is adjacent to the carbon atom combined directly with the tertiary radicle, at a sufficiently high temperature undergo isomeric change in two directions simultaneously: (1) the halogen atom and one of the hydrocarbon groups of the tertiary radicle change places, with the result that the carbon skeleton of the original compound is changed, and the corresponding tertiary isomeride formed; (2) the tertiary compound formed and also the original haloid, as far as the structures of the molecules allow, undergo transformations which are regarded as the result of successive changes of position between halogen and hydrogen atoms without change of the carbon skeleton.

*Phenyltert.-butylcarbinol*,  $CM_3 \cdot CHPh \cdot OH$ , prepared from benzaldehyde and magnesium *tert.*-butyl chloride, forms fine needles, m. p. 45°.

*$\alpha$ -Bromo- $\alpha$ -phenyl- $\beta\beta$ -dimethylpropane*,  $CM_3 \cdot CHPhBr$ , forms a colourless liquid, b. p. 109°/10 mm.,  $D_4^{20}$  1.2563,  $D_4^{20}$  1.2373,  $n_D^{20}$  1.53977, which solidifies to a glassy mass when cooled in a mixture of solid carbon dioxide and ether.

The principal products obtained on heating this bromo-derivative for six hours in a sealed tube at 220° are: I.  $\beta$ -Phenyl- $\gamma$ -methyl- $\Delta^8$ -

butylene (compare Blaise and Courtot, Abstr., 1906, i, 793),  $D_4^0$  0.9080,  $D_4^{20}$  0.8917,  $n_D^{20}$  1.51635, which, when oxidised by means of benzoyl hydroperoxide, yields the corresponding  $\alpha$ -oxide,  $O \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CMe_2 \\ CMePh \end{smallmatrix}$ , in the form of a mobile liquid, b. p.  $89-94^\circ/8$  mm.,  $D_4^0$  0.9976,  $D_4^{20}$  0.9808,  $n_D^{20}$  1.50757. Hydration of this oxide by prolonged treatment with water faintly acidified with sulphuric acid yields  $\beta$ -phenyl- $\gamma$ -methyl-butylene  $\beta$ - $\gamma$ -glycol,  $OH \cdot CMe_2 \cdot CMePh \cdot OH$ , crystallising from light petroleum in small needles, m. p.  $84^\circ$ , which do not distil. Oxidation of this glycol by means of chromic anhydride and potassium hydrogen sulphate yields acetophenone, and, possibly, a small proportion of acetone. II. A colourless liquid,  $C_{11}H_{15}Br$ , b. p.  $116^\circ/9$  mm.,  $D_4^0$  1.2495,  $D_4^{20}$  1.2304,  $n_D^{20}$  1.54052, which is probably the tertiary isomeride of the starting product, that is,  $CMe_2Br \cdot CHMePh$ , as it is found to be formed on bromination of the corresponding alcohol described below.

$\beta$ -Phenyl- $\alpha$ -dimethylpropyl alcohol,  $OH \cdot CMe_2 \cdot CHMePh$ , prepared by the Grignard reaction from acetone and  $\alpha$ -bromoethylbenzene, is a colourless, viscous liquid, b. p.  $66^\circ/0.09$  mm.,  $105-107^\circ/12$  mm.,  $D_4^0$  0.9954,  $D_4^{20}$  0.9794,  $n_D^{20}$  1.51932, and is accompanied by two modifications of  $\beta$ - $\gamma$ -diphenylbutane (see succeeding abstract). Treatment of the alcohol with hydrogen bromide yields  $\beta$ -phenyl- $\gamma$ -methyl- $\Delta^a$ -butylene and  $\beta$ -bromo- $\gamma$ -phenyl- $\alpha$ -methylbutane (see above). T. H. P.

**Stereoisomeric  $\beta$ - $\gamma$ -Diphenylbutanes (Dimethyldibenzyls).** A. I. LEPIN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1190—1196).—The two dimethyldibenzyls obtained in the synthesis of  $\beta$ -phenyl- $\alpha$ -dimethylpropyl alcohol (see previous abstract) have been obtained by Radziszewski (Abstr., 1874, 469), Engler and Bethge (Abstr., 1875, 65), Moritz and Wolfenstein (Abstr., 1899, i, 424), and Klages (Abstr., 1902, i, 666), but their structural relationship has not been ascertained. From their analogy to the tartaric acids, the author regards the liquid modification as the racemic mixture of the two enantiomorphous forms, and the solid one as the internally compensated form. Both give acetophenone on oxidation, and the former is converted into the latter when heated with a crystal of iodine in a sealed tube at  $235-250^\circ$ .

The solid modification forms white crystals, m. p.  $126^\circ$ , whilst the liquid modification has b. p.  $140^\circ/10$  mm.,  $283-284^\circ/752$  mm., m. p.  $8^\circ$ ,  $D_4^0$  0.9906,  $D_4^{20}$  0.9757,  $n_D^{20}$  1.55516; both have about the normal molecular weight in freezing benzene. T. H. P.

**Crystals of 1-Bromo-2:4-dinitrobenzene and Mixed Crystals of 1-Bromo- and 1-Chloro-2:4-dinitrobenzene.** A. K. BOLDYREFF (*Zeitsch. Kryst. Min.*, 1912, 51, 294—295; from *Ann. Inst. Mines, St. Petersburg*, 1908, 1, 20—27).—Two-circle measurements and optical determinations are given for crystals of 1-bromo-2:4-dinitrobenzene and of mixed crystals (50%) of 1-bromo- and 1-chloro-2:4-dinitrobenzene. Although the optical orientation agrees with orthorhombic symmetry, the crystals are regarded as belonging to "the rhombo-prismatic kind of monoclinic syngony." L. J. S.

**2:4:6-Trinitrobenzyl Bromide and its Derivatives.** SIEGMUND REICH, OTTO WETTER, and MAX WIDMER (*Ber.*, 1912, 45, 3055—3061).—2:4:6-Trinitrobenzyl bromide is readily obtained by heating 2:4:6-trinitrotoluene with bromine under pressure (compare Reich, this vol., i, 361). It condenses readily in benzene solution with two molecules of aromatic amine; the toluidines, *o*- and *p*-anisidine, and *m*-nitroaniline, but not *o*- and *p*-nitroaniline, react in this manner. Anthranilic acid readily condenses with trinitrobenzyl bromide, so that the behaviour of the nitroanilines is due to the position of the nitro-groups and not to their acid character. The amines mentioned show the same differences when condensed with 2:4:6-trinitrobenzaldehyde, with which *o*- and *p*-nitroaniline do not react.

A by-product of the bromination of trinitrotoluene is hexabromobenzene.

2:4:6-Trinitrobenzyl bromide crystallises in colourless, glistening platelets, m. p. 67°.

2:4:6-Trinitrobenzyl iodide, prepared by action of the bromide on potassium iodide, forms brown, stunted crystals, m. p. 86—87°.

2:4:6-Trinitrobenzyl alcohol is obtained in short, brown needles, m. p. 100°, on prolonged boiling of the bromide with water.

2:6-Dinitrobenzyl alcohol crystallises in well-formed, slightly brown platelets, m. p. 94°.

2:4:6-Trinitrobenzylaniline forms brown needles, m. p. 151°.

2:4:6-Trinitrobenzyl-*o*-anisidine crystallises in reddish-yellow needles, m. p. 183°.

2:4:6-Trinitrobenzyl-*p*-anisidine yields dark brown needles, m. p. 143°.

2:4:6-Trinitrobenzyl- $\beta$ -naphthylamine gives brown needles, m. p. 150°.

2:4:6-Trinitrobenzyl-*o*-toluidine forms orange-yellow needles, m. p. 140°.

2:4:6-Trinitrobenzyl-*p*-toluidine yields brown needles, m. p. 122°.

2:4:6-Trinitrobenzyl-*m*-nitroaniline forms red needles, m. p. 133°.

2:4:6-Trinitrobenzyl-*o*-aminobenzoic acid gives yellow needles, m. p. 170°.

2:6:2':6'-Tetranitrostilbene,  $C_6H_3(NO_2)_2 \cdot CH:CH \cdot C_6H_3(NO_2)_2$ , prepared by the action of alcoholic potassium hydroxide on dinitrobenzyl bromide, crystallises in short, faintly yellow needles, m. p. 250°.

On reduction, tetra-aminostilbene was obtained in lustrous, colourless crystals, m. p. 164—166°, but not sufficiently pure for analysis.

2:4:6:2':4':6'-Hexanitrostilbene from trinitrobenzyl bromide forms yellow needles, m. p. 211° (decomp.).

E. F. A.

**Preparation of a Monosulphonic Acid of Acenaphthene.** KALLE & Co. (D.R.-P. 248994).—Di- and tri-sulphonated derivatives of acenaphthene have been prepared previously, and a monosulphonic derivative containing the sulphonic radicle in the methylene group has now been obtained as follows.

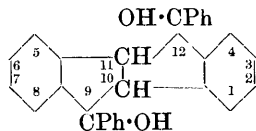
Acenaphthene (15.4 parts) dissolved in nitrobenzene is slowly treated at 3° with chlorosulphuric acid (12 parts), the temperature is

allowed to rise to 15–20°, and the mixture vigorously stirred for some time. The *sodium* salt forms colourless, crystalline leaflets.

F. M. G. M.

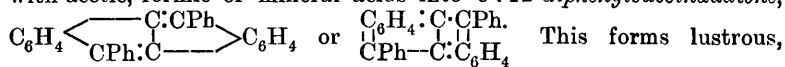
### Coloured Hydrocarbons of the Diphenysuccindene Series.

I. KURT BRAND (*Ber.*, 1912, 45, 3071–3077).—Roser's (Abstr., 1888, 1301) diphenysuccindone (diphenysuccindan-9:12-dione) reacts with magnesium



phenyl bromide, yielding 9:12-*dihydroxy-9:12-diphenyldiphenysuccindane* (annexed formula), which crystallised in stout, colourless needles, m. p. 232–234°, with previous darkening, and is converted by heating

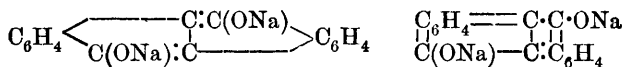
with acetic, formic or mineral acids into 9:12-*diphenylsuccindadiene*,



This forms lustrous, brown crystals, m. p. 259–260°, which become strongly electric when rubbed, and are oxidised by potassium permanganate or chromic acid to *o*-benzoylbenzoic acid.

9:12-*Dihydroxy-9:12-di-p-tolyldiphenysuccindane*,  $\text{C}_{30}\text{H}_{26}\text{O}_2$ , prepared in a similar manner from magnesium *p*-tolyl bromide, forms colourless crystals, which become brown and melt at 248–250°; when boiled with a mixture of formic and acetic acids it yields 9:12-*di-p-tolyldiphenysuccindadiene*,  $\text{C}_{30}\text{H}_{22}$ , which separates from benzene in almost black crystals, having a metallic lustre.

The author mentions that Roser's diphenysuccindone dissolves in aqueous sodium hydroxide, forming solutions of an orange colour, and suggests that the constitution of the sodium salt thus produced is represented by one of the following formulæ:



F. B.

**Condensation of Organic Compounds with the Aid of Iodine.** KNOLL & Co. (D.R.-P. 250236).—The catalytic action of iodine has recently been demonstrated (this vol., i 345) and the following extension is now recorded.

A quantitative yield of dimethylaniline is obtained by heating aniline (93 parts), methyl alcohol (96 parts), and iodine (1 part), together during seven hours at 230°; the analogous preparation of diethylaniline with ethyl alcohol requires ten hours' heating at 235°.

*Diisoamylaniline* is obtained from aniline and *isoamyl* alcohol after ten hours at 240°; aniline (140 parts), methyl alcohol (32 parts), and iodine (1 part) after heating during ten hours at 220° furnishes chiefly methylaniline, whilst molecular proportions of aniline and *p*-benzophenone with 1% iodine yield (at the temperature of water elimination) benzophenoneanil; and acetophenone with 1% iodine at 180–190° gives *s-triphenylbenzene*, m. p. 169–170°.

F. M. G. M.

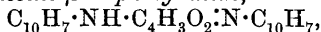
Reactions of Certain Fumaroid and Maleinoid Compounds with Aromatic Amines. WILLIAM H. WARREN and M. R. GROSE (*J. Amer. Chem. Soc.*, 1912, 34, 1600—1613).—Perkin (*Trans.*, 1881, 39, 561) has shown that when an aqueous solution of aniline maleate is evaporated, a derivative of succinimide is produced. Anschütz and Wirtz (*Abstr.*, 1887, 934) have found that the compound is anilino-succinanil, 
$$\text{NHPH} \cdot \text{CH} \begin{array}{c} \text{CH}_2 \cdot \text{CO} \\ \diagup \text{CO} \end{array} \text{NPh.}$$
 It is now shown that both fumaric

and maleic acids react with aniline to form anilinosuccinanil, and that in the production of this compound, two reactions are concerned, one leading to the formation of the imido-ring, and the other involving addition of the amine. These two reactions do not take place simultaneously, but the addition of the amine seems to depend on the presence of the imido-ring. It has been found that  $\beta$ -naphthylamine, *o*-, *m*- and *p*-toluidine, 2:4-xylidine, benzidine, benzylamine, and *p*-phenetidine resemble aniline in their behaviour towards fumaric acid, whilst tribromoaniline, *p*-bromoaniline, and methyl *p*-aminobenzoate fail to react.

*Methyl hydrogen fumarate*,  $\text{CO}_2\text{Me} \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{H}$ , m. p.  $143^\circ$ , obtained by the partial hydrolysis of dimethyl fumarate, forms flattened prisms.

Anilinosuccinanil can be obtained by the action of aniline on methyl hydrogen fumarate, dimethyl fumarate, diethyl fumarate, or fumaric acid; it separates from alcohol in white crystals, and from glacial acetic acid in yellow crystals.

*$\beta$ -Naphthylaminosuccino- $\beta$ -naphthylimide*,



m. p.  $250$ — $255^\circ$  (decomp.), separates in yellow needles from glacial acetic acid, and in white crystals from acetone or alcohol; its *nitroso*-derivative,  $\text{C}_{10}\text{H}_7 \cdot \text{N}(\text{NO}) \cdot \text{C}_4\text{H}_3\text{O}_2 : \text{N} \cdot \text{C}_{10}\text{H}_7$ , m. p. about  $260^\circ$ , forms rhombic crystals.

*o-Tolylaminosuccino-o-tolylimide*, m. p.  $112$ — $113^\circ$ , crystallises in white needles; its *nitroso*-derivative has m. p.  $85^\circ$ . The corresponding *m*- and *p*-tolyl compounds have m. p.  $130^\circ$  and  $209$ — $211^\circ$ , and their *nitroso*-derivatives, m. p.  $120^\circ$  and  $169$ — $170^\circ$  respectively.

2:4-*Dimethylphenylaminosuccino-2:4-dimethylphenylimide*, m. p.  $132$ — $133^\circ$ , crystallises in pale yellow needles; its *nitroso*-derivative has m. p.  $80$ — $90^\circ$ .

Experiments were made on the behaviour of fumaric acid towards *p*-phenylenediamine, but the result was not satisfactory. With benzidine, the compound, 
$$\text{C}_6\text{H}_4 \cdot \text{NH} \begin{array}{c} \text{C}_6\text{H}_4 \cdot \text{N} \\ \diagup \text{N} \end{array} \text{C}_4\text{H}_3\text{O}_2,$$
 was obtained which does not melt below  $300^\circ$ .

By the action of fumaric acid or ethyl fumarate on benzylamine, *benzylaminosuccinobenzylimide*,  $\text{CH}_2\text{Ph} \cdot \text{NH} \cdot \text{C}_4\text{H}_3\text{O}_2 : \text{N} \cdot \text{CH}_2\text{Ph}$ , m. p.  $205^\circ$ , is produced which forms slender, white needles; its *nitroso*-derivative has m. p.  $156^\circ$ . *p*-Ethoxyphenylaminosuccino-*p*-ethoxyphenylimide,  $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{C}_4\text{H}_3\text{O}_2 : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$ , m. p.  $204$ — $205^\circ$ , from *p*-phenetidine, forms slender needles; the *nitroso*-derivative has m. p.  $133$ — $134^\circ$ .

By the interaction of fumaric acid (1 mol.) and methylaniline (3 mols.), *fumaromethylanilide*,  $\text{NPhMe} \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{NPhMe}$ , m. p. 187—188°, is produced, which is identical with the compound obtained by Piutti (Abstr., 1886, 621) by the action of methylaniline on phthalylaspartic acid. It combines with bromine to form *dibromosuccinomethylanilide*, m. p. 214°, which forms short, hexagonal prisms.

When maleinanil (1 mol.) is heated with methylaniline (1 mol.), *methylanilinosuccinanil*,  $\text{NPhMe} \cdot \text{C}_4\text{H}_3\text{O}_2 \cdot \text{NPh}$ , m. p. 173°, is produced, which crystallises in long needles.

*Fumarodiphenylamide*,  $\text{NPh}_2 \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{NPh}_2$ , m. p. 272—273°, obtained by the action of fumaryl chloride on diphenylamine, crystallises in white, slender needles, and is identical with the compound obtained by Piutti (*loc. cit.*) from diphenylamine and fumaric or maleic acid. The substance combines with bromine to form *dibromosuccinodiphenylamide*,  $\text{NPh}_2 \cdot \text{CO} \cdot \text{CHBr} \cdot \text{CHBr} \cdot \text{CO} \cdot \text{NPh}_2$ , m. p. 231°, which crystallises in white, slender needles.

*Diphenylmaleinamic acid*,  $\text{NPh}_2 \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{CO}_2\text{H}$ , m. p. 130°, obtained by the action of maleic anhydride (1 mol.) on diphenylamine (2 mols.), crystallises in radiating needles. E. G.

**Condensation of Formaldehyde with Aniline.** ALEXANDER M. NASTUKOFF and V. I. MALKALN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1196—1200).—The product previously obtained (*J. Russ. Phys. Chem. Soc.*, 1904, 36, 1125) by the condensation of formaldehyde with aniline in presence of concentrated sulphuric and acetic acids is shown to consist of a mixture in approximately equal proportions of an imine closely resembling that described by Orloff (Abstr., 1906, i, 420) and of *aminobenzocyclobutadiene*,  $\begin{array}{c} \text{CH} : \text{C}(\text{NH}_2) \cdot \text{C} - \text{CH} \\ | \qquad \qquad | \qquad | \\ \text{CH} = \text{CH} - \text{C} - \text{CH} \end{array}$ . This was

not obtained in the pure state, but when diazotised in alcoholic solution was found to yield a small proportion of a hydrocarbon, b. p. 104—107°, which is regarded as *benzocyclobutadiene*,  $\begin{array}{c} \text{CH} : \text{CH} \cdot \text{C} - \text{CH} \\ | \qquad \qquad | \\ \text{CH} : \text{CH} \cdot \text{C} - \text{CH} \end{array}$ .

T. H. P.

**Condensation of Formaldehyde with *o*-Toluidine.** ALEXANDER M. NASTUKOFF and P. M. KRONEBERG (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1200—1202).—Condensation of formaldehyde with *o*-toluidine in presence of concentrated sulphuric and acetic acids (compare *J. Russ. Phys. Chem. Soc.*, 1904, 36, 1125) yields as sole product, 6-amino-5-methylbenzocyclobutadiene,  $\begin{array}{c} \text{CMe} : \text{C}(\text{NH}_2) \cdot \text{C} - \text{CH} \\ | \qquad \qquad | \qquad | \\ \text{CH} = \text{CH} - \text{C} - \text{CH} \end{array}$ , which has the normal molecular weight in boiling pyridine.

T. H. P.

**Preparation and Decomposition of Benzylmonochloro- and Benzylchloro-amines.** RASIK LAL DATTA (*J. Amer. Chem. Soc.*, 1912, 34, 1613—1615).—It has been shown in an earlier paper (Trans., 1912, 101, 169) that dichlorocarbamide behaves as a chlorinating agent, and is capable of converting benzylamine into either the monochloro- or dichloro-amine according to the proportion used. The monochloroamine is slowly but quantitatively decomposed by water

with formation of benzaldehyde. The dichloro-compound also yields benzaldehyde under the same conditions, but the change is very slow. When dichlorobenzylamine is left in a stoppered bottle, it gradually changes into a solid crystalline mass consisting of benzoic acid.

E. G.

The Two Isomeric Trinitro-*p*-anisidines and a Trinitro-*p*-phenetidine. FRÉDÉRIC REVERDIN (*Arch. Sci. phys. nat.*, 1912, [iv], 34, 330—338. Compare Abstr., 1910, i, 470).—The constitution of the trinitro-*p*-anisidine of Meldola and Kuntzen (*Trans.*, 1910, 97, 456) and of that prepared by Reverdin (Abstr., 1910, i, 470) is discussed, with particular reference to the position of the mobile nitro-group. Meldola's 2:3:5-trinitro-compound was obtained from a 3:5-dinitro-derivative, but it is suggested that the mobile group might have been displaced in the final nitration, for a trinitrophenol derived from the product resembles a known 2:3:6-trinitrophenol. Reverdin, who relies on Meldola's formula to establish his isomeric 2:3:6-trinitro-*p*-anisidine, could not succeed in methylating this compound or in causing it to condense with chloronitrobenzene, and assumes, therefore, that the amino-group is protected by two nitro-groups in the ortho-position. Similar inactivity in the case of the 2:3:5-compound is attributed by Meldola to the mobility of the nitro-group in position 3. That the mobile nitro-group does occupy position 3 in each case was shown by the formation of 2:6- and 2:5-dinitro-methoxybenzoquinonediazides (*Trans.*, 1910, 97, 1204), and is now supported in the case of Reverdin's compound, by the fact that the reduction of the corresponding hydroxyl compound after elimination of the amino-group, yields a *m*-diamine, and further by the production of an *o*-diamine by the action of alcoholic ammonia. It is hoped to find more direct proofs of the mobility of this nitro-group, among others the conversion of the substance into a known dinitroresorcinol.

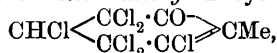
An improved method for the preparation of this trinitro-*p*-anisidine is found in the nitration of 4-*p*-toluenesulphonylanisidine in two stages. The 2:3-dinitro-*p*-toluenesulphonylanisidine (compare Abstr., 1909, 377) when heated at 70° with nitric acid (D 1·4) gives a good yield of *toluene-p-sulphonyltrinitroanisidine*,  $\text{OMe} \cdot \text{C}_6\text{H}(\text{NO}_2)_3 \cdot \text{NH} \cdot \text{C}_7\text{H}_7 \cdot \text{SO}_2$ , a colourless compound, m. p. 221°, accompanied by the *o*-nitrotoluene-sulphonyl derivative of trinitro-*p*-anisidine (Abstr., 1912, i, 183). Both products are readily hydrolysed by concentrated sulphuric acid.

Better results are obtained from 4-*p*-toluenesulphonylphenetidine, which has given rise to a *dinitro*-product, then a *trinitro*-compound, m. p. 215—219°, and finally *trinitro-p-phenetidine*,  $\text{OEt} \cdot \text{C}_6\text{H}(\text{NO}_2)_3 \cdot \text{NH}_2$ , which behaves similarly to the corresponding anisidine. It crystallises in red needles, m. p. 124—125°, and yields an *acetyl* compound, colourless needles, m. p. 241—245°, and also the following derivatives of 2:6-dinitro-*p*-phenetidine: the 3-*methylamino*-, red needles, m. p. 169—170°, by the action of methylamine; the 3-*anilino*-, m. p. 151°, by the action of aniline; the 3-*hydroxy*-, m. p. 167°, by the action of sodium acetate, and the 3-*amino*-, red crystals, m. p. 243—246°, by the action of alcoholic ammonia. The latter is not diazotisable, but gives none of the reactions of *o*-diamines.

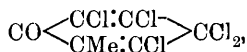
J. C. W.

**Action of Nitric Acid on Halogen Derivatives of *o*-Alkyl-phenols.** THEODOR ZINCKE (*Annalen*, 1912, 394, 1—3).—The product obtained by the fission of tetrabromo-*o*-methylquinnitrole nitrate by alkalis (Zincke and Klostermann, Abstr., 1907, i, 322) can be converted into a substance,  $C_9Br_6O$ , which is apparently perbromindone. The various stages of the change, however, do not proceed quite satisfactorily, consequently the corresponding chlorinated compounds have been prepared and examined (following abstract). C. S.

**Tetrachloro-*o*-cresol and its Conversion into Perchloro-indone.** THEODOR ZINCKE and W. PFAFFENDORF (*Annalen*, 1912, 394, 3—22. Compare preceding abstract).—By keeping for ten to twelve hours a solution of 6-chloro-*o*-toluidine in glacial acetic and concentrated hydrochloric acids saturated with chlorine, 3 : 3 : 4 : 5 : 5 : 6-hexachloro-2-keto-1-methyl- $\Delta^1$ -cyclohexene,



m. p.  $107^\circ$ , is obtained. It crystallises in large, monoclinic prisms, has an odour of camphor, slowly dissolves in alkalis with a yellow colour, liberates iodine from acidified potassium iodide, is scarcely attacked by concentrated sulphuric acid, can be recrystallised from nitric acid (D 1.4), and reacts with sodium acetate in boiling alcohol to form a pentachloro-6-keto-1-methylcyclohexadiene,  $CO \begin{array}{c} \text{CCl}_2 \cdot CCl \\ \text{CMe} : CCl \end{array} CCl$  or



m. p.  $64^\circ$ , b. p.  $165^\circ/15$  mm. By reduction with stannous chloride and acetic and hydrochloric acids, the former ketochloride yields a mixture of tri- and tetra-chloro-*o*-cresol, whilst the latter yields only tetrachloro-*o*-cresol,  $C_7H_4OCl_4$ , m. p.  $190^\circ$ , colourless needles (acetate, m. p.  $136^\circ$ ; methyl ether, m. p.  $114^\circ$ ).

Tetrachloro-*o*-cresol forms a quinnitrole nitrate even under the conditions under which tetrabromo-*o*-cresol forms the quinnitrole (Abstr., 1907, i, 322). It is obtained best by slowly adding tetrachloro-*o*-cresol to nitric acid (D 1.48) with cooling. Tetrachloro-*o*-methylquinnitrole nitrate,  $CCl \begin{array}{c} \text{CCl} \cdot CMe(NO_2) \\ \text{CCl} : CCl \end{array} C(OH) \cdot O \cdot NO_2$ , m. p.  $93-94^\circ$  (decomp.), colourless prisms, is converted into trichloro-*p*-toluquinone above its m. p. or by concentrated sulphuric acid at  $100-120^\circ$ , and by heating with petroleum or formic or acetic acid into tetrachloro-*o*-methylquinol,  $OH \cdot CMe \begin{array}{c} CO \cdot CCl \\ \text{CCl} : CCl \end{array} CCl$ , m. p.  $114-115^\circ$ , faintly yellow prisms (acetate, m. p.  $86^\circ$ , yellow plates; anilide, m. p.  $172^\circ$ , yellow leaflets). The quinnitrole nitrate is not directly reconverted into tetrachloro-*o*-cresol by reduction, but yields it by treatment with boiling glacial acetic acid and subsequently with stannous chloride, the quinol being formed as an intermediate product. The quinol is converted into trichloro-*p*-toluquinone by heating with acetic and sulphuric acids, and yields the quinnitrole nitrate by treating its ethereal solution with nitrous fumes.

The quinnitrole nitrate is decomposed by aqueous sodium carbonate

and yields, after acidification of the solution, a substance,  $C_7H_4O_6N_2Cl_4$ , m. p.  $142^\circ$  (decomp.), colourless needles, to which is ascribed the formula  $NO_2 \cdot CHMe \cdot CCl : CCl : CCl : CCl : CO_2 \cdot NO_2$ , analogous to that of the corresponding brominated compound (*loc. cit.*). The substance has not been converted into tetrachloro-*o*-cresol, but yields trichloro-*p*-toluquinone by heating with acetic anhydride. It is converted by concentrated sulphuric acid at  $105^\circ$  into the substance,  $C_{10}O_2Cl_8$ , m. p.  $164-170^\circ$ , obtained by the action of acetic acid and sodium acetate on pentachlorocyclopentenone (Zincke and Meyer, Abstr., 1909, i, 591). The substance  $C_{10}O_2Cl_8$  forms a *methyl alcoholate*, m. p.  $138^\circ$ , yellow plates, and an *ethyl alcoholate*, m. p.  $99^\circ$ , of hexachloroindone (possibly  $C_6Cl_4 \begin{smallmatrix} \text{---} CCl \text{---} \\ \text{C}(\text{OH})(\text{OR}) \end{smallmatrix} CCl$ ) by boiling with methyl or ethyl alcohol, and yields above its m. p. a substance,  $C_9OCl_8$ , m. p.  $123-124^\circ$ , colourless needles, which has the formula  $CCl \begin{smallmatrix} \text{---} CO \text{---} CCl : CCl : CCl \\ \text{---} CCl : CCl : CCl : CCl \end{smallmatrix}$ ; this substance is converted into hexachloroindone by heating with acetic acid and sodium acetate or by stannous chloride, and yields octachlorohydrindone when carefully heated over a free flame. C. S.

**Rearrangement of Allyl Ethers of Phenols into *C*-Allylphenols.** LUDWIG CLAISEN [and O. EISLEB] (*Ber.*, 1912, 45, 3157—3166).—Whereas *O*-alkyl derivatives of ethyl acetoacetate or of hydroxymethylene compounds can usually be distilled unchanged, the *O*-allyl derivatives readily pass over into *C*-allyl derivatives. The transformation has been investigated in the case of certain phenols and phenol-carboxylic acids.

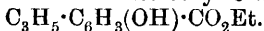
*$\beta$ -Naphthyl allyl ether*,  $C_{10}H_7 \cdot O \cdot C_3H_5$ , before distillation is a colourless, sweet smelling oil, insoluble in sodium hydroxide, and giving no coloration with ferric chloride. When distilled, it undergoes partial conversion into the isomeric 1-allyl- *$\beta$ -naphthol*,  $C_3H_5 \cdot C_{10}H_6 \cdot OH$ ; complete conversion is effected by heating at  $210^\circ$ . The oil, which is faintly yellow-coloured, distils at  $177-178^\circ/12$  mm., and crystallises in well-formed colourless prisms, m. p.  $55^\circ$ . It gives a green coloration with ferric chloride. The *benzoate* separates in colourless crystals, m. p.  $65^\circ$ .

1-Allyl- *$\beta$ -naphthyl allyl ether* is a colourless oil of faint odour, b. p.  $178^\circ/13$  mm. The second allyl group could not be made to wander to the nucleus.

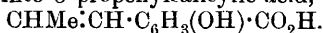
*Guaiacyl allyl ether*,  $OMe \cdot C_6H_4 \cdot O \cdot C_3H_5$ , is a colourless liquid of very little odour, b. p.  $116^\circ/14$  mm.,  $D^{15}_4$  1.058. When heated at  $230^\circ$ , it is converted into *C-allylguaiacol*,  $OMe \cdot C_6H_3(C_3H_5) \cdot OH$ , a colourless oil with an odour of pinks, b. p.  $122^\circ/12$  mm.,  $D^{15}_4$  1.071°. The *sodium* salt forms colourless needles; the *phenylurethane* crystallises in colourless needles, m. p.  $101^\circ$ ; the *p-nitrobenzoate* forms short, flat prisms, m. p.  $97^\circ$ . Although allylguaiacol is very similar to eugenol, the two phenols are probably not identical. *Eugenyl p-nitrobenzoate* crystallises in long, faintly yellow needles, m. p.  $81^\circ$ .

Evidence that the above changes do not involve rearrangement of the allyl group,  $CH_2:CH \cdot CH_2$ , into propenyl,  $CH_3 \cdot CH:CH$ , is

afforded in the case of ethyl *o*-allyloxybenzoate,  $C_8H_5 \cdot O \cdot C_6H_4 \cdot CO_2Et$  which is converted on distillation into ethyl *C*-allylsalicylate,



On hydrolysis with methyl alcoholic potassium hydroxide, *C*-allylsalicylic acid,  $CH_2:CH \cdot CH_2 \cdot C_6H_3(OH) \cdot CO_2H$ , is obtained; when this is heated at  $170^\circ$  with potassium hydroxide and a little water, it undergoes rearrangement into *C*-propenylsalicylic acid,



Scichilone (Abstr., 1883, 335), who observed the conversion of methyl *o*-allyloxybenzoate into allylsalicylic acid, m. p.  $113^\circ$ , obtained in reality a mixture of the *C*-allyl- and *C*-propenyl-salicylic acids.

Ethyl *o*-allyloxybenzoate is an oil, b. p.  $153^\circ/13$  mm., giving no coloration with ferric chloride. On hydrolysis with methyl alcoholic potassium hydroxide, *o*-allyloxybenzoic acid is obtained in colourless platelets, m. p.  $65^\circ$ .

Ethyl *C*-allylsalicylate is an oil, b. p.  $142^\circ/12$  mm.; it gives a deep bluish-violet coloration with ferric chloride. *C*-Allylsalicylic acid crystallises in colourless needles, m. p.  $96^\circ$ . *C*-Propenylsalicylic acid crystallises in long, colourless needles, m. p.  $158^\circ$ , giving an indigo-blue coloration with ferric chloride.

E. F. A.

**Physico-chemical Studies of Photographic Developers. I. Quinol-Sulphite Developer.** NIKOLAI SCHILOFF and S. FEDOTOFF (*Zeitsch. Elektrochem.*, 1912, 18, 929—939).—The nature of the changes accompanying the absorption of oxygen by quinol solutions containing sodium sulphite has been investigated.

In presence of sodium sulphite, not only is a larger quantity of oxygen absorbed by a given quinol solution, but the reaction is unaccompanied by the formation of brown resinous products, and its velocity, although smaller, falls off much less rapidly. In the early stages of the reaction, the oxidation of the quinol induces simultaneous oxidation of the sulphite, but this coupled action soon ceases, as is shown by the data obtained in the estimation of the sulphite and sulphate at successive stages of the reaction. These show that the oxygen absorbed in the later stages of the reaction is unaccompanied by any appreciable alteration of the concentration of sulphite and sulphate. The molecular ratio of the sulphite, which disappears without giving rise to sulphate, to oxidised quinol is as 2 : 1.

Unless the sulphite is present in the quinol solution at the beginning of the reaction, it has no appreciable influence on the course of the change, oxidation and decomposition products of quinol being formed which are incapable of reacting with the sulphite.

The series of colour changes which occur during the progress of the reaction and the changes in the reaction velocity both indicate the formation of three intermediate products which probably all contain sodium sulphite.

On the assumption that the primary oxidation of quinol gives rise to peroxides, evidence of which has been obtained by Sheppard and Mees, the observed facts lead to the view that the following changes are involved: (1) quinol +  $O_2 \rightarrow$  peroxide; (2) peroxide + sodium sulphite  $\rightarrow$  sodium sulphate + intermediate substance *A*; (3) inter-

mediate substance  $A$  + sodium sulphite  $\rightarrow$  additive compound  $A$  ( $A$  + sulphite); (4) additive compound  $A + O_2 \rightarrow$  additive compound  $B + O_2 \rightarrow$  additive compound  $C$ . These additive compounds all contain two molecules of sodium sulphite per molecule of oxidised quinol. The sulphite present in these additive compounds does not react with iodine in neutral or slightly acid solution.

In the absence of sulphite, the absorption of oxygen by quinol solutions involves the changes: (1) quinol +  $O_2 \rightarrow$  peroxide; (2) peroxide + quinol  $\rightarrow$  unstable intermediate substance +  $O_2 \rightarrow$  resinous products. H. M. D.

**Preparation of 3:4-Dihydroxyphenylalkylamines.** KARL W. ROSENMUND, CARL MANNICH, and WILLY JACOBSON (D.R.-P. 247906. Compare this vol., i, 443).—Dihydroxyphenylalkylamines can be readily prepared by reducing oximes of the annexed general formula (where  $R^1$  and  $R^2$  are alkyl groups, and  $R$  alkyl or hydrogen), and subsequently converting the alkyloxy- into a hydroxy-group.

3:4-Dimethoxybenzyl methyl ketone,  $C_6H_3(OMe)_2 \cdot CH_2 \cdot COMe$ , a colourless oil, b. p.  $198^\circ/20$  mm. (prepared from isoeugenyl methyl ether), is converted into its *oxime*; this when reduced with sodium amalgam in acetic acid solution furnishes 3:4-dimethoxyphenylisopropylamine, b. p.  $166-168^\circ/20$  mm. (the hydrochloride has m. p.  $148^\circ$ ), which on hydrolysis by boiling with colourless hydriodic acid (D 1.69) yields 3:4-dihydroxyphenylisopropylamine hydroiodide, a syrup which subsequently becomes crystalline, and is converted into the hydrochloride (m. p.  $190-192^\circ$ ) of the base,



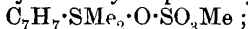
3:4-Dihydroxyphenylethylamine,  $C_6H_3(OH)_2 \cdot CH_2 \cdot CH_2 \cdot NH_2$ , is isolated in the form of its hydrochloride, m. p.  $174-175^\circ$ , and obtained by the reduction of homoveratraldehydeoxime (which was not isolated) to 3:4-dimethoxyphenylethylamine, an oil, b. p.  $188^\circ/15$  mm.; the hydrochloride, a syrup, difficult to crystallise; in this case the hydrolysis of the methoxy-groups is carried out with concentrated hydrochloric acid (4 parts) at  $150^\circ$  during two hours. F. M. G. M.

**Preparation of Di- and Poly-hydroxybenzene Derivatives.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 249939. Compare Abstr., 1885, 145; 1906, i, 559).—When substituted phenols are heated with alkaline earth oxides or hydroxides (the presence of iodine is optional), the substituted group is converted into hydroxyl. Catechol (b. p.  $240-245^\circ$ ) is thus obtained when *o*-chlorophenol (130 parts) is heated during nine hours at  $170^\circ$  with crystalline strontium hydroxide (530 parts) and 500 parts of water, whilst *p*-chlorophenol under similar treatment furnishes quinol.

F. M. G. M.

**Aromatic Sulphine Bases. III.** FRIEDRICH KEHRMANN and GEORGES A. SAVA (*Ber.*, 1912, 45, 2895—2901. Compare Abstr., 1906, i, 83, 949; Smiles, *Trans.*, 1906, 86, 696).—The paper contains

a description of the following compounds. Lead *p*-tolyl mercaptide and methyl sulphate (5 mols.) at 100° for one and a-half hours yield the *methosulphate* of *p*-tolyl dimethylsulphine hydroxide,



the *mercurichloride*,  $\text{C}_9\text{H}_{13}\text{SCl}_2\text{HgCl}_2$ , m. p. 118—120°, colourless needles, *platinichloride*, *picrate*, *perchlorate*, *iodide*, and *dichromate* are described. An aqueous solution of the *base* has a caustic taste and alkaline reaction, liberates ammonia from ammonium salts, and absorbs carbon dioxide; by concentration it yields *p*-tolyl methyl sulphide.  $\beta$ -Naphthyl dimethylsulphine *mercurichloride*, m. p. 114—116° (decomp.), *platinichloride*, *perchlorate*, m. p. 151—153°, and *chloride* are described; the last easily decomposes into methyl chloride and  $\beta$ -naphthyl methyl sulphide, which is also obtained by boiling an aqueous solution of the *base*. The *methosulphate*, *mercurichloride*, and *platinichloride* of  $\beta$ -anthryl dimethylsulphine hydroxide are mentioned. *o*-Anisyl dimethylsulphine hydroxide forms a *mercurichloride*, m. p. 121—122°, *platinichloride*, *iodide*, and *chloride*. *p*-Anisyl dimethylsulphine hydroxide forms a *mercurichloride*, m. p. 121—122°, and *platinichloride*, and the meta-isomeride yields a *mercurichloride*, m. p. 134—135° (decomp.), *platinichloride*, *picrate*, m. p. 130—132°, *dichromate*, m. p. 67—70°, *perchlorate*, m. p. 122°, *chloride*, *bromide*, and *iodide*, m. p. about 122° (decomp.). The *mercurichloride*, m. p. 142—143° (decomp.), *platinichloride*, *iodide*, m. p. 91°, *perchlorate*, m. p. 140—141°, *picrate*, m. p. 140—141°, *ferricyanide*, m. p. 116° (decomp.), and *dichromate* of *o*-phenetyl dimethylsulphine hydroxide, and the *mercurichloride*, m. p. 111—112°, and *platinichloride* of the para-compound are described.  
C. S.

Syntheses in the Fatty-aromatic Series. VIII. Tertiary Derivatives of *o*- and *p*-Aminobenzyl Alcohol. JULIUS VON BRAUN and O. KRUBER (*Ber.*, 1912, 45, 2977—2997).—*p*-Aminobenzylaniline and its derivatives undergo an interesting condensation with aromatic amines with the formation of diphenylmethane derivatives (compare Cohn and Fischer, *Abstr.*, 1900, i, 690). In order to throw light on the method of this condensation, dialkylaminobenzyl alcohols have been prepared by the action of formaldehyde on tertiary amines; the products are yellow, distillable liquids, which exhibit the ordinary reactions for the hydroxyl and tertiary amino-groups, but they condense much less readily than the primary and secondary aminobenzyl alcohols with other aromatic molecules; it is therefore suggested that the easy formation of anhydrides by the primary and secondary amino-compounds is connected with the greater relative reactivity of these substances, the process being really not one of condensation, but an addition of the second molecule to the anhydride molecule. The earlier suggestion (von Braun, *Abstr.*, 1908, i, 684) that the above diphenylmethane derivative formation is due to primary hydrolytic scission of the aminobenzylaniline compound to an aminobenzyl alcohol, which then condenses with the aromatic amine, is relinquished.

Dimethyl-*p*-toluidine when heated for twenty-four hours on the water-bath with an equal weight of concentrated hydrochloric acid and three times the weight of 40% formaldehyde solution undergoes

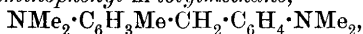
condensation with the formation of 2-dimethylamino-5-methylbenzyl alcohol, a yellow oil of feeble odour, b. p. 250°, with slight decomposition, m. p. 30°; *hydrochloride*, oily; *platinichloride*, red crystals, m. p. 182° (decomp.); *picrate*, yellow leaflets, m. p. 160°; *methiodide*, colourless tablets, m. p. 147° (decomp.). The free amino-alcohol on treatment with concentrated hydrochloric acid in a tube at 100°, or with phosphorus pentachloride in light petroleum solution, gives the *hydrochloride* of 6-dimethylamino-3-methylbenzyl chloride, from which the yellowish-red *platinichloride*, m. p. 195°, can be obtained; the chlorine in the side-chain of the molecule is, however, so loosely attached that it is removed by water and by alkali with the formation of a mixture of the original alcoholic base and 6-dimethylamino-3-methylbenzyl ether,  $(\text{NMe}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}_2)_2\text{O}$ , which is more conveniently prepared by the dehydration of the amino-alcohol with twice its weight of strong sulphuric acid on the water-bath; it is an inodorous, colourless, viscous oil, b. p. 222—224°/19 mm.; *picrate*, m. p. 175°; *methiodide*, m. p. 186°; the ether base can be slowly but completely hydrolysed to the original alcohol base by boiling with dilute sulphuric acid.

Unlike 6-dimethylamino-3-methylbenzyl chloride, the esters with organic acids are stable substances. The *acetate*, colourless liquid, b. p. 144—145°/16 mm., gives a *picrate*, yellow needles, m. p. 117°, a yellowish-red *platinichloride*, m. p. 169°, and an oily *methiodide*. The *benzoate* is a viscid oil, b. p. 226—228°/16 mm. (slight decomp.); *picrate*, m. p. 137—138°. The *m-nitrobenzoate* is a colourless, crystalline solid, m. p. 64°; *picrate*, m. p. 154°.

In the preparation of 6-dimethylamino-3-methylbenzyl alcohol, a too extended heating of the reaction mixture causes partial oxidation to 4-dimethylamino-3-toluic acid,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CO}_2\text{H}$ , which is also obtainable by direct oxidation of the amino-alcohol with chromic acid; the *hydrochloride*, m. p. 188—189° (decomp.), can be converted into the yellow *platinichloride*, m. p. 217—218°. Towards reducing agents, dimethylaminomethylbenzyl alcohol is remarkably resistant, but it is reduced by sodium and alcohol to *as-dimethyl-m-xyldine*,  $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{NMe}_2$ , b. p. 205°; *picrate*, m. p. 123—124°; *platinichloride*, m. p. 219°. The same reduction product was obtained in an endeavour to dehydrate the dimethylaminobenzyl alcohol molecule to an indole ring (compare Paal and Landenheimer, *Abstr.*, 1893, i, 37) by heating with zinc chloride; 1:5-dimethylindole, prepared from *p*-tolylmethylnitrosoamine (compare Hegel, *Abstr.*, 1886, 552) for comparison, has b. p. 138°/17 mm., 262°/753 mm.,  $D_4^{20}$  1.0242, and on reduction with zinc and hydrochloric acid yields the 2:3-dihydro-derivative, falsely expected from the dehydration of the alcoholic base, b. p. 119—120°/18 mm., 233—234°/755 mm.,  $D_4^{20}$  0.9811; *platinichloride*, m. p. 203—204°; *picrate*, m. p. 177°.

Dimethylaminomethylbenzyl alcohol shows but little tendency to condense with other aromatic molecules. With methylaniline it gives a condensation *product*, boiling above 200° in a vacuum. When heated on the water-bath with excess of aniline in 15% hydrochloric acid for twenty-four hours, it gives a small yield of 4'-aminophenyl-6-dimethylamino-*m*-tolylmethane,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , a viscid

liquid, b. p. 220—224°/17 mm. If zinc chloride is used as the condensation agent, the amino-alcohol will condense with tertiary amines; thus, with dimethylaniline at 180°, it then gives colourless 4:6'-tetramethyldiaminophenyl-*m*-tolylmethane,



m. p. 83—84°, b. p. 250—252°/16 mm.; *hydrochloride*, m. p. 203°; *picrate*, reddish-yellow leaflets, m. p. 180—182°; yellow *platinichloride*, m. p. 197° (decomp.); *methiodide*, m. p. 204°. In an analogous manner, dimethyl-*p*-toluidine gives a very viscous, yellow oil, 2:2'-tetramethyldiamino-5:5'-di-*m*-tolylmethane,  $\text{CH}_2(\text{C}_6\text{H}_3\text{Me} \cdot \text{NMe}_2)_2$ , b. p. 212—214°/16 mm. (compare von Braun, *loc. cit.*).

Dimethyl-*o*-toluidine is already known to show considerable resistance towards condensation with aldehydes (Weinberg, *Abstr.*, 1892, 1078; Alexander, *ibid.*, 1320); however, by using a large excess of formaldehyde and extending the time for reaction, 4-dimethylamino-3-methylbenzyl alcohol can be obtained by a similar process to that for the isomeric 2-dimethylamino-5-methylbenzyl alcohol above; it is a yellow liquid, b. p. 147°/11 mm., giving an oily *hydrochloride*, *picrate*, m. p. 119°, a syrupy *methiodide*, colourless *acetate*, b. p. 156—158°/16 mm. (*picrate*, m. p. 133°), *m*-nitrobenzoate, m. p. 64° (*picrate*, m. p. 120°). This alcoholic base shows great resistance to sodium and alcohol, and only a few drops of the *as*-dimethyl-*m*-xylylidine could be obtained; it also condenses with difficulty with dimethylaniline in the presence of zinc chloride, giving a poor yield of 4:4'-tetramethyldiaminophenyl-*m*-tolylmethane,  $\text{NMe}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NMe}_2$ , a colourless, viscous oil, b. p. 247—249°/17 mm.; *platinichloride*, unstable; *picrate*, m. p. 183°.

4-Dimethylaminobenzyl alcohol is obtained in very small amount from the reaction product by treating dimethylaniline with an equal weight of concentrated hydrochloric acid and twice its weight of 40% formaldehyde solution for eight hours on the water-bath. The properties of the product do not agree with those stated by Rousset (*Abstr.*, 1895, i, 176). It is a yellow oil with an odour more pleasant than that of dimethylaniline; *platinichloride*, m. p. 181°; *picrate*, yellow needles, m. p. 130°; *methiodide*, m. p. 126°; the *acetate*, b. p. 142—144°/18 mm., gives a badly crystalline *platinichloride*, and a *picrate*, m. p. 113—114°; the *benzoate* is a viscous oil, b. p. 216—218°/16 mm., which gives an amorphous *platinichloride*, m. p. 179—180°, and a *picrate*, yellow needles, m. p. 117°; the *m*-nitrobenzoate is colourless, m. p. 51°, and gives a *picrate*, m. p. 146°. 4-Dimethylaminobenzyl chloride was produced by the action of hydrochloric acid on the amino-alcohol, as an unstable substance which could be isolated as the yellow *platinichloride*, m. p. 187°. The amino-alcohol condenses easily with dimethylaniline in the presence of zinc chloride, with the formation of *s*-tetramethyldiaminodiphenylmethane.

The condensation of formaldehyde with 1-phenylpiperidine yields some *p*-piperidylbenzyl alcohol, a yellow oil, b. p. 172—176°/12 mm.; *platinichloride*, m. p. 190°. The amino-alcohol condenses with phenylpiperidine in the presence of zinc chloride, giving dipiperidylbiphenylmethane, m. p. 84° (*platinichloride*, decomposes at 235°; *methiodide*, m. p. 217° with decomp.; *dibenzoyl* derivative, m. p. 250°), which

also accompanies the amino-alcohol in its original formation, but which is more satisfactorily obtained by treating an alcoholic solution of *p*-diaminodiphenylmethane with dibromopentane (compare von Braun, *loc. cit.*; also Abstr., 1904, i, 841).

*Diethylaminobenzyl alcohol*, obtained from the condensation of formaldehyde and diethylaniline in hydrochloric acid solution, is surprisingly unstable; it is a yellow liquid, b. p. 165°/9 mm.; *picrate*, m. p. 101°; *methiodide*, m. p. 149°; *acetate*, colourless oil, b. p. 178—180°/17 mm. It is easily decomposed by dilute acids with the formation of *s*-tetraethyldiaminodiphenylmethane, m. p. 41° (*picrate*, m. p. 191°), which therefore accompanies the amino-alcohol in its preparation. On account of its instability, the behaviour of diethylaminobenzyl alcohol towards reduction and condensation with aromatic amines could not be investigated. It is, however, oxidisable to the already known *p*-diethylaminobenzoic acid.

It was found impossible to produce sufficient condensation of formaldehyde with diethyl-*o*- or *p*-toluidine to obtain appreciable quantities of the corresponding aminobenzyl alcohols. D. F. T.

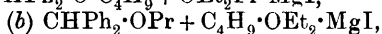
**Oxonium Compounds.** II. GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1219—1247).—In order to confirm his views concerning the mechanism of the Grignard reaction (compare this vol., i, 109), the author has carried out a number of further experiments under conditions excluding the possibility of isomeric change.

The formation of tetraphenylethane on distillation in a vacuum of the product obtained by the action of diphenylmethyl butyl ether on magnesium propyl iodide in the cold shows that the structure of monoetherates of organo-magnesium compounds is expressed by Grignard's formula,  $RR'OR \cdot MgI$ , and not by that of Baeyer,  $RR'OI \cdot MgR$ . The action of alkyl haloid on this compound being expressed by the equation:  $RR'OR \cdot MgI + R'I = MgI_2 + R_2O + R \cdot R'$ , the author regards it as most probable that the first stage of this reaction results in the formation of a tetra-alkyloxonium compound:  $RR'O:RR''$ . With water the decomposition should give rise to an unstable trialkyloxonium compound,  $RR'O:R''H$ , which would decompose with formation of  $R \cdot H$  and  $R \cdot R'$ ; experiment shows that this actually occurs. For instance, in the decomposition by water of the compound  $\begin{matrix} C_4H_9 \\ | \\ CHPh_2 \end{matrix} > O < \begin{matrix} Pr \\ | \\ MgI \end{matrix}$ , 12.5% of the latter gives propane, 14.5% tetraphenylethane, and 38.5% diphenylbutane.

The results of further experiments made to determine the relation of the amount of ether taking part in the reaction to that of the organo-magnesium compound (compare Bredig, *Zeitsch. Elektrochem.*, 1903, 9, 753) are in contradiction to Tschelinzeff's statement that ether plays the part of a catalyst in Grignard's reaction ("Organo-magnesium Compounds," Moscow, 1908, 54). T. H. P.

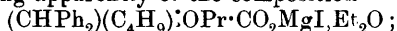
**Action of Carbon Dioxide on Etherates of Magnesium Alkyl Haloids.** GEORGE L. STADNIKOFF and (Mme.) Z. A. KUZMINA-ARON (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1247—1256).—The etherates

formed from ethers and organo-magnesium compounds, when dissolved in benzene or xylene, do not react with carbon dioxide, and the authors have now investigated this action in ethyl ethereal solution. Two possibilities present themselves: (1) According to Tschelinzeff's views ("Organo-magnesium Compounds," Moscow, 1908, 177) and on the assumption that the structure attributed by Stadnikoff (compare preceding abstract) to these etherates is correct, the ethyl ether should displace a molecule of an ether and this displacement should proceed in various ways; thus,  $C_4H_9 \cdot OPr(CHPh_2) \cdot MgI + Et_2O$  should give (a)  $CHPh_2 \cdot O \cdot C_4H_9 + OEt_2Pr \cdot MgI$ ,



and (c)  $C_4H_9 \cdot OPr + CHPh_2 \cdot OEt_2Pr \cdot MgI$ . (2) The etherate may merely dissolve in the ethyl ether. In this case the action of carbon dioxide should yield  $C_4H_9 \cdot OPr(CHPh_2) \cdot CO_2MgI$ , which would be converted by dilute sulphuric acid into the compound,  $C_4H_9 \cdot OPr(CHPh_2) \cdot CO_2H$ . The latter, being unstable, would undergo decomposition, for which three methods are possible: (a)  $CHPh_2 \cdot O \cdot C_4H_9 + Pr \cdot CO_2H$ ; (b)  $CHPh_2 \cdot OPr + C_4H_9 \cdot CO_2H$ , and (c)  $C_4H_9 \cdot OPr + CHPh_2 \cdot CO_2H$ .

The experiments as yet made do not indicate the formation of organic acids in this decomposition, which yields carbon dioxide, propane, butane, ethers, tetraphenylethane, *aa*-diphenylbutane, etc. As product of the action of carbon dioxide, an oily compound has been obtained, this being apparently of the composition



the ether is given up in a vacuum.

T. H. P.

**Reply to Gorsky's "Mechanism of the Grignard Reaction."**  
GEORGE L. STADNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1256—1264).—Polemical against Gorsky (this vol., i, 622).

T. H. P.

**Action of Formic Acid on Triarylcarbinols.** ALFRED GUYOT and A. KOVACHE (*Compt. rend.*, 1912, 155, 838—840. Compare this vol., i, 186; and Kauffmann and Pannwitz, this vol., i, 351).—Crystallisable formic acid, whilst reducing triarylcarbinols, does not have this effect on other molecules containing reducible groups, the reaction being specific for this one class of compounds. A study of the reaction in the case of a large number of such carbinols shows that the reaction is not always quantitative. If, however, a certain quantity of anhydrous sodium formate is previously added to the formic acid, the transformation of the carbinol into hydrocarbon and the evolution of carbon dioxide are theoretical, thus giving a method for the quantitative estimation of such compounds. The part played by the sodium formate is apparently to prevent any dehydrating action of the formic acid.

W. G.

**Betulin. II.** I. K. TRAUBENBERG (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1202—1208).—More energetic oxidation of betulin by means of chromic acid than that previously employed (this vol., i, 260) yields betulinic acid and the ketone,  $C_{24}H_{38}O_2$ , but no diketone,

so that betulin contains only one hydroxyl group of secondary character.

The betulinic acid obtained in the above manner, and regarded by Hausmann (Abstr., 1877, i, 94) as possessing the composition  $C_{36}H_{54}O_6$ , appears to be, not an individual product, but a mixture of an acid,  $C_{12}H_{20}O$ , and a hydrocarbon,  $C_{12}H_{18}$ , the dry distillation of betulin proceeding according to the equation:  $C_{24}H_{40}O_2 = H_2O + C_{12}H_{20}O + C_{12}H_{18}$ .

Oxidation of the betulin by means of fuming nitric acid yields a dinitro-acid,  $C_{22}H_{32}O_{10}N_2$ , m. p. 203—205°. Analysis of the compound obtained by treating this acid with phenylhydrazine gives indefinite results, explainable as due to the formation either of a dihydrazone or of a monohydrazone in which the two nitro-groups are reduced to amino-groups.

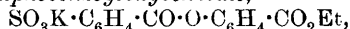
T. H. P.

**Crystalline Form of  $\Delta^1$ -cycloHexene-1- $\alpha$ -isobutyric Acid.** PETR N. TSCHIRWINSKY (*Zeitsch. Kryst. Min.*, 1912, 51, 303; from *Schriften Ural Ges. Naturf.*, 1909, 29, 113—117).—Crystals of the acid,  $C_6H_9 \cdot CMe_2 \cdot CO_2H$ , prepared by O. Wallach (Abstr., 1908, i, 406) are orthorhombic, with  $a : b : c = 0.914 : 1 : 0.359$ .

L. J. S.

**New Aromatic Ethereal Salts Formed by the Interaction of *o*-Sulphobenzoic Anhydride and Phenols in the Presence of Water and an Alkali Hydroxide.** ARNOLD H. C. HEITMAN (*J. Amer. Chem. Soc.*, 1912, 34, 1591—1597).—The following method has been found to yield alkali salts of esters of the general formula,  $SO_3X \cdot C_6H_4 \cdot CO_2R$ . *o*-Sulphobenzoic anhydride (1 mol.) is suspended in about 5 parts of water at 0°, and treated with alkali hydroxide (1 mol.) and a phenol (1 mol.) also dissolved in the same quantity of water at 0°. The mixture is shaken until solution results and is then filtered. The phenol, remaining in the solution, is extracted with ether, the aqueous solution concentrated to about one-fifth of the original volume and allowed to crystallise. The salts are soluble in water or alcohol, stable in the air or in solution, and are readily hydrolysed by warm dilute solutions of alkali carbonates with formation of the phenol and alkali *o*-sulphobenzoate. It is suggested that they may prove of value for the synthesis of physiologically active substances.

The following salts are described: *Potassium phenyl o-sulphobenzoate*,  $SO_3K \cdot C_6H_4 \cdot CO_2Ph$ , m. p. 277—280°. *Barium phenyl o-sulphobenzoate*. *Potassium ethyl o-sulphobenzoyloxybenzoate*,



m. p. 246°, from ethyl salicylate. *Barium guaiacyl o-sulphobenzoate*,  $Ba(SO_3 \cdot C_6H_4 \cdot CO \cdot OC_6H_4 \cdot OMe)_2$ . *Sodium thymyl o-sulphobenzoate*,  $SO_3Na \cdot C_6H_4 \cdot CO \cdot OC_6H_3Me \cdot CHMe_2$ . *Sodium phenolphthalein o-sulphobenzoate*. All these salts are crystalline, with the exception of the last two which are obtained as amorphous powders.

E. G.

**Preparation of Esters of Glycols.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 248255).—The following acids can be employed for the preparation of glycol esters: phenylacetic,  $\alpha$ -phenyl-

propionic,  $\alpha$ -phenylbutyric,  $\alpha$ -phenyl- $\alpha$ -ethylbutyric, and  $\beta$ -phenylpropionic acids.

*Phenyldiethylcarbinylacetic* [ $\alpha$ -Phenyl- $\beta$ -ethylvaleric] acid,



is prepared by the interaction of sodium phenylacetonitrile and diethylcarbinyl bromide and subsequent hydrolysis.

*Glycyl phenylacetate*, b. p. 185—190°/25 mm., is obtained from ethylene glycol and phenylacetic acid, whilst the *ester* from ethylene dichloride and  $\alpha$ -phenylbutyric acid has b. p. 166°/4 mm.

*Glycyl  $\beta$ -phenylpropionate* has b. p. 180°/16 mm. F. M. G. M.

**Preparation of Acids containing an Aryl Group in the  $\alpha$ -Position.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 248777).—The amides and carbamides of  $\alpha$ -aryl acids of general formula  $\text{CRR}^1\text{R}^2\cdot\text{CO}_2\text{H}$  (where R is aryl, and R<sup>1</sup> and R<sup>2</sup> alkyl groups) are of therapeutic value, and the following are now described :

*$\alpha$ -Phenyl- $\alpha$ -propylvaleronitrile*,  $\text{CPhPr}_2\cdot\text{CN}$ , b. p. 157—159°/30 mm. (prepared from phenylacetonitrile), when heated with alcoholic potassium hydroxide during seven hours at 120—130°, furnishes  *$\alpha$ -phenyl- $\alpha$ -propylvaleramide*, prisms, m. p. 91—92°, whilst  *$\alpha$ -phenyl- $\alpha$ -ethylbutyronitrile*,  $\text{CPhEt}_2\cdot\text{CN}$ , an oil, b. p. 139°/22 mm., yields  *$\alpha$ -phenyl- $\alpha$ -ethylbutyramide*, m. p. 53°.

*$\alpha$ -Phenyl- $\alpha$ -ethylbutyrylcarbamide*, prepared from carbamide and  $\alpha$ -phenyl- $\alpha$ -ethylbutyryl chloride, has m. p. 132—133°. F. M. G. M.

**Preparation of Derivatives of  $\alpha$ -Aryl Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 249241. Compare Abstr., 1889, 861, and preceding abstract).—The amides and carbamides of  $\alpha$ -aryl acids of general formula  $\text{R}^1\text{CHR}\cdot\text{CO}_2\text{H}$  (where R<sup>1</sup> is aryl, and R an alkyl group) are quite tasteless, of therapeutic value, and readily prepared by ordinary methods.

*$\alpha$ -Phenyl-*n*-valeric acid*, b. p. 280° (*loc. cit.*), furnishes a *chloride*, which yields the corresponding *amide*, m. p. 83—85°, *carbamide*, *glycide*, and *ethylamide*.

*$\alpha$ -Phenyl-*n*-butyric acid* (phenylethylacetic acid) likewise furnishes a *chloride*, *carbamide*, m. p. 147°, and *amide*, m. p. 86°.

Phenylacetonitrile when treated with sodamide and diethylcarbinol yields *phenylisoamylacetonitrile*; this furnishes the corresponding *acid*, *acid chloride*, and finally *phenylisoamylacetamide*, m. p. 138°.

F. M. G. M.

**Determination of the Configuration of the Stereoisomeric Cinnamic Acids.** RICHARD STOERMER and PAUL HEYMANN (*Ber.*, 1912, 45, 3099—3104).—Fischer (compare this vol., i, 187) has recently called attention to the fact that no definite conclusions can be drawn, regarding the configuration of the cinnamic acids, from the reduction of phenylpropionic acid, since under different conditions both the ordinary and the *allo*- or *iso*-acid may be produced (compare Paal and Hartmann, Abstr., 1909, i, 927). Although the ordinary acid is generally regarded as the *trans*-form, and the *allo*- or *iso*-acid as the *cis*-form, no experimental proof of these configurations has yet been

brought forward. This uncertainty with respect to the configuration of the acids has now been removed, and the correctness of the usual view demonstrated, in the following manner :

Ordinary *o*-nitrocinnamic acid, on exposure to ultra-violet light in pyridine solution, is transformed into a labile isomeride, *allo-o*-nitrocinnamic acid. Both isomerides may be reduced to the corresponding amino-acids, of which the one obtained from the *allo*-acid is at once transformed into carbostyryl by passing carbon dioxide through an aqueous solution of its barium salt, and therefore must possess the *cis*-configuration ; on the other hand, the *o*-aminocinnamic acid described by Baeyer and Jackson, and formed by the reduction of the ordinary *o*-nitro-acid, can be converted into carbostyryl only by indirect methods, and, therefore, has the *trans*-configuration. On diazotisation and reduction, *trans-o*-aminocinnamic acid yields ordinary cinnamic acid, whereas the *cis*-amino-acid gives rise to *allo*-(or *iso*-)cinnamic acid, which, consequently, must have the *cis*-configuration.

The configuration of the isomeric *o*-amino-acids has also been established by diazotisation and boiling the resulting diazonium compound with water. The amino-acid obtained from *allo-o*-nitrocinnamic acid is directly converted into coumarin, whilst Baeyer and Jackson's *o*-amino-acid yields coumaric acid, which can be converted into the anhydride only by indirect methods.

*allo-o*-Nitrocinnamic acid forms stout, yellowish-white crystals, m. p. 143°, dissolves in concentrated sulphuric acid with a blue coloration, and is much more readily soluble in organic solvents than the *trans*-isomeride, into which it may be converted by exposure to sunlight in chloroform solution containing a trace of bromine. Its solubility in benzene at 18° = 0.69% (*trans*-acid = 0.03%). When dissolved in dilute aqueous ammonia and the solution boiled with ferrous sulphate and excess of barium hydroxide, it yields *cis-o*-aminocinnamic acid, which, however, could not be isolated in the free condition, but is converted by passing carbon dioxide through the aqueous solution of its barium salt into carbostyryl. The diazotisation of the *cis-o*-amino-acid was accomplished by dissolving the theoretical amount of sodium nitrite in the aqueous solution of its barium salt and adding the mixture slowly to cold dilute sulphuric acid. Reduction of the resulting diazonium compound with hypophosphorous acid yielded *isocinnamic* acid, which was further identified by its conversion into the aniline salt of *allo*-cinnamic acid. The transformation of *trans-o*-aminocinnamic acid into ordinary cinnamic acid was effected in a similar manner.

F. B.

Sodium Phenyl Carbonate as Intermediate Product in Kolbe's Synthesis of Salicylic Acid. CARL H. SLUITER (*Ber.*, 1912, 45, 3008—3110. Compare this vol., i, 189).—A reply to Tymstra (this vol., i, 859). Sodium salicylate when heated in a sealed tube for three hours at 250°, and then afterwards kept sealed in the cold for eighteen hours, is found to be unaltered ; the carbon dioxide formed in the dissociation of the salicylate evidently undergoes complete re-absorption. If the heating is carried to 290°, there is some charring, and a little free carbon dioxide is formed, whilst the solid

residue contains some sodium hydrogen carbonate. It is suggested that in this case the sodium phenoxide formed from the dissociation of the salicylate undergoes partial decomposition:  $C_6H_5 \cdot ONa = CH_4 + 4C + CO_2 + NaOH$ . These results are held to favour the author's view of the formation of sodium salicylate. D. F. T.

**Terephthalaldehyde and Terephthalaldehydic Acid.** RUDOLF WEGSCHEIDER and HERMANN SUIDA (*Monatsh.*, 1912, 33, 999—1028). —In an investigation as to the possible occurrence of tautomerism with *p*-aldehydic acids analogous to that exhibited by the ortho-isomerides (Wegscheider, *Abstr.*, 1903, i, 562), the authors have obtained only negative results.

Terephthalaldehyde is obtained more satisfactorily by the simultaneous hydrolysis and oxidation of *p*-xylylene bromide with lead nitrate solution (Löw, *Abstr.*, 1885, 1208, and others) than by the oxidation of *p*-xylene (Thiele and Winter, *Abstr.*, 1900, i, 500) with chromic acid. The suggested oxidation of *p*-xylene by manganese dioxide and sulphuric acid (Lassar-Cohn, *Arbeitsmethoden*, 4th ed., 977) was found to yield *p*-toluic acid in place of the desired product.

When terephthalaldehyde is reduced by sodium amalgam in aqueous alcoholic solution, *p*-xylylene glycol is obtained, together with another substance, m. p. 220°.

Terephthalaldehydic acid is best obtained by oxidation of the dialdehyde with potassium dichromate and dilute sulphuric acid; its m. p. is 256° (compare Simonis, this vol., i, 565), but in an open tube appears to be higher on account of oxidation to terephthalic acid.

Nitration of terephthalaldehyde (compare Löw, *loc. cit.*) produces nitroterephthalaldehyde, m. p. 86° (*phenylhydrazone*, m. p. 213—216°; *tetracetate*, m. p. 147—149°), with two nitroterephthalaldehydic acids, m. p. 160° and 184° respectively, and a sparingly soluble acid, m. p. above 300°, as by-products.

The methyl ester of terephthalaldehydic acid, obtained by interaction of methyl iodide and the silver salt of the acid, crystallises in rods, m. p. 62—63°, and can be hydrolysed by alcoholic sodium hydroxide to the original acid; the ester gives a *phenylhydrazone*, yellow needles, m. p. 144—146° (in one experiment a substance, m. p. 116—117°, possibly a labile form, was obtained), a *diacetate*, rods, m. p. 66—68°, a *hydrobenzamide* compound,  $N_2(CH \cdot C_6H_4 \cdot CO_2Me)_3$ , m. p. 140—142°, and is easily oxidised at 100° by air, giving methyl hydrogen terephthalate. When terephthalaldehydic acid is heated at 100° with methyl alcohol containing a little hydrogen chloride, the above methyl ester is produced, but at 140° a mixture of this ester with its *dimethylacetal* derivative,  $CO_2Me \cdot C_6H_4 \cdot CH(OMe)_2$ , m. p. 29—30°, is obtained; in an impure condition the latter substance readily decomposes with formation of the methyl ester.

The ethyl ester of terephthalaldehydic acid, which has already been obtained by Löw (*loc. cit.*), is an oil which crystallises after long standing, possibly on account of oxidation.

Phosphorus pentachloride acts on terephthalaldehydic acid with the formation of *o*-dichloro *p*-toluoyl chloride, m. p. 50—52°. It was not found possible to convert the substance into the above acetal, but

by treatment with methyl alcohol containing suspended calcium carbonate, *methyl o-dichloro-p-toluate*, m. p. 32—35°, was obtained. Attempts to prepare the free dichloro-acid were unsuccessful.

D. F. T.

**Some New Derivatives of the Dihydroxybenzoic Acids.**  
 FRANZ VON HEMMELMAYR (*Monatsh.*, 1912, 33, 971—998).—5-Bromocatecholcarboxylic acid,  $C_7H_5O_4Br \cdot H_2O$ , is obtained when a solution of catecholcarboxylic (2 : 3-dihydroxybenzoic) acid in glacial acetic acid is treated with the requisite quantity of bromine at the ordinary temperature. It forms transparent, colourless, prismatic crystals, m. p. 185°. When the aqueous solution of these crystals is boiled for some time, it deposits, on cooling, white, silky, microscopic needles in addition to the prismatic crystals; these sinter at 211°, and have m. p. 215°. The barium salt,  $(C_7H_4O_4Br)_2Ba \cdot H_2O$ , crystallises in clusters of flat needles.

4 : 5-Dibromocatecholcarboxylic acid (compare Praxmarer, *Abstr.*, 1907, i, 216) is best obtained from the dihydroxybenzoic acid by bromination in glacial acetic acid solution. It forms long, colourless needles, m. p. 241° (decomp.). The barium salt,  $(C_7H_3O_4Br_2)_2Ba \cdot 3H_2O$ , forms spherular aggregates of slender needles. The methyl ester,  $C_8H_5O_4Br_2$ , crystallises in slender needles, m. p. 156—157°.

The two bromo-substitution products of  $\beta$ -resorcylic (2 : 4-dihydroxybenzoic) acid (compare Zehenter, *Abstr.*, 1882, 193; 1887, 924) are best prepared, using glacial acetic acid as the solvent during bromination. Bromo- $\beta$ -resorcylic acid has m. p. 212°; the dibromo-acid has m. p. 220°. Dibromo-2 : 4-diacetoxybenzoic acid,  $C_{11}H_5O_6Br_2$ , crystallises in slender prisms, m. p. 165°. Attempts to prepare the silver salt from the ammoniacal solution were unsuccessful, since the ammonia brings about partial fission of the acetyl group. The aqueous solution of the diacetyl acid is decomposed on boiling; to a slight extent the decomposition proceeds with evolution of carbon dioxide, but for the most part it takes place with fission of one acetyl group, giving dibromoacetoxybenzoic acid,  $C_9H_5O_5Br_2$ , which crystallises in bundle-shaped groups of needles, m. p. 195°.

By the action of nitric acid (D 1·4) on dibromo- $\beta$ -resorcylic acid, 2-bromo-4 : 6-dinitroresorcinol,  $C_6H_3O_6N_2Br$ , is produced. It forms yellow, leaf-like crystals, and has m. p. 192·5°.

By the bromination of nitro- $\beta$ -resorcylic acid in glacial acetic acid solution, even when sufficient bromine is used for the substitution of two hydrogen atoms, 3-bromo-5-nitro- $\beta$ -resorcylic acid,  $C_7H_4O_6NBr \cdot 2H_2O$ , is obtained as yellow needles, m. p. 242° (decomp.). The basic barium salt ( $6H_2O$ ) and silver salts are described. The methyl ester,  $C_8H_5O_6NBr$ , forms long, tabular crystals, m. p. 198—200°. It was not possible to bring about complete acetylation of the acid; treatment of the partly acetylated product with dilute ammonium hydroxide gave orange-red, microscopic prisms of the diammonium salt,  $C_7H_{10}O_6N_3Br$ .

4-Bromo-2 : 6-dinitro- $\alpha$ -resorcylic acid,  $C_4H_2O_8N_2Br \cdot 1$  or  $2H_2O$ , is obtained from monobromo- $\alpha$ -resorcylic acid (Barth and Senhofer, *Abstr.*, 1872, 1014) by the action of nitric acid (D 1·4), the temperature not being allowed to rise very much. It forms yellow, glistening leaflets,

m. p. 210° (decomp.). The basic *barium* salt ( $2\text{H}_2\text{O}$ ) and two *silver* salts were prepared. When the acid is boiled with water, 2-bromo-4:6-dinitroresorcinol separates, owing to decomposition; when acetylated with acetic anhydride the carboxyl group is eliminated, and *bromo-dinitroresorcinol diacetate*  $\text{C}_{10}\text{H}_7\text{O}_8\text{N}_2\text{Br}$ , obtained as yellow needles, m. p. 113°.

2:4-Dibromo- $\alpha$ -resorcylic acid,  $\text{C}_7\text{H}_4\text{O}_4\text{Br}_2 \cdot 3\text{H}_2\text{O}$ , is obtained by the bromination of  $\alpha$ -resorcylic (3:5-dihydroxybenzoic) acid in glacial acetic acid solution. It crystallises in colourless, spherular aggregates of tabular crystals, m. p. 192°. The *barium* ( $10\text{H}_2\text{O}$ ) and *silver* ( $4\text{H}_2\text{O}$ ) salts are described. The *diacetyl* derivative,  $\text{C}_{11}\text{H}_8\text{O}_6\text{Br}_2$ , forms large, colourless crystals, m. p. 182—183°. Nitration of the acid with 1:4 nitric acid gives yellow needles of 2:4-dibromo-6-nitro- $\alpha$ -resorcylic acid, m. p. 208° (decomp.). The basic *barium* ( $6\text{H}_2\text{O}$ ) and *silver* ( $\text{H}_2\text{O}$ ) salts are described.

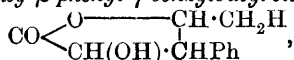
The aqueous solutions of the various acids mentioned above, together with those of 2:4-, 2:5-, 2:6- and 3:4-dihydroxybenzoic acids, nitro- and dinitro-2:4-dihydroxybenzoic acid, monobromo-2:5-, dibromo-2:6- and tribromo-3:4-dihydroxybenzoic acids were investigated with respect to the stability of the carboxyl group on boiling. With the exception of nitro-2:4-, monobromo-2:5-, monobromo-3:4-, 4:5-dibromo-2:3- and the 2:5- and 3:4-dihydroxybenzoic acids, more or less elimination of carbon dioxide takes place. T. S. P.

An  $\alpha$ -Hydroxy-lactone from Phenylacetaldehyde. ERNST SPÄTH (*Monatsh.*, 1912, 33, 1029—1054).—The author has found a second example of the characteristic condensation of an aldehyde with potassium cyanide previously observed with isobutaldehyde (Kohn, Abstr., 1899, i, 328).

An aqueous-alcoholic solution of a mixture of phenylacetaldehyde and potassium cyanide slowly deposits colourless needles of  $\beta$ -hydroxy- $\alpha$ -*diphenylbutaldehydecyanohydrin*,



m. p. 146—148°; the mother liquor contains a brown, amorphous substance,  $\text{C}_{32}\text{H}_{28}\text{O}(\text{OH})_2$ , the two hydroxyl groups being detected by Zerewitinoff's method (Abstr., 1907, ii, 509). The cyanohydrin is easily hydrolysed by dilute acids, preferably in alcoholic solution, the product being  $\alpha$ -hydroxy- $\beta$ -phenyl- $\gamma$ -benzylbutyrolactone,



needles, m. p. 114—115°, b. p. 264—265°/16 mm. (compare Erlenmeyer and Reis, Abstr., 1904, i, 1018); on warming with dilute potassium hydroxide solution the lactone is converted into sparingly soluble *potassium  $\alpha$ - $\gamma$ -dihydroxy- $\beta$ - $\delta$ -diphenylvalerate*, m. p. 228° (decomp.), which at 250° in a vacuum decomposes with formation of  $\alpha$ -diphenylpropylene (compare Dieckmann and Kämmerer, Abstr., 1906, i, 820). The lactone gives an oily *acetate* and a *benzoate*, m. p. 126—127°, which is also obtained by the action of benzoyl chloride and potassium hydroxide solution on the cyanohydrin.

The lactone shows the tendency to esterify to give esters of the corresponding hydroxy-acid, but by the action of methyl iodide on the

silver salt of the acid, *methyl  $\alpha$ -dihydroxy- $\beta$ - $\delta$ -diphenylvalerate* was obtained in needles, m. p. 124—126° (decomp.); the *ethyl* ester, obtained in an analogous manner, forms needles, m. p. 122—123° (decomp.); both esters at 130° decompose quantitatively into the lactone and the corresponding alcohol.

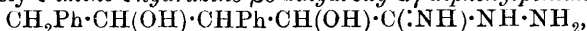
On reduction of the lactone with hydriodic acid at 200°, a mixture of 2-phenylnaphthalene, leaflets, m. p. 101—102°, with an oil, b. p. 184—187°/14 mm., which is probably 2-phenyltetrahydronaphthalene, is obtained. With magnesium methyl iodide the lactone gives  *$\alpha$ - $\gamma$ -diphenyl- $\epsilon$ -methylhexane- $\beta$  $\delta$ -triol*, colourless crystals, m. p. 134—135°.

The lactone in warm alcoholic solution forms *additive* compounds with phenylhydrazine, hydrazine (applied as the hydrate), and methylamine, the products being of uncertain structure, and the m.p.'s 184° (decomp.), 184—185°, and 174—175° respectively. All three products are easily hydrolysed by dilute mineral acid into their constituents.

The cyanohydrin behaves similarly with the above three bases; phenylhydrazine produces colourless needles of  *$\epsilon$ -imino- $\epsilon$ -phenylhydrazino- $\beta$  $\delta$ -dihydroxy- $\alpha$ - $\gamma$ -diphenylpentane*,



m. p. 142—147°, which when heated with aqueous alcohol loses the elements of water, giving a heterocyclic substance,  $\text{C}_{23}\text{H}_{22}\text{O}_2\text{N}_2$ , of uncertain structure, colourless needles, m. p. 184°; *hydrochloride*, sparingly soluble needles. Hydrazine and methylamine produce respectively  *$\epsilon$ -imino- $\epsilon$ -hydrazino- $\beta$  $\delta$ -dihydroxy- $\alpha$ - $\gamma$ -diphenylpentane*,



m. p. 183—184°, and  *$\epsilon$ -methylamino- $\epsilon$ -imino- $\beta$  $\delta$ -dihydroxy- $\alpha$ - $\gamma$ -diphenylpentane*, a slowly solidifying syrup. The latter substance on cautious hydrolysis by keeping in cold aqueous alcoholic solution gives a product identical with the additive compound of the lactone and methylamine. These addition compounds of cyanohydrin with the above bases are all hydrolysable by mineral acids to the lactone and the corresponding base.

D. F. T.

**Preparation of 1-Aminoanthraquinone-2-carboxylic Acid and its Derivatives.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 247411).—1-Aminoanthraquinone-2-carboxylic acid or its substituted derivatives are readily obtained by the action of ammonia or of primary or secondary amines on anthraquinone-2-carboxylic acids, which are negatively substituted in the  $\alpha$ -position.

*1-Aminoanthraquinone-2-carboxylic acid*, yellow needles, m. p. 280°, is prepared by boiling 1-chloroanthraquinone-2-carboxylic acid (86 parts) and copper oxide (3 parts) with 300 parts of water and an equal quantity of 15% ammonium hydroxide solution during six hours under reflux; the *alkali* salts dissolve in water to form a red solution. *Methylaminoanthraquinone-2-carboxylic acid*, bluish-red needles, m. p. 240°, is obtained when the ammonium hydroxide in the foregoing example is replaced by methylamine; the *alkali* salts furnish bluish-coloured aqueous solutions.

*1-Anilinoanthraquinone-2-carboxylic acid*, glistening, brown leaflets, m. p. 297—298°, is prepared by boiling 1-nitroanthraquinone-2-carboxylic acid (86 parts) with aniline (860 parts).

1 : *p*'-Chloroanilinoanthraquinone-2-carboxylic acid is obtained as a red powder from *p*-chloroaniline and 1-chloroanthraquinone-2-carboxylic acid with copper oxide and sodium carbonate; the sodium salt separates in glistening, golden leaflets.

1-β-Naphthylaminoanthraquinone-2-carboxylic acid is a dark violet powder; its alkali salts are very sparingly soluble in water with a violet coloration; the sodium salt forms graphite-like crystals.

1-Piperidylaminoanthraquinone-2-carboxylic acid forms red flakes.

1-Glycylanthraquinone-2-carboxylic acid, red needles, is obtained by the action of sodium glycine on 1-chloroanthraquinone-2-carboxylic acid in the presence of copper powder in aqueous solution.

Nitro-1-β-naphthylaminoanthraquinone-2-carboxylic acid, a black powder, is prepared from 1-chloronitroanthraquinone-2-carboxylic acid and β-naphthylamine; the sodium salt separates as a dark violet powder, whilst the compound obtained by heating 1-chloroanthraquinone-2-carboxylic acid with 3-amino-*p*-toluoylbenzoic acid is a violet powder dissolving in alkali with a violet coloration.

The 1-chloroanthraquinone-2-carboxylic acid employed in these preparations was prepared by the oxidation of 1-chloro-β-anthraquinone-aldehyde (Abstr., 1907, i, 224); it forms yellow needles and has *m. p.* 267°.

F. M. G. M.

**Preparation of Condensation Products Containing Sulphur in the Anthraquinone Series.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 248996). — 1-Anilino-4-*p*-tolylthiolanthraquinone-2-carboxylic acid, a bluish-violet powder, is prepared by condensing 4-chloro-1-anilinoanthraquinone-2-carboxylic acid with *p*-thiocresol; by further condensation it furnishes an *acridone*, which can also be obtained by the action of *p*-thiocresol on 4-chloroanthraquinone-2 : 1-acridone.

1-β-Naphthylamino-4-*p*-tolylthiolanthraquinone-2-carboxylic acid, a green powder, is obtained in a similar manner from 4-chloro-1-β-naphthylaminoanthraquinone-2-carboxylic acid, whilst 1 : 4-di-*p*-tolylthiolanthraquinone-2-carboxylic acid, a red powder, is prepared from 1 : 4-dichloroanthraquinone-2-carboxylic acid. These compounds are all readily converted into the corresponding *acridones*. F. M. G. M.

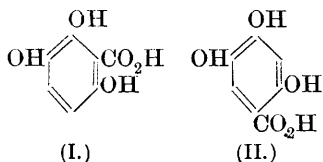
**Action of Alkalis on Bisdiphenylacetylhydrazide Chloride.** ROBERT STOLLÉ and F. SCHMIDT (*Ber.*, 1912, 45, 3113—3116).—On treatment with alcoholic sodium ethoxide at a low temperature, or when boiled with aqueous sodium hydroxide, bisdiphenylacetylhydrazide chloride,  $\text{CHPh}_2\cdot\text{CCl}:\text{N}\cdot\text{N}:\text{CCl}\cdot\text{CHPh}_2$  (Abstr., 1911, i, 508), loses hydrogen chloride and is converted into tetraphenylsuccinonitrile. It is probable that the compound (I)  $\text{CPh}_2\cdot\text{C}:\text{N}\cdot\text{N}:\text{C}:\text{CPh}_2$  is immediately formed in the reaction, but, owing to the instability of the group  $\text{C}:\text{C}:\text{N}\cdot\text{N}:\text{C}:\text{C}$ , at once undergoes rearrangement with the formation of the nitrile. That the rupture of the nitrogen-linking is not due to a special action of the alkali is shown by the behaviour of 3 : 6-bisdiphenylmethylen-3 : 6-dihydro-1 : 2 : 4 : 5-tetrazine (see this vol., i, 1036). When heated alone or in solution, this loses nitrogen (1 mol.), yielding tetraphenylsuccinonitrile, the above-mentioned compound (I) no doubt being formed as an intermediate

product. Insufficient cooling during the action of sodium ethoxide on the hydrazide chloride causes the formation of diphenylacetoneitrile.

*Tetrachlorotetraphenylsuccinonitrile*,  $C_{28}H_{16}N_2Cl_4$ , prepared by chlorinating tetraphenylsuccinonitrile in the light of a mercury lamp, crystallises in stout prisms, m. p.  $164^\circ$ .

Phenyliminodiphenylacetyl chloride reacts with sodium methoxide, yielding *methyl phenyliminodiphenylacetate*,  $C_{21}H_{19}ON$ , crystallising in colourless needles, m. p.  $150^\circ$ . The *ethyl* ester, prepared in a similar manner, forms prisms, m. p.  $131^\circ$ . F. B.

**Some Derivatives of Hydroxyquinol. VIII.** GUIDO BARGELLINI and ERMANNOMARTEGIANI (*Gazzetta*, 1912, 42, ii, 351—356. Compare this vol., i, 292).—The hydroxyquinolcarboxylic acid of Thiele and Jäger has been stated by von Hemmelmayr (Abstr., 1911, i, 983) to have the constitution (I), but the authors now advance evidence in favour of formula (II). When the acid is treated with methyl sulphate, asaronic acid is formed (compare Fabinyi and Széki, Abstr., 1907, i, 45), and the position of the methoxyl groups in this



compound is established by the fact that it can be obtained by oxidation of 2:4:5-trimethoxyacetophenone. The esterification of the hydroxyquinolcarboxylic acid with methyl sulphate does not proceed quantitatively, for hydroxyquinol trimethyl ether and hexamethoxydiphenyl are also formed.

*Asaronanilide*,  $C_{16}H_{17}O_4N$  (prepared with phenylcarbimide), forms dirty white scales, m. p.  $144$ — $146^\circ$ . *Asaronthioanilide*,  $C_{16}H_{17}O_3NS$ , is a yellow crystalline substance, m. p.  $159$ — $160^\circ$ . When it is treated in alkaline solution with potassium ferri-cyanide, an oxidation product,  $C_{16}H_{15}O_3NS$ , is obtained. It is a yellow substance, m. p.  $193$ — $195^\circ$ , and to it is assigned the constitution of 2:4:5-trimethoxyphenylbenzthiazole (annexed formula). R. V. S.

**Preparation of o-Aminoanthraquinonecarboxylic Acid.** ACTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 248838).—

When *o-aminocarboxybenzoyl-o-benzoic acid* (annexed formula) is heated with sulphuric acid or other condensing reagents it usually yields about 70% of 3-aminoanthraquinone-2-carboxylic acid with 30% of 1-aminoanthraquinone-2-carboxylic acid, red crystals, m. p.  $280^\circ$  (about); the separation of these products is effected by means of the relative insolubility of sodium 3-aminoanthraquinone-2-carboxylate in excess of alkali.

*Nitroterephthaloyl-o-benzoic acid* and *o-aminoterephthaloyl-o-benzoic acid*, yellow leaflets, m. p.  $265^\circ$ , were also obtained during the preparation of the foregoing *o-aminocarboxybenzoyl-o-benzoic acid* from *p-toluoil-o-benzoic acid* (Abstr., 1898, i, 322). F. M. G. M.

**Constitution of Orsellinic Acid.** ALFRED THIEL (*Annalen*, 1912, 394, 108—110).—A proof that one hydroxyl group in orsellinic acid is in the para-position to the carboxyl group (Fischer and Hoesch, this vol., i, 859) has already been given by Thiel, Schumacher, and Roemer (Abstr., 1906, i, 22). C. S.

**Preparation of Halogen Derivatives of Benzaldehyde.** JAN J. BLANKSMA (*Chem. Weekblad*, 1912, 9, 862—870. Compare Abstr., 1909, i, 936).—A number of halogen derivatives of benzaldehyde have been prepared from ring-substituted *p*-aminobenzaldehydes. Aniline converts 3:5-dibromo-4-aminobenzaldehyde into 3:5-*dibromo-4-aminobenzylideneaniline*,  $C_6H_5 \cdot N : CH \cdot C_6H_2Br_2 \cdot NH_2$ , pale yellow crystals, m. p. 99°. Diazotisation of 3:5-dibromo-4-aminobenzaldehyde in hydrobromic acid and treatment with cuprous bromide in the same solvent yields 3:4:5-*tribromobenzaldehyde* in colourless crystals, m. p. 108°, readily sublimed and volatile in steam. Boiling with aqueous potassium permanganate converts it into 3:4:5-*tribromobenzoic acid*, m. p. 235° (compare Sudborough, Abstr., 1894, i, 244); acetic anhydride and concentrated sulphuric acid give a *diacetyl* derivative,  $C_6H_2Br_3 \cdot CH(OAc)_2$ , colourless crystals, m. p. 100°; aniline produces 3:4:5-*tribromobenzylideneaniline*, colourless crystals, m. p. 99°; *p*-toluidine forms 3:4:5-*tribromobenzylidene-p-toluidine*, m. p. 98°.

Bromine water converts 2-bromo-4-aminobenzaldehyde into 2:3:5-*tribromo-4-aminobenzaldehyde*, m. p. 182°, which is converted by diazotisation in sulphuric acid into 2:3:5-*tribromobenzaldehyde*, colourless crystals, m. p. 114°, volatile with steam, and by aqueous potassium permanganate into 2:3:5-*tribromobenzoic acid*, m. p. 187° (compare Rosanoff and Prager, Abstr., 1909, ii, 32; Ullmann and Kopetschni, Abstr., 1911, i, 292).

*m*-Aminobenzaldehyde is transformed by bromine water into 2:4:6-*tribromo-m-aminobenzaldehyde*, m. p. 139° (compare Anilin-farben- & Extrakt-Fabriken, vormals J. R. Geigy, Abstr., 1910, i, 175), from which diazotisation yields 2:4:6-*tribromobenzaldehyde*, colourless crystals, m. p. 99°, volatile with steam; it is converted by potassium permanganate into 2:4:6-*tribromobenzoic acid*, m. p. 186°; and by aniline into 2:4:6-*tribromobenzylideneaniline*, pale yellow needles, m. p. 90°.

Diazotisation and treatment with cuprous bromide in hydrobromic acid convert 2:4:6-*tribromo-4-aminobenzaldehyde* into 2:3:4:6-*tetrabromobenzaldehyde*, a colourless substance volatile with steam, m. p. 116°, which is transformed by warming with aniline into 2:3:4:6-*benzylideneaniline*, m. p. 108°.

On nitration, *p*-acetylaminobenzaldehyde yields 3-nitro-*p*-acetylaminobenzaldehyde, m. p. 155°, which is saponified to 3-nitro-4-aminobenzaldehyde, m. p. 190° (compare Cohn and Springer, Abstr., 1903, i, 492), a substance converted by bromine water into 3-bromo-5-nitro-4-aminobenzaldehyde, pale yellow crystals, m. p. 168°, or by excess of bromine water into 2:4-dibromo-6-nitroaniline, m. p. 127°. On diazotisation, 3-bromo-5-nitro-4-aminobenzaldehyde is converted into 3-bromo-5-nitrobenzaldehyde, pale yellow needles volatile with steam,

m. p. 100°, which is oxidised by potassium permanganate to 3-bromo-5-nitrobenzoic acid, colourless crystals, m. p. 162°.

With bromine water, 3-bromo-5-aminobenzaldehyde yields 2 : 4 : 5 : 6-tetrabromo-3-aminobenzaldehyde, pale yellow needles, m. p. not below 270°, which is converted by Sandmeyer's method into pentabromobenzaldehyde, colourless crystals, m. p. not below 270°. This substance is oxidised by potassium permanganate to pentabromobenzoic acid colourless crystals, m. p. 252° (not 235° as given by Reinecke, *Zeitsch. Chem.*, 1869, 110).

3-Nitro-4-aminobenzaldehyde is converted by Sandmeyer's reaction into 4-chloro-3-nitrobenzaldehyde, colourless crystals, m. p. 65°, oxidised by potassium permanganate to 4-chloro-3-nitrobenzoic acid, m. p. 178°. The corresponding bromo-derivative is prepared similarly, has m. p. 106°, and is oxidised by potassium permanganate to 4-bromo-3-nitrobenzoic acid, m. p. 199°.

3-Bromo-5-nitro-4-aminobenzaldehyde yields by Sandmeyer's method 3 : 4-dibromo-5-nitrobenzaldehyde, colourless crystals, m. p. 99°, oxidised by potassium permanganate to 3 : 4-dibromo-5-nitrobenzoic acid, colourless crystals, m. p. 183°.

Bromine water reacts with 2-chloro-4-aminobenzaldehyde, forming 2-chloro-3 : 6-dibromo-4-aminobenzaldehyde, pale yellow needles, m. p. 174°, which by Sandmeyer's method yields 2-chloro-3 : 4 : 5-tribromobenzaldehyde, colourless crystals, m. p. 121°.

2-Chloro-4-acetylaminobenzaldehyde is converted by nitric acid into 2-chloro-5-nitro-4-acetylaminobenzaldehyde, pale yellow crystals, m. p. 98°. Elimination of the acetyl group by concentrated hydrochloric acid produces 2-chloro-5-nitro-4-aminobenzaldehyde, yellow crystals, m. p. 194°, which is converted by Sandmeyer's method into 2 : 4-dichloro-5-nitrobenzaldehyde, m. p. 74° (compare Anilinfarben- & Extrakt Fabriken vormals J. R. Geigy, D.R.-P. No. 198809).

A. J. W.

**Asymmetric Synthesis Produced by the Action of Catalysts.** GEORG BREDIG and P. S. FISKE (*Biochem. Zeitsch.*, 1912, 46, 7—23).—Under the influence of optically active alkaloids as catalysts, benzaldehyde cyanohydrin can be produced by the interaction of benzaldehyde and hydrocyanic acid, the alkaloid acting in a similar way to emulsin in this respect. When quinine is employed, the product of the asymmetric synthesis is dextrorotatory, and yields a levorotatory mandelic acid, whereas under the influence of quinidine the products of reaction show the rotations in the reverse directions. As the molar amounts of alkaloids necessary to produce the reactions are less than those of the products produced, the action must be of catalytic character. The alkaloids appear to enter into combination with the cyanohydrins, as they cannot be removed from solutions in organic solvents containing both alkaloid and cyanohydrin by simply washing with strong aqueous hydrochloric acid; indeed, such solutions in inorganic solvents can remove the alkaloid from a solution of its hydrochloride in water.

S. B. S.

**Synthesis of Aromatic Aldehydes. III. LUDWIG GATTERMANN** (*Annalen*, 1912, 393, 215—233. Compare Abstr., 1906, i, 589; 1908, i, 28).—Many aromatic aldehydes which cannot be prepared by either of the author's earlier methods have been obtained by the interaction of magnesium aryl haloids with ethyl formate or ethoxymethylene-aniline in ether, preferably at  $-50^{\circ}$ . The yields are in many cases less than 10%, but at times, especially at low temperatures, exceed 60% of the theoretical.

The two processes are as follows: The cold ethereal solution of the magnesium aryl haloid is slowly added to a cold ethereal solution of ethyl formate. After the reaction, the mixture is acidified with cold hydrochloric acid, the ether and the excess of ethyl formate are removed on the water-bath, and the aldehyde is then distilled with steam and purified through the sodium hydrogen sulphite compound. The method with ethoxymethyleneaniline is performed thus: the ethereal solution of the magnesium aryl haloid is heated just to boiling, and is slowly treated with an ethereal solution of ethoxymethylene-aniline (prepared from the dry silver salt of formanilide and ethyl iodide), the mixture is cooled after the reaction, acidified with dilute hydrochloric acid, and is then treated as above for the isolation and purification of the aldehyde.

*o*-Tolualdehyde is obtained from *o*-bromotoluene in 50% and 55% yield respectively by the ethyl formate and ethoxymethyleneaniline methods. 2:5-Dimethylbenzaldehyde,  $C_6H_3Me_2 \cdot CHO$ , b. p.  $219-220^{\circ}/738$  mm., colourless, pleasantly odorous liquid, obtained in 45% yield from bromo-*p*-xylene by the ester method at  $-60^{\circ}$ , yields 2:5-dimethylcinnamic acid, m. p.  $128.5^{\circ}$ , by Claisen's method, and reacts with acetone to form 2:5-dimethylstyryl methyl ketone,  $C_{12}H_{14}O$ , b. p.  $154-156^{\circ}/15$  mm. (azine,  $C_{24}H_{28}N_2$ , m. p.  $163^{\circ}$ , yellow needles; semicarbazone,  $C_{13}H_{17}ON_3$ , m. p.  $204^{\circ}$ , colourless needles; dibromo-additive compound,  $C_{12}H_{14}OBr_2$ , m. p.  $128^{\circ}$ , colourless leaflets). It is extremely remarkable that the nitration of 2:5-dimethylbenzaldehyde by potassium nitrate and concentrated sulphuric acid at about  $-15^{\circ}$  yields 6-nitro-2:5-dimethylbenzaldehyde, m. p.  $120^{\circ}$ , yellow needles or leaflets. The nitrated aldehyde forms an azine,  $C_{18}H_{18}O_4N_4$ , m. p.  $162^{\circ}$ , yellow needles; semicarbazone, m. p.  $183^{\circ}$ , colourless needles, yields tetramethylindigotin, blue needles, by treating its alcoholic solution with acetone and aqueous sodium hydroxide, and forms 6-amino-2:5-dimethylbenzaldehyde, m. p.  $52^{\circ}$ , amber crystals, by reduction with ferrous sulphate and aqueous ammonia.

*p*-Bromobenzaldehyde, obtained from *p*-dibromobenzene in 40% yield by the ester method at  $-50^{\circ}$ , forms a phenylhydrazone, m. p.  $112-113^{\circ}$ , brownish-yellow needles; azine, m. p.  $221^{\circ}$ , long, yellowish-green leaflets, and acetal, m. p.  $89-90^{\circ}$ , yellow crystals.

4-Bromo-2:5-dimethylbenzaldehyde, m. p.  $63.5^{\circ}$ , needles or leaflets, obtained in 10% yield from 2:5-dibromo-*p*-xylene at  $-50^{\circ}$  by the ester method, forms an azine, m. p.  $219^{\circ}$ , green needles, and oxime, m. p.  $113^{\circ}$ , colourless needles.

*o*-Ethoxybenzaldehyde, obtained in 30% yield from *o*-bromophenetole by the ester method at  $-60^{\circ}$ , forms an azine, m. p.  $136^{\circ}$ , yellow crystals, and semicarbazone, m. p.  $219^{\circ}$ , long, colourless needles

condenses with benzidine to form *di-o-ethoxybenzylidenebenzidine*, m. p. 137—138°, large leaflets, reacts with magnesium phenyl bromide to form ultimately *o-ethoxybenzhydrol*, m. p. 75°, stout, colourless crystals, and yields by nitration with potassium nitrate and concentrated sulphuric acid at 0° *nitro-o-ethoxybenzaldehyde*, m. p. 69° (*azine*, m. p. 284—285°, yellow leaflets; *semicarbazone*, m. p. 223°, pale yellow prisms; *phenylhydrazone*, m. p. 203—204°, red needles).

*p-Methylthiolbenzaldehyde*,  $C_8H_8OS$ , m. p. 78°, yellow leaflets, obtained only by the ethoxymethyleneaniline method from *p*-iodophenyl methyl sulphide in about 60% yield, forms an *azine*, m. p. 193°, yellow leaflets; *semicarbazone*, m. p. 213°, colourless needles; *phenyl hydrazone*, m. p. 136°, yellow leaflets, and condensation product,  $C_{15}H_{15}NS_2$ , m. p. 145°, with *p*-thioanisidine, and yields *p-methylthiolbenzoic acid*, m. p. 190°, by oxidation with potassium permanganate.

*p-Ethylthiolbenzaldehyde*, b. p. 244—245°, yellow oil, obtained in a similar manner from *p*-iodophenyl ethyl sulphide in 32% yield, forms an *azine*, m. p. 151—152°, yellow leaflets; *phenylhydrazone*, m. p. 115°, colourless leaflets; *semicarbazone*, m. p. 193°, colourless needles, and condensation product,  $C_{17}H_{19}NS_2$ , m. p. 114—115°, yellow leaflets, with *p*-thiophenetidine.

$\alpha$ -Naphthaldehyde is obtained from  $\alpha$ -bromonaphthalene in 45—50% yield by the ethoxymethyleneaniline method; it forms a *semicarbazone*, m. p. 221°, colourless needles, and condensation product with benzidine,  $C_{34}H_{24}N_2$ , m. p. 199°, yellow leaflets.  $\beta$ -Naphthaldehyde, obtained in 40% yield in a similar manner, forms an *azine*, m. p. 232°, yellow needles, *phenylhydrazone*, m. p. 205—206° (decomp.), colourless leaflets, *semicarbazone*, m. p. 245°, colourless needles, and  *$\beta$ -naphthylideneaniline*, m. p. 113°; with malonic acid and alcoholic ammonia it forms  *$\beta$ -naphthylacrylic acid*,  $C_{10}H_7 \cdot CH : CH \cdot CO_2H$ , m. p. 203°, colourless needles, from which  *$\beta$ -naphthylpropionic acid*, m. p. 129—130°, colourless leaflets, is obtained by reduction with sodium amalgam.

*Bromothiophenalddehyde*, a yellow oil with the odour of bitter almonds, is obtained in about 10% yield from dibromothiophen by the ester method; it forms an *azine*, m. p. 157—158°, yellow needles, *semicarbazone*, m. p. 200—201°, colourless leaflets, and *phenylhydrazone*, m. p. 105°, colourless leaflets, and yields the acid, m. p. 139·5°, by oxidation.

Bromothiophen is obtained in 70% yield by converting dibromothiophen into magnesium bromothiophen bromide, and treating this with hydrochloric acid in the cold. Thiophenalddehyde, obtained from it in 15% yield by the ester method at  $-20^\circ$ , forms an *azine*,  $C_{10}H_8N_2S_2$ , m. p. 154°, long, yellow needles.

*p*-Nitrophenyl mercaptan, obtained from *p*-chloronitrobenzene and potassium hydrosulphide in boiling alcohol, is converted by alcoholic sodium methoxide and methyl iodide on the water-bath into *p-nitrophenyl methyl sulphide*,  $NO_2 \cdot C_6H_4 \cdot SMe$ , m. p. 72°, long, yellow plates. By reduction with tin and hydrochloric acid it yields *p-aminophenyl methyl sulphide*, b. p. 272—273°, which forms an *acetyl* derivative, m. p. 130·5°, colourless needles, and *benzoyl* derivative, m. p. 177—178°, leaflets, and is converted into *p-bromophenyl methyl sulphide*, m. p. 38°,

and *p*-iodophenyl methyl sulphide, m. p.  $45^{\circ}$ , by diazotisation and the usual subsequent treatment.

*p*-Aminophenyl ethyl sulphide, b. p.  $280-281^{\circ}$ , yellow oil, obtained from *p*-nitrophenyl ethyl sulphide, m. p.  $44^{\circ}$ , long, yellow needles, forms an acetyl derivative (thiophenacetin), m. p.  $116-117^{\circ}$ , colourless needles, and is converted into *p*-iodophenyl ethyl sulphide, b. p.  $146-147^{\circ}$ /11 mm., by the usual process. C. S.

**A Colour Reaction of Unsaturated Ketones.** GUSTAVE REDDELIEN (*Ber.*, 1912, 45, 2904—2908).— $\alpha\beta$ -Unsaturated ketones dissolve in concentrated sulphuric acid with the formation of intensely-coloured solutions, which when sufficiently dilute show a characteristic colour change on the addition of a small quantity of nitric acid. Other substances, such as water, hydrochloric acid, hydrobromic acid, bromine water, hydrogen peroxide, or phosphoric acid, do not cause an analogous change. The behaviour of nitric acid appears to be independent of the concentration (from D 1.5 to 1/10 *N*), and the colour change once effected is not altered by further gradual addition of nitric acid provided a rise of temperature is avoided. The phenomenon seems to depend on the instantaneous nitration of the unsaturated ketone and the feebler halochromy (compare Pfeiffer, *Abstr.*, 1910, i, 852; *ibid.*, 1911, i, 788) of the nitro-ketones compared with the ketones themselves. The ready nitration of unsaturated ketones is doubtless connected with the ready addition of nitric acid to form nitrates, and the quantitative transformation of the latter into the corresponding nitro-compounds on solution in concentrated sulphuric acid.

To some extent this reaction is also shown by saturated ketones, such as acetophenone and benzophenone. In these cases, however, the substances are dissolved by concentrated sulphuric acid with the production of solutions so feebly coloured that a colour change can scarcely be detected. Readily oxidisable substances also show the reaction, but the colour change is then dependent on the quantity of nitric acid added. Certain readily oxidisable unsaturated ketones (for example, pulegone, carvenone, carvone) also show this reaction.

In practice, a trace of the ketone is dissolved in concentrated sulphuric acid (10 c.c.) and the solution divided into two parts. To one of these, a drop of nitric acid (D 1.4) is added. To the other, a drop of nitric acid (10%). The colorations produced must be similar. A considerable number of examples are cited.

*Distyryl ketone nitrate*,  $C_{17}H_{14}O$ ,  $HNO_3$ , was obtained in orange-coloured crystals, m. p.  $48-49^{\circ}$ , by the addition of finely powdered distyryl ketone to nitric acid (D 1.4) at  $50-55^{\circ}$ . When preserved, it gradually lost nitric acid.

*Phenyl styryl ketone nitrate*,  $C_{15}H_{12}O \cdot HNO_3$ , was formed as a reddish-yellow oil by addition of the ketone to nitric acid (D 1.4) at the ordinary temperature.

*Styryl methyl ketone nitrate* was a pale yellow oil, which, when placed over nitric acid, absorbed nearly an additional molecule of the latter.

*Cinnamylideneacetophenone nitrate*,  $C_{17}H_{14}O$ ,  $HNO_3$ , was obtained as a dark red, viscous, difficulty decomposed oil. H. W.

**Supposed Isomerism in the Case of Methyl- $\Delta^1$ -cyclohexene-3-one.** PAUL RABE and ERNEST POLLOCK (*Ber.*, 1912, 45, 2924—2927).—Knoevenagel (*Abstr.*, 1897, i, 606) and Rabe and Ehrenstein (*Abstr.*, 1907, i, 626) have stated that methyl- $\Delta^1$ -cyclohexene-3-one exists in two isomeric forms, one of which is readily, the other sparingly, soluble in water. Further investigation has shown that this is not the case. Methyl- $\Delta^1$ -cyclohexene-3-one is miscible with water at the ordinary temperature, whilst the sparingly soluble isomeride consists of different substances, which have not yet been fully investigated.

Specimens which are not completely soluble in water (previously termed  $\beta$ -methylcyclohexenone) can only be obtained by treatment of the oily ethyl methylenebisacetoacetate with 10% sulphuric acid. By systematic fractional solution of the sparingly soluble portion in water, a small quantity of an oil, b. p. 198—210°/750 mm., was obtained, analysis of which showed it to contain an excess of 6% of carbon and 1% of hydrogen above that required for methyl- $\Delta^1$ -cyclohexene-3-one.

For the preparation of the latter substance in a pure state, the authors now recommend the decomposition of methylcyclohexanolone-dicarboxylic esters by potassium hydroxide instead of by sulphuric acid (*loc. cit.*). The following physical constants are given for the ketone (Roy, *Diss.*, Jena, 1910): m. p. ca - 21°,  $n_D^{20}$  1.49475,  $n_{H_A}^{30}$  1.49005,  $n_{H_B}^{30}$  1.50522,  $n_{H_C}^{30}$  1.51465;  $\eta^{30}$  0.01763; dielectric constant,  $K$  24.32; electrical conductivity of the pure substance,  $\kappa_{20}$   $2.321 \times 10^{-7}$ ; mol. heat of combustion, 942.8 Cal. at constant volume, 944.0 Cal. at constant pressure.

Aqueous ferric chloride solution oxidises the ketone to *m*-cresol, whilst reduction by hydrogen in the presence of palladium yields methylcyclohexanone. The previous observations (*loc. cit.*) concerning the sodium salt of the ketone are withdrawn.

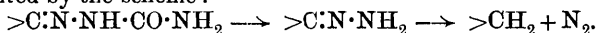
H. W.

**Some Derivatives of 3:4-Dimethoxypropiophenone.** ERMANNO MARTEGIANI (*Gazzetta*, 1912, 42, ii, 346—350. Compare Bargellini and Martegiani, *Abstr.*, 1911, i, 854).—3:4-Dimethoxypropiophenone (identical with that of Hell and Portmann, *Abstr.*, 1895, i, 657) is obtained from propionyl chloride and veratrole in the presence of aluminium chloride. Another substance, probably propionylguaiacol, may be formed also. The *oxime*,  $C_{11}H_{15}O_3N$ , crystallises in small, colourless, prismatic needles, m. p. 63—65°. The *semicarbazone*,  $C_{12}H_{17}O_3N_3$ , forms colourless needles, m. p. 190—192°. The *phenylhydrazone*, m. p. 108—110°, is a yellow, crystalline powder, which rapidly alters even in dry air.

The *monoxime*,  $C_6H_3(OMe)_2 \cdot CO \cdot CMe \cdot NOH$  (prepared with amyl nitrite), forms colourless needles, m. p. 161—162°. From it the diketone could not be obtained. The substance yields veratric acid when boiled with an excess of amyl nitrite. The dioxime is identical with the  $\beta$ -dioxime which Malagnini obtained from diisonitrosomethylisoeugenol peroxide (*Abstr.*, 1895, i, 35). The *oximephenylhydrazone*,  $C_{17}H_{19}O_3N_3$ , crystallises in woolly needles, and has m. p. 209°. It dissolves in sulphuric acid, giving a yellowish-green coloration.

R. V. S.

**Replacement of Oxygen in Ketones and Aldehydes by Hydrogen.** LUDWIG WOLFF (*Annalen*, 1912, 394, 86—108).—The semicarbazones of certain ketones are converted by aqueous sodium hydroxide at 150° into the hydrocarbons corresponding with the ketones, hydrazones being formed as intermediate products. Some hydrazones, therefore, are converted into hydrocarbons in a similar manner; others yield azines. When heated with an absolute alcoholic solution of sodium ethoxide, the hydrazones and semicarbazones of all aliphatic, aromatic, and cyclic ketones and aldehydes, and of ketonic acids are converted into hydrocarbons corresponding with the parent carbonyl compound, in 75—90% yield. The course of the reaction is represented by the scheme:



The amount of sodium ethoxide which apparently acts catalytically is of little importance. For the decomposition of semicarbazones, 96—98% alcohol can be employed. The temperature at which the decomposition is effected varies within wide limits. Generally, heating at 160° for six to eight hours is sufficient; the hydrazones of cyclic ketones require a higher temperature (up to 200°) or more prolonged heating. Similar decompositions have not been observed with phenylhydrazones.

[With GERHARD WEILAND.]—Benzophenonesemicarbazone or hydrazone and 7% aqueous alcoholic sodium hydroxide yield diphenylmethane at 150—160°. Acetophenonehydrazone or semicarbazone and alcoholic sodium ethoxide at 180° yield ethylbenzene. By similar means *p*-aminoacetophenonehydrazone yields *p*-aminoethylbenzene, dibenzyl ketone hydrazone yields dibenzylmethane, and the hydrazone of Michler's ketone yields *p*-dimethylaminodiphenylmethane.

[With E. THIELEPAPE.]—Hexane is obtained from the hydrazone or semicarbazone of methyl butyl ketone, menthane from menthonehydrazone, and camphane from camphorhydrazone.

[With E. NOLTE.]—Fenchone and hydrazine hydrate at 210° yield *fenchonazine*,  $\text{C}_{20}\text{H}_{32}\text{N}_2$ , m. p. 106—107°, and *fenchonehydrazone*,  $\text{C}_{10}\text{H}_{18}\text{N}_2$ , m. p. 56—57°, b. p. 230—231° (decomp.),  $[\alpha]_D$  46.4°, in 11% alcoholic solution; the latter is converted quantitatively by alcoholic sodium ethoxide at 180° in twenty hours into *fenchane*,  $\text{C}_{10}\text{H}_{18}$ , b. p. 149°,  $D^{20}_D$  0.8316,  $n^{20}_D$  1.4462,  $[\alpha]_D$  -18.11° in alcohol.

[With HANS MAYEN.]—Ethyl lævulate and hydrazine hydrate yield hydrated 3-methyl-6-pyridazinone (Curtius's lævulic acid hydrazide),  $\text{C}_5\text{H}_8\text{ON}_2\cdot\text{H}_2\text{O}$ , m. p. 82—83°. The anhydrous substance has m. p. 104—105° (not 94° as given by Curtius), b. p. 267°. The hydrated compound and alcoholic sodium ethoxide at 170—180° yield valeric acid.

Anisaldehydesemicarbazone yields anisazine and a little *p*-tolyl methyl ether by heating with alcoholic sodium hydroxide at 160°; the latter is obtained in larger yield by using alcoholic sodium ethoxide at 170°. By similar methods vanillinsemicarbazone yields the azine and 3-methoxy-*p*-cresol. *Furfuralhydrazone*, b. p. 105—110°/12 mm., and hot alcoholic sodium ethoxide yield 2-methylfuran, b. p. 62.5—63°/746 mm.,  $D^{21}_D$  0.912.

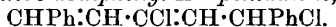
[With E. THIELEPAPE.]—By heating with hydrazine hydrate,

citronellal yields *citronellalazine*, b. p. 209—213°/15 mm., and *citronellalhydrazone*,  $C_{20}H_{36}N_2$ , b. p. 125—140°/15 mm. The latter, which is better obtained from hydrazine hydrate at 160°, reacts with alcoholic sodium ethoxide at 170° to form citronellol and  $\beta\zeta$ -dimethyl- $\Delta^8$ -octene,  $CH_2:CMc[CH_2]_3\cdot CHMeEt$  (assuming that a shifting of the double linking does not occur), b. p. 162°,  $D_4^{20}$  0.7558,  $n_D^{20}$  1.4303,  $[\alpha]_D^{20}$  9.27° in alcoholic solution.

[With H. MAYEN.]—By heating with alcoholic sodium ethoxide at 165° for twenty hours, benzaldehydephenylhydrazone yields ammonia, aniline, benzoic acid, and a little acetic acid. At 210°, ethylaniline is also formed. When the phenylhydrazone is gently boiled for half an hour, it decomposes into ammonia, stilbene, aniline, benzaldehyde, and benzonitrile. In a similar manner, furfuralphenylhydrazone and alcoholic sodium ethoxide yield ammonia, aniline, and pyromucic acid; benzophenonephenylhydrazone yields ammonia, aniline, ethylaniline, diphenylcarbinol, acetic acid, and tetraphenylethane, and acetophenonephenylhydrazone yields ammonia, aniline, phenylmethylcarbinol, acetic acid, and 2-phenylindole, the last in 40% yield. C. S.

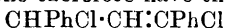
Dibenzylideneacetone [Distyryl Ketone] and Triphenylmethane. VIII. So-called Keto-haloids of Unsaturated Ketones and their Transformation Products. FRITZ STRAUS (*Annalen*, 1912, 393, 235—337. Compare Abstr., 1910, i, 563, 565).—The author has found that the keto-chlorides of unsaturated ketones undergo an apparently simple and smooth substitutive change, namely the replacement of the halogen by a methoxy-group, yielding products which can have been formed only by a complicated re-distribution of the double linkings. All previous conclusions based on processes of substitution therefore become uncertain. The mutual relations between keto-chlorides and their transformation products must be tested by reactions in which it is certain that the first step is addition at a double linking.

Dichlorodistyrylmethane, obtained by the action of phosphorus pentachloride (Abstr., 1906, i, 859) or of oxalyl chloride (Staudinger, Abstr., 1909, i, 905) on distyryl ketone, is reconverted into the ketone by hydrolysis. Both reactions are processes of substitution in an unsaturated ketone; therefore, the constitution of the keto-chloride is not safely established by them. By treating the keto-chloride in carbon tetrachloride at  $-15^\circ$  to  $-10^\circ$  with 9—10% ozone and decomposing the resulting ozonide with water, the author has obtained benzaldehyde, benzoic acid,  $\alpha$ -chlorophenylacetaldehyde (isolated as its hydrolysed derivative, benzoylcarbinol), and  $\alpha$ -chlorophenylacetic acid (isolated as  $\alpha$ -methoxyphenylacetic acid). Consequently the keto-chloride of distyryl ketone is not dichlorodistyrylmethane as hitherto supposed, but  $\gamma\epsilon$ -dichloro- $\alpha\epsilon$ -diphenyl- $\Delta^{\gamma\epsilon}$ -pentadiene,

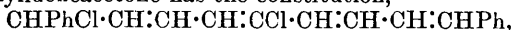


By similar fissive decomposition, the ozonide of the keto-chloride of phenylstyryl ketone yields benzoic acid,  $\alpha$ -chlorophenylacetic acid, benzaldehyde, mandelic acid, benzoylcarbinol, and benzoyl chloride; the ozonide of the keto-chloride of cinnamylideneacetophenone yields the same products. The keto-chlorides of phenyl styryl ketone and

cinnamylideneacetophenone therefore have the constitutions



and  $\text{CHPhCl} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CPhCl}$  respectively. Also the keto-chloride of dicinnamylideneacetone has the constitution,

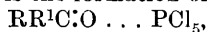


containing a system of four conjugated double linkings. (In the fissive decomposition of the preceeding ozonides, glyoxal [isolated as the *p*-nitrophenylosazone] is always obtained, being formed probably by the rupture of a benzene nucleus, and oxalic acid is produced when the keto-chloride contains a system of conjugated ethylenic linkings.) Cinnamylidene dichloride has the customary constitution

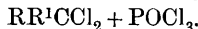


because the decomposition of its ozonide by water results in the formation of benzoic acid and benzaldehyde, dichloroacetic acid and dichloroacetaldehyde, and glyoxal.

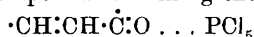
In view of the large number of additive compounds of metallic chlorides and carbonyl compounds now known, the author is of opinion that the initial reaction between an aldehyde or ketone and phosphorus pentachloride is the formation of a complex,



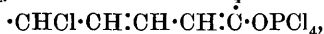
which subsequently changes to  $\text{RR}^1\text{CCl} \cdot \text{OPCl}_4$ , and finally to



Similar schemes are advanced to explain the conversion of acids and their esters or their amides into acid chlorides or iminochlorides respectively by phosphorus pentachloride. In the cases of the preceding unsaturated ketones containing conjugated double linkings, the primary additive compound containing the group

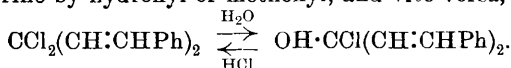


or  $\cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH} \cdot \dot{\text{C}} \cdot \text{O} \dots \text{PCl}_5$  changes, by a transference of chlorine to the other extremity of the conjugated system, to a substance containing  $\cdot \text{CHCl} \cdot \text{CH} \cdot \dot{\text{C}} \cdot \text{OPCl}_4$  or

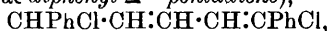


from which the final product is obtained by the elimination of phosphoryl chloride. The formation of the same (so-called) keto-chlorides from the preceeding unsaturated ketones and oxalyl chloride can be explained in a similar manner by assuming that the acid chloride is first attached to the carbonyl oxygen atom of the ketone by means of its residual affinity, the resulting additive compound then undergoing changes analogous to those given above. With the former view of the constitution of keto-chlorides, one difficulty in explaining the replacement of the halogen lies in the fact that, although both chlorine atoms are similarly bound, only one enters into substitutive reactions. Another difficulty arises in connexion with the varying additive activity of the ethylenic linkings; the keto-chloride of distyryl ketone contains, according to the old formulation, two exactly similar double linkings, yet the substance reacts additively only with one molecule of bromine. These difficulties disappear with the acceptance of the constitution of keto-chlorides now advanced. (The name keto-chloride is retained for brevity.)

Keto-chlorides react rapidly with water or methyl alcohol, one chlorine atom being replaced by the hydroxyl or methoxy-group with the formation of the (so-called) chlorocarinols or their methyl ethers; from these the keto-chlorides are regenerated by hydrochloric acid. Hitherto these reactions have been regarded as a simple direct replacement of chlorine by hydroxyl or methoxyl, and vice versa,



However, by oxidising the methyl ethers of the preceding keto-chlorides (of distyryl ketone, cinnamylideneacetophenone, dicinnamylideneacetone) in acetone by potassium permanganate at 15–20° a constant product of the oxidation is  $\alpha$ -methoxyphenylacetic acid. Consequently they all contain the group  $\text{OMe}\cdot\text{CHPh}\cdot\text{CH}:\text{C}$ , and the keto-chlorides themselves, therefore, have the new constitutions given above. The same result is attained by reducing the chlorocarinols by a modification of Skita's process. Thus the chlorocarinol of distyryl ketone in aqueous alcohol containing sodium methoxide, gum, and palladous chloride is reduced by hydrogen at 1.5 atmospheres to  $\alpha\epsilon$ -diphenylpentan- $\alpha$ -ol,  $\text{CH}_2\text{Ph}\cdot[\text{CH}_2]_3\cdot\text{CHPh}\cdot\text{OH}$ , b. p. 200–204°/20 mm., which yields  $\alpha\epsilon$ -diphenylpentan- $\alpha$ -one, m. p. 44–45°, by oxidation in acetic acid by potassium dichromate and sulphuric acid. This ketone, which has also been obtained by reducing cinnamylideneacetophenone in acetone by hydrogen and colloidal palladium in the presence of gum, has been obtained in two modifications; the stable form has m. p. 45–45.2°, and forms an oxime, m. p. 79–80.2°, whilst the labile form (only certainly isolated once) has m. p. 24.5–25.2°, and forms an oxime, m. p. 65.5–67° (compare Borsche, this vol., i, 194). The *keto-chloride* of cinnamylideneacetophenone ( $\alpha\epsilon$ -dichloro- $\alpha\epsilon$ -diphenyl- $\Delta^{88}$ -pentadiene),



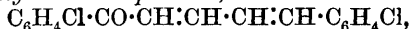
m. p. 55–56°, forms a dark violet, crystalline *stannichloride*, dissolves in liquid sulphur dioxide with an intense violet colour, reacts with water and with methyl alcohol to form an oily *chlorocarinol*,  $\text{OH}\cdot\text{CHPh}\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CPhCl}$ , and the corresponding *methyl ether* respectively, the latter being reconverted into the keto-chloride by hydrogen chloride.

It follows from the preceding results that the keto-chlorides and their chlorocarinols and chloromethyl ethers are similarly constituted, and that their conversions into one another are cases of simple substitution.

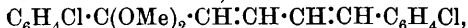
Distyryl ketone can be converted into cinnamylideneacetophenone by the following series of reactions. The ketone is converted successively into its keto-chloride and the methyl ether of the corresponding chlorocarinol,  $\text{OMe}\cdot\text{CHPh}\cdot\text{CH}:\text{CCl}\cdot\text{CH}:\text{CHPh}$ . By boiling the last substance with 2% sodium methoxide in methyl alcohol for fifty to sixty hours, it is converted into the *acetal* of cinnamylideneacetophenone,  $\text{CPh}(\text{OMe})_2\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CHPh}$ , m. p. 60–60.5°, b. p. 216–218°/18–20 mm., from which cinnamylideneacetophenone is obtained by the addition of a little concentrated sulphuric acid to its methyl alcoholic solution. The same acetal is obtained from the keto-

chloride of cinnamylideneacetophenone by a similar series of reactions. The positions of the methoxy-groups are not indubitably proved by the oxidation of the acetal to phenylglyoxylic acid by potassium permanganate in acetone. The proof is furnished, however, by treating the acetal in methyl alcohol containing 5% sodium methoxide, gum, and palladous chloride with hydrogen under a pressure of 1.5 atmospheres, whereby the *acetal*,  $\text{CPh(OMe)}_2 \cdot [\text{CH}_2]_3 \cdot \text{CH}_2\text{Ph}$ , b. p. 194—197°/20 mm., of  $\alpha$ -diphenylpentan- $\alpha$ -one is produced, from which the diphenylpentanone, m. p. 44.5—45°, is obtained by hydrolysis.

In a similar manner di-*p*-chlorodistyryl ketone is converted into di-*p*-chlorocinnamylideneacetophenone,

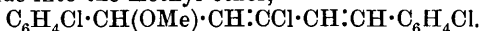


m. p. 162—162.5°, broad, yellow needles, which is also produced from *p*-chlorocinnamaldehyde, m. p. 62—62.5°, b. p. 155—156°/14 mm., and *p*-chloroacetophenone. The *acetal*,

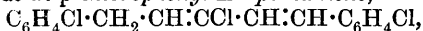


b. p. about 198°/0 mm., cannot be conveniently purified. Also, dicinnamylideneacetophenone has been converted into  $\alpha$ -diphenyl- $\Delta^{88,9}$ -nonatetrene- $\alpha$ -one,  $\text{COPh} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CH} \cdot \text{CHPh}$ , m. p. 126—126.5°, golden-yellow needles, which dissolves in concentrated sulphuric acid with a reddish-violet colour changing to brownish-violet, and forms an *acetal*, m. p. 115.5—116.5°.

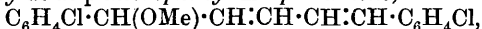
With the object of obtaining a general method of preparing the non-halogenated, unsaturated alcohols corresponding with the preceding keto-chlorides and chlorocarinols, di-*p*-chlorostyryl ketone has been converted successively into the following substances, the constitutions of most of which have been controlled by an examination of their products of oxidation. Di-*p*-chlorostyryl ketone is converted through the ketochloride into the methyl ether,



The latter is reduced by zinc dust and glacial acetic acid on the water-bath to  $\gamma$ -chloro- $\alpha$ -di-*p*-chlorophenyl- $\Delta^{88}$ -pentadiene,



m. p. 103—104°, colourless prisms or leaflets, which yields *p*-chlorobenzaldehyde, *p*-chlorobenzoic acid, and *p*-chlorophenylacetic acid by oxidation in acetone by potassium permanganate, and is converted into  $\alpha$ -methoxy- $\alpha$ -di-*p*-chlorophenyl- $\Delta^{88}$ -pentadiene,

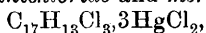


m. p. 79—79.5°, by boiling 0.5% methyl alcoholic sodium methoxide. The methoxy-compound dissolves in concentrated sulphuric acid with a reddish-blue colour and crimson fluorescence, which changes to yellowish-green and brownish-red fluorescence, and is oxidised in acetone by potassium permanganate to *p*-chlorobenzoic acid and  $\alpha$ -methoxy-*p*-chlorophenylacetic acid,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CH(OMe)} \cdot \text{CO}_2\text{H}$ , m. p. 85—86°. The latter acid has been prepared by converting *p*-chloro-mandelic acid into  $\alpha$ -*p*-dichlorophenylacetyl chloride,  $\text{C}_6\text{H}_4\text{Cl} \cdot \text{CHCl} \cdot \text{COCl}$ , b. p. 129—132°/20 mm., by phosphorus pentachloride, and converting the latter into the required acid by boiling methyl alcoholic sodium methoxide and subsequent hydrolysis.

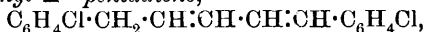
When a benzene solution of  $\gamma$ -chloro- $\alpha$ -di-*p*-chlorophenyl- $\Delta^{88}$ -pentadiene is treated with sodium methoxide in the cold for twenty-four

hours and is occasionally warmed to 45—50°,  $\alpha$ -methoxy- $\alpha$ -di-*p*-chlorophenyl- $\Delta^{\beta\delta}$ -pentadiene is obtained, together with an *isomeride*, probably  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}(\text{OMe})\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Cl}$ , m. p. 108—108·5°, white leaflets.

$\gamma$ -Chloro- $\alpha$ -di-*p*-chlorophenyl- $\Delta^{\beta\delta}$ -pentadiene in boiling aqueous acetone is converted by 4% sodium hydroxide into  $\alpha$ -di-*p*-chlorophenyl- $\Delta^{\beta\delta}$ -pentadien- $\alpha$ -ol,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Cl}$ , m. p. 111—112°, stout, white prisms, which yields the methyl ether, m. p. 79—79·5°, by treatment with boiling methyl alcohol containing two drops of concentrated hydrochloric acid. By treating this methyl ether or the *isomeride*, m. p. 108—108·5°, with phosphorus pentachloride in benzene, or the di-*p*-chlorophenylpentadienol itself in benzene with hydrogen chloride and calcium chloride,  $\alpha$ -chloro- $\alpha$ -di-*p*-chlorophenyl- $\Delta^{\beta\delta}$ -pentadiene,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CHCl}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Cl}$ , m. p. 88—89°, yellow, round crystals, is obtained. This substance forms a dark-coloured *stannichloride* and *mercurichloride*,

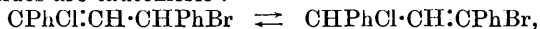


regenerates the pentadienol or its methyl ether by treatment with water or methyl alcohol, and forms an ozonide, by the decomposition of which by water, *p*-chlorobenzoic acid, *p*-chlorobenzaldehyde,  $\alpha$ -*p*-dichlorophenylacetic acid (isolated as *p*-chloromandelic acid), and  $\alpha$ -*p*-dichlorophenylacetaldehyde (isolated as *p*-chlorobenzoylcarbinol) are produced. *p*-Chlorobenzoylcarbinol,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH}$ , m. p. 122—123°, with sublimation, is obtained by boiling *p*-chloro- $\omega$ -bromoacetophenone with acetic acid and sodium acetate, and hydrolysing the resulting *acetate*, m. p. 65·5—66·5°, b. p. 174—175°/20 mm., broad leaflets, by boiling water and barium carbonate. By reduction with zinc dust and boiling glacial acetic acid,  $\alpha$ -methoxy- $\alpha$ -di-*p*-chlorophenyl- $\Delta^{\beta\delta}$ -pentadiene yields  $\alpha$ -di-*p*-chlorophenyl- $\Delta^{\beta\delta}$ -pentadiene,



m. p. 67—68°, broad needles, which does not react smoothly with bromine; the hydrogen atoms of the methylene group are not reactive, since the substance does not condense with diazobenzenesulphonic acid, and produces only a brown coloration with alcoholic potassium hydroxide and *m*-dinitrobenzene (under these conditions, fluorene produces an intense reddish-violet coloration).

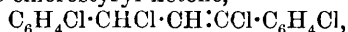
The chlorobromides of the preceding unsaturated ketones, obtained by the action of hydrogen bromide on the chlorocarbinols (Abstr., 1910, i, 119, 565), are, in accordance with the views developed above, formulated as, for example,  $\text{CPhCl}\cdot\text{CH}\cdot\text{CHBrPh}$ . The fact previously noted that the chlorobromides yield a mixture of the halogen hydrides and of the halogenated carbinols or their methyl ethers by treatment with water or methyl alcohol is explained by assuming that the chlorobromides are tautomeric:



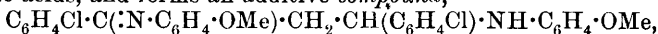
although this explanation is attended by certain difficulties which have not been overcome.

[With W. HEITZ.]—The formation of arylimines by the interaction of primary aromatic amines and the keto-chlorides of unsaturated ketones (Straus and Ackermann, Abstr., 1910, i, 241), which is directly explicable with the old formulation of the latter, must, in

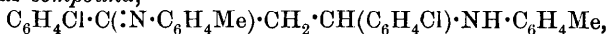
view of their new constitutions, be regarded as the result of the following changes:  $\text{CRCl:CH:CHRCI} \rightarrow \text{CRCl:CH:CHR}\cdot\text{NHR}' \rightarrow \text{CHRCI}\cdot\text{CH}_2\cdot\text{CR:NR}' \rightarrow \text{CHR:CH:CR:NR}'$ . Thus the keto-chloride of *p*-chlorophenyl *p*-chlorostyryl ketone,



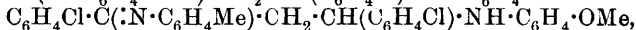
and *p*-anisidine (3 mols.) in benzene yield, after keeping for forty-five hours in darkness, *p*-anisylimino-*p*-chlorophenyl-*p*-chlorostyrylmethane,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH:CH}\cdot\text{C}(\text{C}_6\text{H}_4\text{Cl})\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$ , m. p.  $173\cdot5^\circ$ , yellow crystals (a colourless isomeride has not been detected; compare Straus and Ackermann), which forms a *hydrochloride*,  $\text{C}_{22}\text{H}_{17}\text{ONCl}_2\cdot\text{HCl}$ , m. p.  $166^\circ$  (decomp.), yellow flocks, and a *picrate*, m. p.  $151\text{--}151\cdot5^\circ$  (decomp.), reddish-yellow needles, yields *p*-anisidine and *p*-chlorophenyl *p*-chlorostyryl ketone by treatment with acetic and concentrated hydrochloric acids, and forms an additive *compound*,



m. p.  $122\cdot5^\circ$ , colourless leaflets, with *p*-anisidine in boiling benzene. A similar *compound*,



m. p.  $124\cdot5\text{--}125\cdot5^\circ$ , glistening leaflets, is obtained from *p*-toluidine and Straus and Ackermann's yellow *p*-tolylimino-*p*-chlorophenyl-*p*-chlorostyrylmethane (not from the colourless isomeride) in boiling benzene. In boiling benzene, *p*-toluidine and *p*-anisylimino-*p*-chlorophenyl-*p*-chlorostyrylmethane or *p*-anisidine and yellow *p*-tolylimino-*p*-chlorophenyl-*p*-chlorostyrylmethane yield the same additive *compound*,  $\text{C}_6\text{H}_4\text{Cl}\cdot\text{C}(\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OMe})\cdot\text{CH}_2\cdot\text{CH}(\text{C}_6\text{H}_4\text{Cl})\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}$  or



m. p.  $127\text{--}128^\circ$ , glistening leaflets.

C. S.

**Studies in the cyclopentadiene Series. I. 5-Nitro-2:3-diacetylcyclopentadiene.** WILLIAM J. HALE (*J. Amer. Chem. Soc.*, 1912, **34**, 1580—1590).—It has already been shown (this vol., i, 566) that acetylacetone condenses with nitromalonaldehyde in presence of sodium hydroxide to form 5-nitro-2:3-diacetylcyclopentadiene,  $\text{NO}_2\cdot\text{C}_5\text{H}_3\text{Ac}_2$ . An account is now given of the *sodium*, *potassium*, and *barium* salts and certain derivatives of this compound. The *oxime*, m. p.  $155^\circ$  (decomp.), crystallises in lustrous, orange-yellow leaflets. The dioxime could not be obtained. The *anil*, m. p.  $166\cdot5^\circ$ , forms clusters of yellow needles. The *phenylhydrazone*, m. p.  $175\text{--}180^\circ$  (decomp.), crystallises in slender, yellow needles, and the *hydrazone*, m. p.  $185\text{--}190^\circ$  (decomp.), forms small nodules.

By the action of benzaldehyde (4 mols.) on the sodium salt of 5-nitro-2:3-diacetylcyclopentadiene (1 mol.) in presence of excess of sodium hydroxide, the *sodium* salt of 5-nitro-2:3-dicinnamoylcyclopentadiene is produced, which is converted by acetic acid into 5-nitro-2:3-dicinnamoylcyclopentadiene,  $\text{NO}_2\cdot\text{C}_5\text{H}_3(\text{CO}\cdot\text{CH:CHPh})_2$ , m. p.  $253\text{--}255^\circ$  (decomp.), which forms small, orange-yellow needles.

When 5-nitro-2:3-diacetylcyclopentadiene (1 mol.) is oxidised with potassium permanganate in presence of excess of potassium hydroxide, there are formed as potassium salts, acetic acid (2 mols.), oxalic acid (1 mol.), and carbonic acid (3 mols.). It is shown that this result affords good evidence of the structure of the cyclopentadiene. The

compound does not combine with bromine, hydrogen bromide, or hydrogen iodide. E. G.

**Some Derivatives of Acetophenoneacetone.** CESARE FINZI (*Gazzetta*, 1912, 42, ii, 356—363).—The author has established the constitution of the monoxime of this substance (Paal, Abstr., 1884, i, 599), for when treated with benzenesulphonyl chloride (compare Werner and Pignet, Abstr., 1905, i, 66) it yields carbylamine and a substance,  $C_{17}H_{17}O_4NS$ , which crystallises in colourless needles, m. p.  $74^\circ$ . This substance yields phenylcarbylamine when boiled with alcoholic potassium hydroxide, and the residue gives phenol when fused with alkali. In consequence of these reactions, the author ascribes to it the formula

$$\begin{array}{c} SO_2Ph \cdot O \cdot C \cdot CH_2 \cdot CH_2 \cdot COMe \\ | \\ PhN \end{array}, \text{ the original}$$

oxime being therefore the *cis*oxime,

$$\begin{array}{c} Ph \cdot C \cdot CH_2 \cdot CH_2 \cdot COMe \\ | \\ HO \cdot N \end{array}$$

*Acetophenoneacetone monosemicarbazone*,  $C_{12}H_{15}O_2N_3$ , has m. p.  $191^\circ$ . In some preparations of the semicarbazone, another substance, m. p.  $255-256^\circ$ , was obtained. Acetic acid appears to convert the semicarbazone into a substance of the same composition, but of m. p.  $210^\circ$ . R. V. S.

**Dioximes of Benzil.** W. E. GARNER (*Chem. News*, 1912, 106, 202).—The usual method of formulation of the three dioximes of benzil does not readily account for the fact that the  $\gamma$ -oxime loses water more readily than the  $\alpha$ -oxime with formation of diphenylfurozan, but it is shown that if the two hydroxyl groups lie outside the plane of the remainder of the molecule these difficulties are removed. G. S.

**Preparation of Dihalogenated Nitroanthraquinones.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 249721. Compare Abstr., 1903, i, 498).—1:5-Dichloro-4-nitroanthraquinone, yellow needles, is prepared by dissolving 1:5-dichloroanthraquinone (20 parts) in 400 parts of fuming sulphuric acid, and adding nitric acid (20%) at a temperature of  $40-50^\circ$ . When 1:8-dichloroanthraquinone dissolved in concentrated sulphuric acid at  $20^\circ$  is treated with an excess of nitric acid (2 mols.), it furnishes 1:8-dichloro-4-nitroanthraquinone, yellow prisms; whilst 1:5-dibromo-4-nitroanthraquinone, yellow needles, is obtained in a similar manner. F. M. G. M.

**Preparation of Arylaminoanthraquinone Derivatives.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 248655).—Numerous condensation products from aminoanthraquinones and halogenated compounds have been prepared previously; the reaction has now been extended to compounds of the general formula:  $Z \cdot C_6H_4 \cdot X \cdot C_6H_4 \cdot Z$  and  $Z \cdot C_6H_3 \cdot \begin{smallmatrix} Y \\ < \\ Y \end{smallmatrix} C_6H_3 \cdot Z$  (where X is oxygen, sulphur, or an imino-group, Y a radicle with two free valencies, such as CO or NH, and Z a halogen atom), which condense with two molecules of  $\alpha$ -aminoanthraquinone; and the preparation of compounds from this base with dibromodiphenyl ether, *pp*-dichlorodiphenyl sulphide, *pp*-dibromodiphenylamine, and

with 2:7-dibromoxanthone are described in the original; they form red or reddish-brown crystals, and their solutions in different solvents exhibit marked colour reactions. F. M. G. M.

F. M. G. M.

[Preparation of Anthraquinone Derivatives.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 248997).—Condensation products of halogenated anthraquinones with aminoanthraquinones have previously been prepared; this reaction has now been extended to  $\omega$ -chloroacetyl-aminoanthraquinones, and yields compounds (in their most simple form) of the type  $\text{NHX} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{NHX}$  ( $\text{X}$  = anthraquinone).

The compound from 2-aminoanthraquinone and *o*-chloroacetyl-2-aminoanthraquinone forms orange crystals; its tinctorial properties with those of other analogous compounds are tabulated in the original.

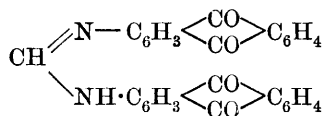
F. M. G. M.

[Preparation of Anthracene Derivatives.] FRITZ ULLMANN (D.R.-P. 248999. Compare Abstr., 1907, i, 224).—When the compound, m. p. 188° (obtained from benzaldehyde and 1:3-dibromo-2-aminoanthraquinone), is heated at 200—240° in the presence of copper powder, it furnishes a *dibromodiaminodianthraquinonyl*, a pale yellow, crystalline powder, m. p. 290°. F. M. G. M.

F. M. G. M.

Preparation of Condensation Products in the Anthraquinone Series. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 248656. Compare this vol., i, 811).—The *amidine* (annexed formula)

is obtained when 2-aminoanthraquinone is heated at 130—140° with ethyl orthoformate.



*Benzoyl-2-anthraquinonylimide chloride* is prepared by the action of phosphorus pentachloride on benzoyl-2-aminoanthraquinone, and this when

condensed with 2-aminoanthraquinone furnishes the *amidine*,  $\text{C}_6\text{H}_5 \cdot \text{C} \begin{smallmatrix} \nearrow \text{N} \cdot \text{C}_{14}\text{H}_7\text{O}_2 \\ \searrow \text{NH} \cdot \text{C}_{14}\text{H}_7\text{O}_2 \end{smallmatrix}$ , yellow needles, m. p. 334—335°, which can be obtained by heating together 2-aminoanthraquinone, benzotrichloride, and nitrobenzene at 150—160° during several hours.

F. M. G. M.

**Preparation of Hydroxyanthrimides.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 249938. Compare Abstr., 1909, i, 242).—*Hydroxy-1:1'-dianthrimide*,  $\text{OH}\cdot\text{C}_{14}\text{H}_6\text{O}_2\cdot\text{NH}\cdot\text{C}_{14}\text{H}_7\text{O}_2$ , dark violet needles, is obtained when 1:1'-dianthrimide is heated at  $170^\circ$  with concentrated sulphuric acid, sodium nitrite, and boric acid, whilst *hydroxy-1:5-trianthrimide*, glistening, violet leaflets (from nitrobenzene), is obtained in a similar manner from 1:5-trianthrimide.

F. M. G. M.

**Derivatives of Anthraquinone.** WOLFGANG LENHARD (*Zeitsch. angew. Chem.*, 1912, 25, 2152—2155).—1-Amino-2-thiolanthraquinone, prepared from 2-bromo-1-aminoanthraquinone by the action of alcoholic sodium sulphide, gives rise to a *disulphide*, *esters*, and *ethers*, which

may be converted into the corresponding *acetyl* and *benzoyl* derivatives; the *phenyl* and *tolyl* ethers are obtained by heating 2-bromo-1-aminoanthraquinone with phenyl and tolyl mercaptans in an alkaline alcoholic solution. The sodium salt of 1-amino-2-thiolanthraquinone reacts with ethylene dibromide to form the *di-1-amino-2-anthraquinonyl ether* of *dithioethylene glycol*, and with *s*-dichloroethane, yielding the corresponding *ether* of *dithiolacetylene* (*dithioethylene*); with cyanogen iodide it forms 1-amino-2-anthraquinonyl thiocyanate.

Attempts to replace the amino-group of 2-bromo-1-aminoanthraquinone by the thiol group were unsuccessful; the amino-compound readily diazotises and yields a crystalline *diazonium thiocyanate*, which, however, is transformed by boiling with water into a mixture of 2-bromo-1-anthraquinonyl thiocyanate and 1:2-dithiocyananthraquinone.

Ethers of *dithioalizarin* (1:2-dithiolanthraquinone) have been prepared from the above-mentioned 1-amino-2-thiolanthraquinone ethers by introducing the thiocyano-group in the 1-position, followed by hydrolysis and treatment with alkyl haloids; in this manner, the *dimethyl*, *methylethyl*, *diethyl*, and *methylbenzyl* ethers were obtained.

The sodium salt of 1-amino-2-thiolanthraquinone, and also the methyl, ethyl, and benzyl ethers, react with benzoyl chloride, yielding a *thiazole*; with ethyl chlorocarbonate the sodium salt forms an *ethyl thiocarbonate*, which, by the action of glacial acetic acid or alcoholic potassium hydroxide, is converted into a *ketohydrothiazole* or a *hydroxyl thiazole*. With ethyl chloroacetate it gives rise to an *ethyl thiolacetate*, from which a *dihydrothiazine* of anthraquinone is produced by boiling with acetic acid.

Thiazole derivatives containing a thiol group in the thiazole ring have hitherto not been prepared in the anthraquinone series; a *thiazole* of this kind has now been obtained by heating the sodium salt of 1-amino-2-thiolanthraquinone with carbon disulphide; on treatment with alcoholic potassium hydroxide and alkyl haloids, it yields the corresponding ethers.

1-Amino-2-thiolanthraquinone condenses with acetone (1 mol.) to form a *dimethylthiazole*.

In attempting to prepare di-1-thiocyananthraquinonyl 2-disulphide from *di-1-aminoanthraquinonyl 2-disulphide* by means of the diazo-reaction, *anthraquinone-1:2-diazosulphide* was obtained.

When heated at 200°, di-1-aminoanthraquinonyl 2-disulphide is transformed into the *monosulphide* (*di-1-aminoanthraquinonyl 2-sulphide*), m. p. above 350°, which has also been prepared by heating 2-bromo-1-aminoanthraquinone with the sodium salt of 1-amino-2-thiolanthraquinone.

The sodium salt just-mentioned reacts with *s*-tetrabromoethane in the presence of sodium sulphide, yielding *di-1-aminoanthraquinonyl 2-trisulphide*, slender, red needles, m. p. 262°; attempts to prepare trisulphides from the sodium salts of 1-thiol-, 2-thiol-, and 1-amino-2:4-dithiol-anthraquinones by the same method were unsuccessful.

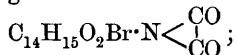
The above trisulphide is also obtained by crystallising di-1-aminoanthraquinonyl 2-disulphide from pyridine.

With the object of determining whether the transformation of

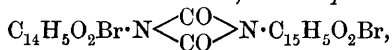
disulphides is accompanied by the liberation of sulphur in the free condition as suggested by Beilstein, or to the simultaneous formation of a trisulphide, as was found by Hinsberg in the benzene and naphthalene series, the author has examined the behaviour of a number of disulphides, and finds that the simple 1- and 2-disulphides when heated are quite stable, whilst the 1-amino-derivatives of the disulphides and 2:4-disulphides lose an atom of sulphur and give rise to monosulphides; in no case was a trisulphide obtained. From these results the conclusion is drawn that the formation of monosulphides in the anthraquinone series takes place in the manner suggested by Beilstein, and is restricted to those compounds having the disulphide group in the 2-position.

Replacement of the halogens in 2:4-dibromo-1-aminoanthraquinone by the thiol group yields 1-amino-2:4-dithiolanthraquinone. This gives rise to *methyl*, *ethyl*, and *benzyl ethers*, and reacts with ethylene dibromide (1 mol.) to form an *ether of dithioethylene glycol*. It is oxidised by potassium ferricyanide to a *bidisulphide*, which, on crystallisation from pyridine, loses sulphur and is converted into a *monodisulphide*.

2:4-Dibromo-1-aminoanthraquinone reacts with oxalyl chloride in ethereal solution, yielding 2:4-dibromo-1-anthraquinonyloximide,



in carbon tetrachloride solution at 130°, the compound,



is produced.

F. B.

**Mercaptans of Anthraquinone.** LUDWIG GATTERMANN (*Annalen*, 1912, 393, 113—197).—Since by the action of sodium alkylloxides, 1-nitroanthraquinone is converted into 1-alkyloxanthraquinones, the author hoped to obtain 1-thiolanthraquinone from 1-nitroanthraquinone by the action of potassium hydrosulphide; the substance produced, however, is 1-aminoanthraquinone. The action of potassium aryl mercaptides on 1-nitroanthraquinone yields 1-anthraquinonyl aryl sulphides,  $\text{C}_6\text{H}_4\begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array}\text{C}_6\text{H}_3\cdot\text{SAr}$ , from which the aryl group cannot be removed even by aluminium chloride.

1-Thiolanthraquinone can be obtained by diazotising 1-aminoanthraquinone in sulphuric acid, boiling the diazonium sulphate with aqueous potassium thiocyanate, and boiling the resulting 1-thiocyananthraquinone with 10% alcoholic potassium hydroxide, whereby the potassium salt of the thiolanthraquinone is produced. Substituted 1-aminoanthraquinones undergo similar changes.

The sulphate of the aminoanthraquinone is diazotised in the usual manner, but when an aminoanthraquinone which does not form a sulphate in dilute sulphuric acid is used, its solution in concentrated sulphuric acid is diazotised at the ordinary temperature by nitroso-sulphuric acid. In either case, the solution is diluted with water or ice, treated with an excess of 20% aqueous potassium thiocyanate in the cold (whereby a crystalline diazonium thiocyanate occasionally is

precipitated), and the mixture is heated on the water-bath and finally over a naked flame until the evolution of nitrogen ceases and the precipitated thiocyananthraquinone has coagulated.

After the thiocyananthraquinone has been boiled with 10% alcoholic potassium hydroxide until a clear solution has been obtained, an equal volume of water is added and the solution is ready for the numerous transformations of the thiolanthraquinones mentioned below. By acidification the solution yields the free thiolanthraquinone, which, however, changes very readily to the disulphide.

The thiocyananthraquinones all crystallise extremely easily, and are yellow or yellowish-brown if hydroxyl or basic groups are not present; those containing hydroxyl or basic groups are orange or reddish-violet to violet respectively.

1-Thiocyananthraquinone,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_3 \cdot SCN$ , m. p.  $241^\circ$ , crystallises in yellow needles. The dark violet, alkaline solution of 1-thiolanthraquinone obtained by its decomposition as above yields the *disulphide*,  $C_{28}H_{14}O_4S_2$ , m. p. above  $350^\circ$ , yellow, rhombic plates, quantitatively by oxidation with aqueous potassium ferricyanide, and reacts with methyl iodide to form 1-methylthiolanthraquinone,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_3 \cdot SMe$ , m. p.  $208^\circ$ , yellow needles. The corresponding 1-ethylthiol, m. p.  $183^\circ$ , crystallises in yellow prisms; the 1-benzylthiol, m. p.  $241^\circ$ , in golden-yellow needles, and the ethylenethiol,  $C_{14}H_7O_2 \cdot S \cdot CH_2 \cdot CH_2 \cdot S \cdot C_{14}H_7O_2$  (from ethylene dibromide), m. p. above  $350^\circ$ , in canary-yellow needles. By oxidation with chromic and acetic acids, these four ethers are oxidised to the respective *sulphones*, m. p.  $251^\circ$ ,  $210^\circ$ ,  $231^\circ$ , and  $185^\circ$ . 1-Thiolanthraquinone forms a *benzoyl* derivative, m. p.  $207^\circ$ , yellow needles.

2-Thiocyananthraquinone, m. p.  $205^\circ$ , crystallises in golden-yellow needles. 2-Thiolanthraquinone, m. p.  $206^\circ$ , stout, yellow needles, obtained as above or by heating 2-chloroanthraquinone with sodium sulphide under pressure, yields the following derivatives: *disulphide*, m. p.  $257^\circ$ , pale yellow needles; *methyl thio-ether*, m. p.  $162^\circ$ , yellow needles (*sulphone*, m. p.  $230^\circ$ , yellow prisms); *ethyl thio-ether*, m. p.  $138^\circ$ , golden needles (*sulphone*, m. p.  $154^\circ$ , pale yellow prisms); *benzyl thio-ether*, m. p.  $138^\circ$ , golden-yellow needles (*sulphone*, m. p.  $212^\circ$ , yellow prisms); *ethylene thio-ether*,  $C_{20}H_{18}O_4S_2$ , m. p.  $302^\circ$ , yellow needles; *allyl thio-ether*, m. p.  $126^\circ$ , yellow needles (*sulphone*, m. p.  $159^\circ$ , pale yellow needles), and *benzoyl* derivative, m. p.  $180^\circ$ , small, yellow needles.

1-Thiocyano-2-methylantraquinone, m. p.  $193$ — $194^\circ$ , pale yellow needles, is obtained from 1-amino-2-methylantraquinone. From the alkaline solution of 1-thiol-2-methylantraquinone have been prepared the *disulphide*, m. p.  $247^\circ$ , yellow needles; *methyl thio-ether*, m. p.  $124^\circ$ , orange-red needles (*sulphone*, m. p.  $198^\circ$ , yellowish-red plates); *ethyl thio-ether*, m. p.  $99^\circ$ , orange-red leaflets; and *benzyl thio-ether*, m. p.  $139^\circ$ , orange-red needles.

1-Thiocyano-4-methoxyanthraquinone, m. p.  $245^\circ$ , yellow needles, is obtained from 1-amino-4-methoxyanthraquinone. The corresponding mercaptan yields a *disulphide*, m. p.  $282$ — $283^\circ$ , red needles; *benzyl*

*thio-ether*, m. p. 200°, dark red leaflets (*sulphone*, m. p. 197°, pale red prisms), and *ethyl thio-ether*, m. p. 148°, red needles.

1-Thiocyano-4-aminoanthraquinone, m. p. 256°, reddish-violet needles, is obtained from 1:4-diaminoanthraquinone. Its *acetyl* derivative,  $C_{17}H_{10}O_3N_2S$ , m. p. 263°, crystallises in red needles. 4-Amino-1-thiolanthraquinone forms a *disulphide*, m. p. above 300°, violet needles; *methyl thio-ether*, m. p. 200° (decomp.), violet-red needles (*acetyl* derivative, m. p. 226° [decomp.], red needles); *benzyl thio-ether*, m. p. 225°, violet needles (*sulphone*, m. p. 264°, brownish-yellow needles, by oxidation with 15% hydrogen peroxide), and *allyl thio-ether*, m. p. 175°, reddish-violet needles.

1-Thiocyano-4-methylaminoanthraquinone, m. p. 242—243°, dark violet needles, is obtained from 1-amino-4-methylaminoanthraquinone (*diacetyl* derivative,  $C_{19}H_{16}O_4N_2$ , m. p. 278°). 4-Methylamino-1-thiolanthraquinone forms a *disulphide*, m. p. 280°, dark violet needles, and *methyl thio-ether*, m. p. 210°, violet needles.

1-Thiocyano-4-dimethylaminoanthraquinone, m. p. 241°, crystallises in Bordeaux-red needles. The corresponding mercaptan yields a *disulphide*, m. p. 220° (decomp.), bluish-violet crystals, and *methyl thio-ether*, m. p. 247°, violet needles, the *sulphone* of which, m. p. 193°, forms reddish-brown needles.

1-Thiocyano-4-hydroxyanthraquinone, m. p. 231°, brownish-red needles, is obtained from 1-amino-4-hydroxyanthraquinone. The corresponding mercaptan yields a *disulphide*, m. p. above 300°, reddish-brown needles; *methyl thio-ether*, m. p. 194°, reddish-brown needles, and *benzyl thio-ether*, m. p. 242°, bluish-red needles (*sulphone*, m. p. 216°, yellow needles).

1-Thiocyano-3:4-dihydroxyanthraquinone, m. p. above 350°, obtained from 4-aminoalizarin, crystallises in yellowish-red needles. The corresponding mercaptan forms a *disulphide*, m. p. above 300°, red needles, and *methyl thio-ether*, m. p. 248°, red needles.

1:4-Dithiocyanoanthraquinone, m. p. above 300°, yellow needles, is obtained directly by boiling diazotised 4-nitro-1-aminoanthraquinone or 4-chloro-1-aminoanthraquinone with aqueous potassium thiocyanate. The corresponding dimercaptan forms a *dimethyl thio-ether*, m. p. 127°, reddish-brown needles (*disulphone*, m. p. 280°, pale yellow needles); *diethyl thio-ether*, m. p. 117°, reddish-yellow needles (*disulphone*, m. p. 217°, yellow needles), and *dibenzyl thio-ether*, m. p. 230°, red leaflets (*disulphone*, m. p. 263°, yellow needles). 1-Iodo-4-nitroanthraquinone, m. p. 259°, yellow needles, is obtained by boiling diazotised 4-nitro-1-aminoanthraquinone with aqueous potassium iodide.

1:5-Dithiocyanoanthraquinone, m. p. above 350°, yellow needles, yields the dimercaptan, the *diethyl thio-ether* of which has m. p. 230°, and crystallises in red needles.

1-Thiocyano-5-aminoanthraquinone, m. p. 235°, dark red crystals, is obtained from 1:5-diaminoanthraquinone. It yields 5-amino-1-thiolanthraquinone, the *benzyl thio-ether* of which crystallises from pyridine in green metallic needles, m. p. 196°, containing  $2C_5NH_5$ .

5-Chloro-1-aminoanthraquinone, m. p. 210°, dark red needles (*acetyl* derivative, m. p. 216°, yellow leaflets), yields 5-chloro-1-thiocyanoanthraquinone, m. p. 287°, golden-yellow needles; the mercaptan forms

a *disulphide*, m. p. above  $360^{\circ}$ , yellowish-brown needles, and *methyl thio-ether*, m. p.  $228^{\circ}$ , brownish-red needles.

1-Thiocyano-5-methylaminoanthraquinone, m. p.  $268^{\circ}$ , dark reddish-violet needles, yields a mercaptan, the *disulphide* of which, red crystals, has m. p.  $321^{\circ}$ , and the *methyl thio-ether*, tufts of dark red needles, has m. p.  $248^{\circ}$ .

1-Thiocyano-5-dimethylaminoanthraquinone, m. p.  $212^{\circ}$ , reddish-violet needles, yields a mercaptan which forms a *disulphide*, m. p.  $272^{\circ}$ , red needles, and *methyl thio-ether*, m. p.  $176.5^{\circ}$ , red needles.

5-Piperidyl-1-aminoanthraquinone,  $C_5NH_{10} \cdot C_6H_8 \begin{smallmatrix} <CO \\ <CO \end{smallmatrix} C_6H_3 \cdot NH_2$ , m. p.  $149^{\circ}$ , brownish-red plates, yields 1-thiocyano-5-piperidylanthraquinone, m. p.  $164^{\circ}$ , violet needles; the mercaptan forms a *benzyl thio-ether*, m. p.  $210^{\circ}$ , almost black needles.

8-Piperidyl-1-aminoanthraquinone, m. p.  $180^{\circ}$ , dark violet crystals, yields 1-thiocyano-8-piperidylanthraquinone, m. p.  $164^{\circ}$ , dark violet needles; the mercaptan forms a *methyl thio-ether*, m. p.  $187^{\circ}$ , brownish-red needles.

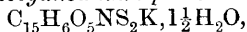
1:8-Dithiocyanoanthraquinone, m. p. above  $300^{\circ}$ , yellow needles, yields 1:8-dithiolanthraquinone, which forms a *dimethyl thio-ether*, m. p.  $221^{\circ}$ , brownish-red needles; *diethyl thio-ether*, m. p.  $169^{\circ}$ , red needles, and *dibenzyl thio-ether*, m. p.  $240^{\circ}$ , orange-red needles.

1:4-Diaminoanthraquinone is diazotised by 1 mol. of nitrous acid, and an aqueous paste of the resulting sulphate is heated with cuprous cyanide. By hydrolysing the product with 10% sodium carbonate at  $150^{\circ}$  and acidifying, 1-aminoanthraquinone-4-carboxylic acid, m. p.  $246-248^{\circ}$  (decomp.), dark brown needles, is obtained. It yields 1-thiocyanoanthraquinone-4-carboxylic acid, decomp.  $280^{\circ}$ , greyish-yellow needles; the *methyl thio-ether*, m. p.  $278^{\circ}$ , of the corresponding mercaptan crystallises in yellowish-red needles.

1-Amino-5-cyanoanthraquinone, m. p.  $300^{\circ}$ , dark red leaflets, yields 1-aminoanthraquinone-5-carboxylic acid, m. p.  $265^{\circ}$ , red prisms, by hydrolysis, from which 1-thiocyanoanthraquinone-5-carboxylic acid, m. p.  $307^{\circ}$ , yellowish-brown needles, is obtained; the corresponding mercaptan forms a *methyl thio-ether*, m. p.  $276^{\circ}$ ; yellowish-brown needles.

1-Aminoanthraquinone-5-sulphonic acid is obtained by reducing 1-nitroanthraquinone-5-sulphonic acid with aqueous sodium sulphide; its *potassium* salt crystallises in reddish-violet prisms containing  $H_2O$ . 1-Thiocyanoanthraquinone-5-sulphonic acid forms a *potassium* salt,  $C_{15}H_6O_5NS_2K \cdot H_2O$ , yellowish-brown leaflets. The corresponding mercaptan forms a *disulphide*,  $C_{25}H_{12}O_{10}S_4K_2$ , yellow needles or large, red prisms, and *methyl thio-ether*,  $C_{15}H_9O_5S_2K \cdot 2H_2O$ , orange-red crystals.

1-Aminoanthraquinone-8-sulphonic acid forms a *potassium* salt, red prisms. *Potassium* 1-thiocyanoanthraquinone-8-sulphonate,



brown prisms, yields a mercaptan which does not form a *disulphide*, and the *methyl thio-ether*,  $C_{15}H_9O_5S_2K$ , of which crystallises in orange-red needles.

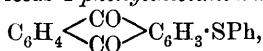
*Potassium* 1-aminoanthraquinone-6-sulphonate,  $C_{14}H_8O_5NSK \cdot 3\frac{1}{2}H_2O$ , red prisms, yields *potassium* 1-thiocyanoanthraquinone-6-sulphonate,

$C_{15}H_6O_5NS_2K \cdot H_2O$ , yellow needles; the corresponding mercaptan forms a *disulphide*,  $C_{28}H_{12}O_{10}S_4K_2$ , yellow prisms, and *methyl thio-ether*,  $C_{15}H_9O_5S_2K \cdot 2H_2O$ , orange-red prisms.

1-Aminanthraquinone-7-sulphonic acid, violet-red, stellate needles, yields 1-thiocyananthraquinone-7-sulphonic acid, the potassium salt of which,  $C_{15}H_6O_5NS_2K \cdot H_2O$ , pale yellow, rectangular prisms, forms a mercaptan, of which the *disulphide*,  $C_{28}H_{12}O_{10}S_4K_2 \cdot 5H_2O$ , pale yellow plates, and *methyl thio-ether*,  $C_{15}H_9O_5S_2K$ , orange-red needles, are mentioned.

In solution, the alkali salts of the preceding mercaptans exhibit colours which are nearer the blue end of the spectrum than those of the alkali salts of the corresponding hydroxyanthraquinones.

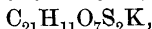
Anthraquinonyl aryl sulphides are obtained from nitroanthraquinones and potassium aryl mercaptides in boiling alcohol. Thus 1-nitroanthraquinone yields 1-phenylthiolanthraquinone,



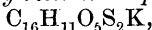
m. p.  $185^\circ$ , yellowish-red needles, and the corresponding 1-o-tolylthiol derivative, m. p.  $216^\circ$ , reddish-brown needles, and p-tolylthiol compound, m. p.  $235^\circ$ , orange-red needles; 1:5-dinitroanthraquinone yields

1:5-diphenylthiolanthraquinone,  $SPh \cdot C_6H_3 \begin{array}{c} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} C_6H_3 \cdot SPh$ , m. p.

$250^\circ$ , reddish-brown leaflets, and the corresponding di-p-tolylthiol compound, m. p. above  $300^\circ$ , golden-yellow needles. The following are obtained in a similar manner: potassium 1-phenylthiolanthraquinone-5-sulphonate,  $C_{20}H_{11}O_5S_2K$ , yellowish-red needles, and the corresponding p-tolyl derivative,  $C_{21}H_{13}O_5S_2K$ , golden-yellow needles; benzyl derivative,  $C_{21}H_{13}O_5S_2K \cdot 2H_2O$ , golden-yellow needles; salicyl derivative,

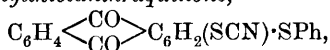


orange-red leaflets; p-nitrophenyl derivative,  $C_{20}H_{10}O_7NS_2K$ , yellow needles; p-aminophenyl derivative,  $C_{20}H_{12}O_5NS_2K$ , brown needles (by reduction of the preceding compound by alcoholic sodium sulphide); potassium 1-phenylthiolanthraquinone-8-sulphonate,  $C_{20}H_{11}O_5S_2K$ , orange needles, and the corresponding p-tolyl derivative,  $C_{21}H_{13}O_5S_2K$ , brick-red needles; potassium 1-ethylthiolanthraquinone-6-sulphonate,



yellow leaflets, and the corresponding phenyl derivative,  $C_{20}H_{11}O_5S_2K$ , yellow needles; p-tolyl derivative,  $C_{21}H_{13}O_5S_2K$ , yellow needles; salicyl derivative,  $C_{21}H_{11}O_7S_2K$ , yellow leaflets; 1-amino-4-phenylthiolanthraquinone,  $C_{20}H_{13}O_2NS$ , m. p.  $201^\circ$ , bluish-red needles (acetyl derivative, m. p.  $224^\circ$ , reddish-brown needles); 1-amino-4-p-tolylthiolanthraquinone, m. p.  $218^\circ$ , bluish-red leaflets (acetyl derivative, m. p.  $278^\circ$ , reddish-brown needles); 1-amino-4-salicylthiolanthraquinone, as potassium salt,  $C_{21}H_{12}O_4NSK$  (ethyl ester, m. p.  $166^\circ$ , bluish-red needles), and 1-amino-4-a-naphthylthiolanthraquinone, m. p.  $232^\circ$ , dark red needles.

1-Thiocyano-4-phenylthiolanthraquinone,



m. p.  $228^\circ$ , yellowish-red needles, obtained by boiling diazotised 1-amino-4-phenylthiolanthraquinone with aqueous potassium thiocyanate, is

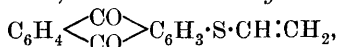
converted by alcoholic potassium hydroxide and subsequent treatment with methyl iodide into 4-phenylthiol-1-methylthiolanthraquinone, m. p. 182°, red needles. 1-Thiocyano-4-p-tolylthiolanthraquinone, m. p. 241°, reddish-yellow needles, m. p. 241°, yields 4-p-tolylthiol-1-methylthiolanthraquinone, m. p. 215°, red leaflets; the disulphide, m. p. above 330°, of the mercaptan crystallises in orange-red needles.

New types of sulphur compounds, which can be isolated on account of their pronounced tendency to crystallise, have been obtained from the mercaptans of the anthraquinone series. Thus anthraquinonylthiol-

acetic acid,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 250°, yellow needles,

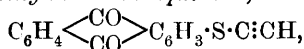
is obtained from 1-thiolanthraquinone and chloroacetic acid in boiling alkaline solution; it forms an ethyl ester, m. p. 148°, yellow needles, and a sulphoxide, m. p. 240, pale yellow needles, the ethyl ester of which has m. p. 144°. Also an aqueous alcoholic alkaline solution of 1-thiolanthraquinone by treatment with ethylene dibromide yields

1-β-bromoethylthiolanthraquinone,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2\text{Br}$ , m. p. 180°, yellow needles, from which 1-vinylthiolanthraquinone,



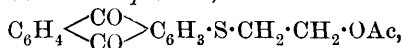
m. p. 163°, brownish-red needles, is obtained by the action of boiling alcoholic potassium hydroxide. By the addition of bromine in cold chloroform, the vinyl compound yields 1-αβ-dibromoethylthiolanthra-

quinone,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{S} \cdot \text{CHBr} \cdot \text{CH}_2\text{Br}$ , m. p. 160°, golden-yellow needles, which is converted by boiling aqueous alcoholic potassium hydroxide into 1-acetenylthiolanthraquinone,



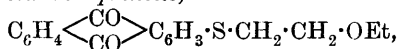
m. p. 198—199°, golden-yellow needles or plates (silver derivative, red, slightly explosive powder).

1-β-Acetoxyethylthiolanthraquinone,



m. p. 148°, yellow needles, obtained by heating the bromo-compound with acetic acid, acetic anhydride, and potassium acetate, is hydrolysed by aqueous potassium hydroxide, yielding 1-β-hydroxyethylthiolanthra-

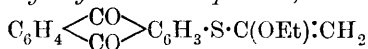
quinone,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{S} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$ , m. p. 178°, orange-red needles; the benzoate, m. p. 201°, crystallises in yellow needles. By heating with alcohol at 130°, 1-β-bromoethylthiolanthraquinone yields 1-β-ethoxyethylthiolanthraquinone,



m. p. 129°, reddish-yellow needles.

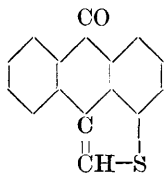
1-αβ-Dibromoethylthiolanthraquinone yields 1-αβ-dimethoxyethylthiolanthraquinone,  $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{S} \cdot \text{CH}(\text{OMe}) \cdot \text{CH}_2 \cdot \text{OMe}$ , m. p. 156°, yellow needles, or the corresponding diethoxy-compound, m. p. 156°, by

heating with methyl or ethyl alcohol. By heating with alcoholic potassium hydroxide under suitable conditions, the dibromo-compound yields 1- $\alpha$ (or  $\beta$ )-ethoxyvinylthiolanthraquinone,



or  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{S} \cdot \text{CH} : \text{CH} \cdot \text{OEt}$ , m. p. 197—198°, dark red leaflets; the corresponding *methoxy*-compound, m. p. 215°, crystallises in red needles. By boiling an aqueous methyl alcoholic alkaline solution of 1-thiolanthraquinone with *s*-dichloroethylene, 1- $\beta$ -chlorovinylthiolanthraquinone,  $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} \text{C}_6\text{H}_3 \cdot \text{S} \cdot \text{CH} : \text{CHCl}$ , m. p. 174—175°, red needles, and the preceding acetenyl derivative are produced. The substance,  $\text{C}_2\text{H}_2(\text{S} \cdot \text{C}_4\text{H}_7\text{O}_2)_2$ , m. p. 341°, dark red leaflets, can be obtained from alkaline 1-thiolanthraquinone and *s*-dichloroethylene under suitable conditions, or by heating 1- $\alpha\beta$ -dibromoethylthiolanthraquinone with pyridine at 150°; in the latter method, methylene bromide must be eliminated.

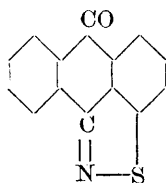
The following substances have been obtained by similar methods: 2-anthraquinonylthiolacetic acid, m. p. 202°, yellow needles (*methyl ester*, m. p. 131°; *ethyl ester*, m. p. 112°; *sulphoxide*, m. p. 247°, yellow prisms [*ethyl ester*, m. p. 215°]); 2- $\beta$ -bromoethylthiolanthraquinone, m. p. 172°, pale yellow needles; 2-vinylthiolanthraquinone, m. p. 133°, golden-yellow needles; 2- $\alpha\beta$ -dibromoethylthiolanthraquinone, m. p. 133·5°, yellow plates; 2- $\beta$ -hydroxyethylthiolanthraquinone, m. p. 137° (*acetate*, m. p. 128°; *benzoate*, m. p. 128·5°; *ethyl ether*, m. p. 110°); 2- $\alpha\beta$ -diethoxyethylthiolanthraquinone, m. p. 106°; 2-acetenylthiolanthraquinone, m. p. 323°, red leaflets; 4-methoxyanthraquinonylthiolacetic acid, m. p. 220°, pale red needles; 4-aminoanthraquinonylthiolacetic acid, m. p. 206° (decomp.), red needles; 4-methylaminoanthraquinonylthiolacetic acid, m. p. 232°, dark violet leaflets; 5-chloroanthraquinonylthiolacetic acid, m. p. 278°, pale yellow needles; 5-dimethylamino-1- $\beta$ -bromoethylthiolanthraquinone, m. p. 186°, red leaflets; 5-dimethylamino-1-vinylthiolanthraquinone, m. p. 161·5°, reddish-brown leaflets; 5-dimethylamino-1- $\alpha\beta$ -dibromoethylthiolanthraquinone, m. p. 143°, dark brown leaflets; 5-dimethylamino-acetenylthiolanthraquinone, m. p. 197°, reddish-brown prisms.



By heating with acetic anhydride under pressure, anthraquinonylthiolacetic acids are converted into anthraquino-1-thiophens. In some cases the tendency to ring closure is so pronounced that the thiophens are produced in the usual method of preparing the thiolacetic acids. *Anthraquino-1-thiophen*, m. p. 179—180° (annexed formula), crystallises in pale yellow needles. 2-Methylanthraquino-1-thiophen,  $\text{C}_{16}\text{H}_{10}\text{OS}$ , m. p. 186°, yellow needles, 2-methylanthraquino-1-thiophencarboxylic acid, m. p. 271°, citron-yellow needles, and 4-methoxyanthraquino-1-thiophen, m. p. 202—203°, yellowish-brown leaflets, are described.

By heating with concentrated aqueous ammonia at 130°, 1-thiocyananthraquinone is converted into *anthraquino-1-thiazole* (annexed

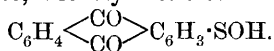
formula), m. p. 221°, yellow needles. The following thiazoles have also been prepared; 2-methylantraquino-1-thiazole, m. p. 218°, pale yellow needles; 4-aminoantraquino-1-thiazole, m. p. 251°, golden plates or needles; 4-methylaminoantraquino-1-thiazole, m. p. 219°, greenish metallic leaflets; 4-dimethylaminoantraquino-1-thiazole, m. p. 212°; anthraquino-1:4-dithiazole, m. p. 226°, citron-yellow needles; anthraquino-1-thiazole-4-carboxylic acid, m. p. 260°;



yellow needles; 4-tolylthiolantraquino-1-thiazole, m. p. 210°, yellow leaflets; 5-aminoantraquino-1-thiazole, m. p. 250°, reddish-brown needles with green reflex; 5-thiocyanooantraquino-1-thiazole, m. p. 276°, golden needles; 5-methylthiolantraquino-1-thiazole, m. p. 245°, orange needles; 5-methylaminoantraquino-1-thiazole, m. p. 185°, reddish-violet needles; 5-dimethylaminoantraquino-1-thiazole, m. p. 152°, brownish-red needles, and anthraquino-1:5-dithiazole, m. p. 287°, yellow needles.

The dyeing properties of many of the preceding substances are described. C. S.

**$\alpha$ -Anthraquinonesulphenic Acid.** KARL FRIES (*Ber.*, 1912, 45, 2965—2973).—The author has succeeded in obtaining in the anthracene group, halogen thiols of the type recently described by Zincke (*Abstr.*, 1911, i, 368; this vol., i, 762). The  $\alpha$ - and  $\beta$ -chloro- and bromo-thiolantraquinones resemble in general properties the analogues previously described, but the  $\alpha$ -compounds are relatively more stable; also with alcohols the  $\alpha$ -compounds react in an unusual manner with formation of alkyloxy-sulphur derivatives which behave as esters of, and are hydrolysable to, a feebly acetic substance,



This is the first substance of this type to be isolated, and the generic name *sulphenic acid* is suggested. It is possible that the free substance is in reality a  $\psi$ -acid, and that the salts are of the structure  $\text{R} \cdot \text{S} \begin{array}{c} \diagup \text{X} \diagdown \\ \diagdown \text{O} \diagup \end{array}$ ,

where X represents the metal atom.

[With E. ENGELBERTZ.]—When  $\alpha$ -anthraquinone disulphide suspended in chloroform is treated with the theoretical quantity of bromine or chlorine,  $\alpha$ -bromothioloantraquinone ( $\alpha$ -anthraquinonesulphenyl bromide), orange needles, m. p. 214°, or  $\alpha$ -chlorothioloantraquinone ( $\alpha$ -anthraquinonesulphenyl chloride), orange needles, m. p. 224°, is respectively obtained. The substances agree in chemical behaviour; aqueous alkali slowly attacks them, forming  $\alpha$ -anthraquinonesulphinic acid together with the original disulphide; alcoholic potassium hydroxide gives the same result more rapidly, but the products are accompanied by a little of the alkali salt of the sulphenic acid, which colours the solution bluish-green. They react in the usual manner with ammonia, amines, and phenols, for example, the bromine compound when heated with  $\beta$ -naphthol gives hydrogen bromide and  $\alpha$ -anthraquinonyl  $\alpha$ -[ $\beta$ -hydroxynaphthyl]-sulphide, golden-yellow tablets, m. p. 254°; the alkali salts form bronze, prismatic needles.

If the above chlorine or bromine compounds are boiled for some

time with methyl alcohol, orange-red needles of *methyl α-anthraquinone-sulphenate*, m. p. 189°, separate; this substance gives a red solution in acetic acid, which turns yellow on boiling with the formation of α-anthraquinone disulphide and disulphoxide, together with some of the sulphinic acid. Ethyl alcohol acts on the above halogen compounds, producing *ethyl α-anthraquinonesulphenate*, red needles, m. p. 149°. If the above methyl ester is boiled for a short time with an alcoholic solution of potassium hydroxide, the *potassium* salt separates in short, almost black needles with a feeble green lustre; the aqueous solution of this salt on acidification with acetic acid deposits the free α-anthraquinone-sulphenic acid,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_3 \cdot SOH$ , which crystallises from aqueous

acetone in red needles, which do not melt even at 300°, although decomposition has occurred; the *alkali* salts are easily soluble in water, the *lead* and *barium* salts sparingly so, the colour of the solid in all cases being black with a feeble green lustre. The acid reacts with hydrogen chloride and bromide, forming the above anthraquinonyl sulphur chloride and bromide; with methyl sulphate in methyl-alcoholic solution it yields the methyl ester, but when shaken in alcoholic alkaline solution with methyl sulphate there is produced *methyl α-anthraquinonyl sulphoxide*,  $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_6H_3 \cdot \begin{smallmatrix} S \\ | \\ O \end{smallmatrix} Me$ , yellow needles, m. p.

226°, which by warming with hydrobromic acid gives *methyl-α-anthraquinonyl sulphide*, yellow needles, m. p. 218°; this substance is also obtainable by the action of methyl sulphate on α-anthraquinone mercaptan, and on oxidation with nitric acid (D 1·4) or hydrogen peroxide it regenerates the sulphoxide. Oxidation of the alcoholic alkaline solution of sulphenic acid by potassium ferricyanide gives rise to α-anthraquinonesulphinic acid, needles, which do melt below 300°; the same oxidation occurs slowly when an alkaline solution of the acid is exposed to air; on boiling its acetic acid solution, the sulphinic acid undergoes simultaneous oxidation and reduction to α-anthraquinone-sulphonic acid and a mixture of the disulphide and disulphoxide respectively. The sulphenic acid when its acetic acid solution is boiled undergoes similar decomposition to its methyl ester. It is reduced by sodium sulphide to α-anthraquinone mercaptan, and condenses with phenols when heated, for example, giving the above α-anthraquinonyl α-[β-hydroxynaphthyl]-sulphide with β-naphthol.

D. F. T.

[Preparation of Anthracene Derivatives.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 250273).—When substituted anthraquinone-sulphonic acids are condensed in aqueous solution with arylmercaptols, products are formed which contain at least one sulphonic group. The compounds from *p*-tolyl mercaptan with 1:4-dichloroanthraquinone-6-sulphonic acid (a yellowish-red powder) and with 1:5-diamino-4:8-dibromoanthraquinone-2:6-disulphonic acid (a glistening, bronze, crystalline powder) are described together with their tinctorial properties.

F. M. G. M.

Cold Vulcanisation of Caoutchouc. GUSTAV BERNSTEIN (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 185—191).—If the gelatinous substance

obtained by the action of sulphur monochloride on purified Para caoutchouc in xylene solution at room temperature is extracted in a Soxhlet apparatus with benzene, then with carbon disulphide, and finally with ethyl alcohol according to the procedure adopted by Weber, the residual product is found to contain much larger quantities of sulphur and chlorine than that which is obtained after extraction with carbon disulphide only. The latter method yields a yellow powder which contains sulphur and chlorine in approximate agreement with the formula  $(C_{10}H_{16})_2S_2Cl_2$ . The higher values yielded by the product obtained by extracting according to Weber's method are shown to be due to decomposition of the substance under the influence of hot benzene and alcohol.

From more dilute xylene solutions, the substance resulting from the action of sulphur chloride or caoutchouc separates in the form of a powder, and under these conditions the influence of large variations in the relative quantities of the two substances has been examined. In all cases, the product appears to be that represented by  $(C_{10}H_{16})_2S_2Cl_2$ .

It is shown that the changes occurring in the xylene solution can be followed by measurements of the viscosity. H. M. D.

**Theory of the Vulcanisation of Caoutchouc.** F. WILLY HINRICHSSEN and ERICH KINDSCHER (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 191—193).—The product obtained by the action of sulphur on caoutchouc in cumene solution at  $170^\circ$  has been found to correspond with the formula  $C_{10}H_{16}S_2$ . The composition of the dark brown powder, which is obtained, remains practically unchanged when the ratio of caoutchouc to sulphur is varied from 2 : 1 to 1 : 4.

Certain statements made by Spence and Young (this vol., ii, 706), and by Loewen (this vol., ii, 914, 215) are subjected to criticism.

H. M. D.

**The Cerebrosides of the Brain.** PHCEBUS A. LEVENE and WALTER A. JACOBS (*J. Biol. Chem.*, 1912, 12, 389—398).—Many cerebrosides (galactosides) have been described by various workers, and in most cases each has received several names. An attempt is made to unravel the resulting confusion. The list is finally reduced to three, but they differ only in optical activity, and in solubilities which enable their separation to be accomplished with some difficulty; it is proposed that as the real difference is stereochemical to substitute a new nomenclature, namely, *d*-cerebrin (=cerebrin, cerebron, and phrenosin of other writers), *dl*-cerebrin (=kerasin and homocerebrin of other writers), and *l*-cerebrin.

W. D. H.

**Thiocarbimides: the Glucoside of Cheirolin.** WILHELM SCHNEIDER and WILHELM LOHMANN (*Ber.*, 1912, 45, 2954—2961).—It has already been conjectured (Schneider, *Abstr.*, 1910, i, 658) that cheirolin is present in wallflower seeds in the form of a glucoside. This can actually be isolated by extracting dry fat-free wallflower seed with alcohol; the glucoside, which could not be obtained pure, is a brown, hygroscopic powder, the solution of which is turned greenish-yellow by alkali. It contains the elements sulphur, nitrogen, and potassium apparently in the atomic proportions 3 : 2 : 1;

the sulphur appears to be present in three different forms, as hydrolysis with hydrochloric acid produces hydrogen sulphide (from the thiocarbimide group of cheirolin) and sulphuric acid, whilst the sulphone group (present in cheirolin) can only be detected by oxidation with fuming nitric acid. After hydrolysis with hydrochloric acid, the presence of dextrose could be detected by the formation of the osazone. The glucoside also, like sinigrin, undergoes scission when treated with silver nitrate, producing dextrose and a precipitate, *cheirolin silver sulphate*,  $C_5H_9O_2NS_2 \cdot Ag_2SO_4$ , which, however, is not merely a double salt. After oxidation of the glucoside with fuming nitric acid, barium methanesulphonate can be isolated. Myrosin from white mustard seed hydrolyses the glucoside, and cheirolin can be easily isolated from the product; on the other hand, wall-flower seeds, as also cauliflower seeds, contain an enzyme which is capable of liberating mustard oil from black mustard seed (myrosin free). D. F. T.

**Oxidation of Picrotoxin.** GEORGE BARGER and REGINALD W. L. CLARKE (*Ber.*, 1912, 45, 3166—3167. Compare Sielisch, this vol., i, 790).—On oxidation of picrotoxin by boiling with concentrated nitric acid, an *acid* is obtained sparingly soluble in warm acetic acid, and crystallising in large, tabular crystals, decomp.  $300^\circ$ . The acid,  $C_{18}H_{14}O_9$ , is dibasic. E. F. A.

**Picrotin.** PAUL HORRMANN and KARL SEYDEL (*Ber.*, 1912, 45, 3080—3086. Compare Sielisch, this vol., i, 790).—It has been shown previously that picrotin possesses the properties of a lactone, although neither the corresponding acid nor any of its derivatives could be isolated. The authors now find that the action of potassium hydroxide or methoxide in methyl alcohol solution gives rise to two isomeric monobasic acids,  $C_{15}H_{20}O_8$ , which are termed  $\gamma$ - and  $\delta$ -picrotic acids. The latter is isolated in the form of its methyl ester, whilst the  $\gamma$ -acid separates out from the reaction product as the potassium salt. Exactly similar results were obtained by the action of potassium hydroxide and ethoxide in ethyl alcoholic solution.

The pronounced reducing properties of picrotin are not shared by the two acids, and it is, therefore, probable that the addition of water to the lactone linking is accompanied by some other change in the structure of the molecule.

$\gamma$ -Picrotic acid forms stout crystals (decomp.  $204$ — $205^\circ$ ) and differs from the  $\delta$ -acid in reducing alkaline permanganate. The *potassium* salt crystallises from methyl alcohol in slender needles containing the solvent (1 mol.), and has  $[\alpha]_D^{17.5} - 3^\circ 57'$  in aqueous solution; it sinters and becomes brown at  $245^\circ$  (decomp.  $260^\circ$ ).

$\delta$ -Picrotic acid, prepared by the hydrolysis of its esters with aqueous sodium hydroxide, has  $[\alpha]_D^{17.5} + 71^\circ 58'$  (decomp.  $258^\circ$ ); the *methyl* ester crystallises from water in slender needles, m. p.  $239^\circ$ ,  $[\alpha]_D^{17.5} + 77^\circ 11'$  in alcohol; the *ethyl* ester has m. p.  $199^\circ$ ,  $[\alpha]_D^{17.5} + 74^\circ 25'$  in alcohol.

In addition to the above mentioned products, the action of potassium hydroxide or alkyl oxides on picrotin leads to the formation of a substance,  $C_{15}H_{18}O_7$ , *picrotin-lactone*, which is isomeric with picrotin,

and is also produced during the hydrolysis of the esters of  $\delta$ -picrotic acid.

The action of excess of alkali on picrotin yields a dibasic acid,  $C_{15}H_{22}O_9$ . F. B.

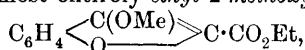
**Hydroxycarboxylic Esters of Coumarone, Thionaphthen, and Indole, and their Products of Alkylation.** KARL VON AUWERS (*Annalen*, 1912, 393, 338—383).—The chief interest of the paper lies in the alkylation experiments. Ethyl 2-hydroxycoumarilate

(acetate,  $C_6H_4 \begin{smallmatrix} \text{C(OAc)} \\ \text{O} \end{smallmatrix} \rangle C \cdot CO_2Et$ , m. p. 76—77°; benzoate, m. p. 124°)

and the corresponding thionaphthen and indole derivatives yield mainly *O*-ethers by treatment with methyl sulphate or ethyl sulphate and aqueous alkali, their formation being attributed to the interaction of the ions of the alkyl sulphate and of the sodium derivative of the strongly acidic hydroxy-ester. Alkylation by an alkyl iodide and sodium alkoxide yields mainly the *C*-ether (except in the case of ethyl 2-hydroxythionaphthen-1-carboxylate, where the *O*-ether is the main product), produced by the addition of the alkyl iodide and subsequent elimination of sodium iodide.

Whilst the parent substances are stable, their ethers are easily hydrolysed or decomposed by boiling alcoholic alkalis; the *O*-ethers yield the corresponding carboxylic acids (from which 2-alkyloxy coumarone and the corresponding thionaphthen and indole derivatives are easily obtained by heating, and coumaranone and the corresponding thionaphthen and indole derivatives by the action of acids), and the *C*-ethers experience rupture of the heterocyclic nucleus in the case of the thionaphthen compound and yield 1-alkylcoumaranones from the coumarone derivatives.

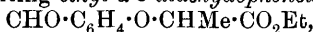
Thus by treatment at 0° with methyl sulphate and 15% potassium hydroxide, the former being always in excess, ethyl 2-hydroxycoumarilate yields almost entirely *ethyl 2-methoxycoumarilate*,



m. p. 59°. This ether yields coumaranone by treatment with boiling oxalic acid solution or 1% sulphuric acid, and 2-methoxycoumarilic acid,  $C_{10}H_8O_4$ , m. p. 166—170° (decomp.), by hydrolysis with alcoholic alkalis; above its m. p. the acid yields 2-methoxycoumarone, b. p. 109—110°/17 mm.,  $D_4^{19.4}$  1.1442. Ethyl 2-hydroxycoumarilate, ethyl sulphate, and aqueous potassium hydroxide at about 30° yield 2-ethoxycoumarilic acid, m. p. 166—170° (decomp.) (ethyl ester, b. p. 180°/13 mm.,  $D_4^{14.6}$  1.1678, from the silver salt and ethyl iodide), from which coumaranone and 2-ethoxycoumarone, b. p. 117°/16 mm.,  $D_4^{17.2}$  1.1068, are obtained by methods similar to those above.

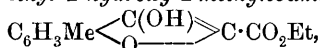
Ethyl 2-hydroxycoumarilate, methyl-alcoholic sodium methoxide (1 mol.), and methyl iodide (2—3 mols.), heated in a sealed tube at 100° for one and a-half to two hours, yield almost entirely *ethyl 1-methylcoumaranone-1-carboxylate*,  $C_5H_4 \begin{smallmatrix} \text{CO} \\ \text{O} \end{smallmatrix} \rangle CMe \cdot CO_2Et$ ; this, however, could not be isolated as such, but was converted by aqueous alcoholic sodium hydroxide into 1-methylcoumaranone, identified by its disemicarbazide

derivative, m. p. 234—235°. An unsuccessful attempt was made to prepare the pure *C*-methyl ether by heating salicylaldehyde, methyl  $\alpha$ -bromopropionate, and alcoholic sodium ethoxide on the water-bath, hydrolysing the resulting *ethyl  $\alpha$ -o-aldehydophenoxypropionate*,

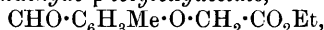


b. p. 181—183°/19 mm. (*semicarbazone*, m. p. 120°, after drying at 100°), oxidising the *acid*, m. p. 63—73°, by potassium permanganate to  $\alpha$ -salicyloxypropionic [ $\alpha$ -*o*-carboxyphenyloxypropionic] *acid*, m. p. 136°, and treating the *ethyl ester*, b. p. 192—194°/17—18 mm., of this in benzene with sodium. By treatment with ethyl iodide and alcoholic sodium ethoxide, ethyl 2-hydroxycoumarilate yields *ethyl 1-ethyl coumaranone-1-carboxylate* (containing a little of the *O*-ether), b. p. 173·5—178·5°/17 mm.,  $D_4^{19.8}$  1·1537, when prepared at atmospheric pressure, b. p. 170—175°/15 mm.,  $D_4^{18}$  1·1563, when prepared in a sealed tube, which is converted into 1-ethylcoumaranone by treatment with alcoholic alkali.

The following substances are the intermediate compounds required in the preparation of *ethyl 2-hydroxy-4-methylcoumarilate*,



m. p. 96°, long, white needles (*acetate*, m. p. 68—68·5°; *benzoate*, m. p. 126°): *ethyl 2-aldehyde-p-tolylloxyacetate*,



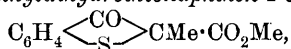
m. p. 54·5°, prepared from *p*-homosalicylaldehyde and ethyl bromoacetate, and the corresponding *acid*,  $\text{C}_{10}\text{H}_{10}\text{O}_4$ , m. p. 151°, white needles; *p*-homosalicyloxyacetic [*o*-carboxy-*m*-tolylloxyacetic] *acid*,  $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$ , m. p. 182—183°, and its *diethyl ester*, b. p. 195°/15 mm., the coumarone derivative being obtained by the action of sodium on the latter in dry benzene. By treatment with methyl sulphate and 10% potassium hydroxide at the ordinary temperature, ethyl 2-hydroxy-4-methylcoumarilate yields *ethyl 2-methoxy-4-methylcoumarilate*,  $\text{C}_6\text{H}_3\text{Me} \left\langle \begin{array}{c} \text{C(OMe)} \\ \text{O} \end{array} \right\rangle \text{C} \cdot \text{CO}_2\text{Et}$ , b. p. 199°/18 mm., m. p. 29—30° (after long keeping),  $D_4^{22.7}$  1·1702; the *acid*,  $\text{C}_{11}\text{H}_{10}\text{O}_4$ , m. p. 178—180°, is obtained by hydrolysing the preceding ester by alcoholic alkali or by treating ethyl 2-hydroxy-4-methylcoumarilate with an excess of alkali and methyl sulphate. The acid yields *2-methoxy-4-methylcoumarone*, b. p. 149°/36 mm.,  $D_4^{24.3}$  1·1074, above its m. p. *2-Ethoxy-4-methylcoumarilate*,  $\text{C}_{12}\text{H}_{12}\text{O}_4$ , m. p. 173°, prepared by gently warming ethyl 2-hydroxy-4-methylcoumarilate with ethyl sulphate and aqueous alkali, forms an *ethyl ester*, m. p. 47—48° (from the silver salt), and yields *2-ethoxy-4-methylcoumarone*, b. p. 133°/15·5 mm.,  $D_4^{16.5}$  1·0827, by loss of carbon dioxide.

1 : 4-*Dimethylcoumaranone*,  $\text{C}_6\text{H}_3\text{Me} \left\langle \begin{array}{c} \text{CO} \\ \text{O} \end{array} \right\rangle \text{CHMe}$ , m. p. 63° (di-semicarbazide derivative, m. p. 225°), and *ethyl 1 : 4-dimethylcoumaranone-1-carboxylate*,  $\text{C}_6\text{H}_3\text{Me} \left\langle \begin{array}{c} \text{CO} \\ \text{O} \end{array} \right\rangle \text{CMe} \cdot \text{CO}_2\text{Et}$ , are obtained by heating ethyl 2-hydroxy-4-methylcoumarilate with methyl iodide and methyl-alcoholic sodium methoxide. The ester has b. p. 170—172°/15 mm.,  $D_4^{20.1}$  1·1606, when prepared at atmospheric pressure, and

b. p. 179—182°/18.5 mm.,  $D_4^{21}$  1.1533, when obtained in a sealed tube; it contains a little of the *O*-ether, and therefore yields 2-methoxy-4-methylcoumarilic acid as well as 1:4-dimethylcoumaranone by warming with alcoholic alkali. In an attempt to prepare the pure ester, the following have been obtained: *α*-2-aldehydo-4-methylphenoxypropionic acid, m. p. 111—112°, and its methyl ester, m. p. 57°; ethyl ester, b. p. 206°/35 mm., and oxime, m. p. 168—169°, from the last *α*-2-cyano-4-methylphenoxypropionic acid, m. p. 121—122°, being obtained by boiling acetic anhydride.

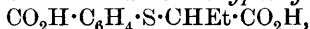
The ethylation of ethyl 2-hydroxy-4-methylcoumarilate by ethyl iodide and alcoholic sodium ethoxide in a sealed tube yields a mixture of the *O*- and the *C*-ethers, since the product yields with boiling alcoholic alkali 4-methyl-1-ethylcoumaranone, m. p. 40°, and 2-ethoxy-4-methylcoumarilic acid.

Methyl 2-hydroxythionaphthen-1-carboxylate, methyl-alcoholic sodium methoxide (1 mol.), and methyl iodide (2 mols.), heated in a sealed tube at 100° for two hours, yield a mixture of methyl 2-methoxythionaphthen-1-carboxylate,  $C_6H_4 \begin{smallmatrix} \text{C(OMe)} \\ \text{---S---} \end{smallmatrix} C \cdot CO_2Me$ , m. p. 68—68.5°; and methyl 2-keto-1-methyldihydrothionaphthen-1-carboxylate,



m. p. 74°, which is separated by the sparing solubility of the latter in petroleum of low b. p., or in methyl alcohol. The *O*-ether, which is the chief product by this method of methylation, is the only product when an aqueous alkali and an excess of methyl sulphate are used; it yields 2-methoxythionaphthen-1-carboxylic acid, m. p. 171—173°, by hydrolysis by alcoholic alkali. This acid is readily converted into 2-methoxythionaphthen above its m. p. The *C*-ether is rapidly decomposed by cold alcoholic alkali, yielding *α*-o-carboxyphenylthiolpropionic acid,  $CO_2H \cdot C_6H_4 \cdot S \cdot CHMe \cdot CO_2H$ , m. p. 194—195°, colourless leaflets, which is also obtained from thiosalicylic acid and *α*-bromopropionic acid and dilute sodium hydroxide on the water-bath; it cannot be transformed back to the thionaphthen derivative.

Methyl 2-hydroxythionaphthen-1-carboxylate reacts with ethyl iodide and sodium ethoxide at 100° in a sealed tube to form a mixture of the *O*- and the *C*-ethyl ethers. Since these could not be separated, the product was treated with alcoholic alkali, whereby the former yields 2-ethoxythionaphthen-1-carboxylic acid, m. p. 158°, stout prisms, and the latter is converted into *α*-o-carboxyphenylthiolbutyric acid,



m. p. 171—172°. 2-Ethoxythionaphthen has b. p. 154°/19 mm., and  $D_4^{17.6}$  1.1591.

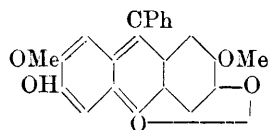
Ethyl indoxylate, methyl sulphate, and dilute potassium hydroxide at the ordinary temperature yield ethyl 3-methoxyindole-2-carboxylate,  $C_6H_4 \begin{smallmatrix} \text{C(OMe)} \\ \text{---NH---} \end{smallmatrix} C \cdot CO_2Et$ , m. p. 92—93°; by hydrolysis with alcoholic alkali, the ester yields the acid,  $C_{10}H_9O_3N$ , m. p. 147—148° (decomp.), which is converted by heating into 3-methoxyindole, m. p. 69—70°, b. p. about 170°/18—19 mm., flattened needles. Methoxyindole develops a brownish-violet coloration with concentrated sulphuric

acid, produces a brownish-red coloration on a pine shaving moistened with hydrochloric acid, and yields indigotin by warming with ferric chloride and hydrochloric acid.

The methylation of ethyl indoxylate by methyl iodide and methyl alcoholic sodium methoxide at 100° in a sealed tube yields a mixture of methylated derivatives which has not yet been thoroughly examined. C. S.

**Ethers of Hydroxyquinolbenzein** [2:3:7-Trihydroxy-9-phenylfluorone]. FRIEDRICH KEHRMANN and M. GÜNTHER (*Ber.*, 1912, 45, 2884—2891).—An examination of the oxonium haloids obtained from substituted phenylxanthhydrols would indicate that the presence of an esterified carboxyl group in the ortho-position in the phenyl group is essential for the existence of normal haloid salts (compare Kehrman and Dengler, *Abstr.*, 1909, i, 249; Gomberg and Cone, *ibid.*, 1910, i, 55; Kehrman and Knop, this vol., i, 43). That this is not so is proved by the following example.

2:3:7-Trihydroxy-9-phenylfluorone is readily obtained in 70% yield by keeping equal weights of hydroxyquinol and benzo-trichloride for twenty-four hours at the ordinary temperature, for eighteen hours at 60—70°, and finally for one hour at 100°, and decomposing the resulting chloride by boiling water. When heated with the calculated



amount of dilute aqueous sodium hydroxide and an excess of methyl iodide, the benzein yields a mixture of 3-hydroxy-2:7-dimethoxy-9-phenylfluorone (annexed formula), m. p. 287—288°, dark red crystals with blue metallic reflex, and the corresponding trimethyl ether,  $C_{22}H_{18}O_5$ , m. p. 277°, golden leaflets. The dimethyl ether forms a red

sodium salt, and a chloride, orange-red leaflets, and acetate, both of which are hydrolysed by water; the acetate of the trimethyl ether does not give a precipitate by the addition of water to its solution in acetic acid.

By treating the trimethyl ether in nitrobenzene at 150° with methyl sulphate, a tetramethyl ether is obtained, which is isolated by hydrochloric acid in the form of 2:3:6:7-tetramethoxy-9-phenylxanthonium chloride,  $C_6H_2(OMe)_2 \llbracket \begin{smallmatrix} CPh \\ OCl \end{smallmatrix} \rrbracket C_6H_2(OMe)_2$ , red leaflets. The corre-

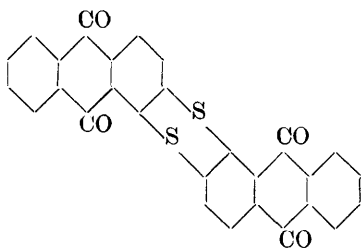
sponding platinichloride,  $2C_{23}H_{21}O_5 \cdot PtCl_6$ , brick-red leaflets, and dichromate are described. The chloride dissolves in water without hydrolysing. The solution is bitter, and remains unchanged for a short time even after the addition of sodium hydrogen carbonate, but ultimately decomposes, yielding the tetramethoxyphenylxanthanol, colourless needles (methyl alcoholate, m. p. 171—172°). An ethereal solution of the carbinol forms with carbon dioxide a yellow, fluorescent solution, which probably contains the xanthonium carbonate. C. S.

**Action of Hydrogen Peroxide on Trithienyl.** MAURICE LANFRY (*Compt. rend.*, 1912, 155, 836—838).—By the action of hydrogen peroxide (10 vols.) on a boiling solution of trithienyl in

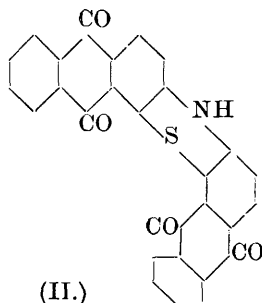
dilute acetic acid two compounds are formed according to the duration of the reaction. After thirty minutes, a compound,  $C_{12}H_8S_2O_2$ , m. p. 231—233°, is obtained, crystallising in colourless prisms, insoluble in water, but soluble in benzene or chloroform. It is not acted on by aqueous alkalis or dilute sulphuric acid. If the reaction is prolonged to one hour, the compound,  $C_{12}H_8S_2O_4$ , m. p. 338°, already prepared by Renard (compare Abstr., 1891, 427) by the oxidation of trithienyl with fuming nitric acid, is obtained. It is not acted on by bromine in the cold or on heating.

W. G.

**Preparation of Anthraquinone Derivatives Containing Sulphur.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 248171).—When 1 : 2-dihalogen- or 1 : 2-halogenamino-anthraquinones are boiled during some hours in nitrobenzene solution with 1 : 2-dimercaptol- or 1 : 2-aminomercaptol-anthraquinones condensation occurs.



(I.)



(II.)

*Diphthalylthianthren* (formula I.), red needles with a metallic lustre, is thus prepared from anthraquinone-1 : 2-dimercaptol and 1 : 2-dichloroanthraquinone, whilst 1 : 2-dichloroanthraquinone and 2-aminoanthraquinone-1-mercaptol furnishes *thiodianthraquinonylamine* (formula II.).

A complete analysis of these compounds is given in the original.

F. M. G. M.

**Preparation of Compounds from Quinine and Dialkyl-barbituric Acids.** EMANUEL MERCK (D.R.-P. 249908).—A salt from codeine and diethylbarbituric acid has previously been prepared (compare this vol., i, 209), and the reaction has now been extended to other nearly related alkaloids.

*Quinine diethylbarbiturate* crystallises in fine needles, m. p. 136°, whilst *quinine dipropylbarbiturate* forms colourless needles, m. p. 127—128°.

F. M. G. M.

**Preparation of Esters of Hydroquinine.** VEREINIGTE CHININ-FABRIKEN ZIMMER & Co. (D.R.-P. 250379. Compare Abstr., 1888, 69, and 1911, ii, 219).—*Hydroquinine ethyl carbonate*, tasteless, colourless needles, m. p. 75—78°, is prepared by boiling together equimolecular proportions of hydroquinine and ethyl chlorocarbonate in benzene solution during ten minutes.

*Benzoylhydroquinine*, colourless crystals, m. p. 102—107°, is obtained

by the reaction of benzoyl chloride on hydroquinone; it forms a *salicylate*, colourless needles, m. p. 193.5°.

*Hydroquinine salicylate*, large, colourless crystals, m. p. 115—119°, is prepared by heating hydroquinine with salol during six hours at 130—140°.

*p*-Nitrobenzoylhydroquinine, m. p. 163—164°, is obtained by the action of *p*-nitrobenzoyl chloride on hydroquinine in boiling benzene solution; on reduction it furnishes *p*-aminobenzoylhydroquinine, yellow needles, m. p. 155—157.5°. *Hydroquinine carbonate* is prepared by the action of carbonyl chloride on hydroquinine; these compounds are of therapeutic value. F. M. G. M.

**Peculiar Relation between the Strengths of Acids and their Activity.** II. PAUL RABE [with EBERHARD FELLE] (*Ber.*, 1912, 45, 2927—2932. Compare Rabe and McMillan, *Abstr.*, 1911, ii, 33).—The author has extended his previous work on the catalytic influence of acids in accelerating the conversion of cinchonine into cinchotoxine, and has now examined the effect of hydrochloric and acetic acids on cinchonine, cinchonidine, hydrocinchonine, quinine, quinidine, and hydroquinine. Hydrochloric acid did not effect the transformation in any of the observed cases. The change, however, takes place slowly in dilute alcoholic solution (80%), and still more slowly in benzene solution.

In the case of narcotine, the following reactions are possible: (1) racemisation with the formation of so-called gnoscopine; (2) hydrolysis to nornarceine; (3) hydrolytic decomposition into cotarnine and meconine (compare Rabe and McMillan, *Abstr.*, 1911, i, 77). On treatment with 3*N*-acetic acid at 98° during thirty hours, narcotine yields small quantities of nornarceine, meconine, and cotarnine, together with traces of gnoscopine; with *N*-hydrochloric acid, on the other hand, no decomposition product was obtained after treatment during ten hours at 98°, whilst, after thirty hours, only traces of nornarceine were detected.

Choline when heated at about 98° during seventy-two hours with *N*-hydrochloric and *N*-acetic acids respectively yielded 70% and 66% of unchanged material. Trimethylamine could not be detected. A portion of the choline apparently suffered change in some unknown direction.

Oleic acid when heated with acetic acid or with acetic acid and water at 98° during thirty-six hours was not converted into elaidic acid. H. W.

**Hæmanthine.** LOUIS LEWIN (*Arch. expt. Path. Pharm.*, 1912, 70, 302).—Polemical against Tutin (this vol., i, 797). Hæmanthine (from *Haemanthus toxicarius* [*Buphane disticha*]) is a pure substance with characteristic chemical reactions, and a constant toxic action.

W. D. H.

**Preparation of apoScopolamine.** F. HOFFMANN, LA ROCHE & Co. (D.R.-P. 247819).—apoScopolamine, C<sub>17</sub>H<sub>19</sub>O<sub>3</sub>N, needles, m. p. 97—98°, is readily prepared by dissolving two parts of scopolamine

sulphuric acid (this vol., i, 896) in hot water (50 parts), cooling until crystallisation commences, and then adding 20 parts of 2*N*-sodium hydroxide, when the product separates after half an hour in crystalline form; it furnishes a crystalline *nitrate*. *Chloroscopolamine* is obtained by the action of thionyl chloride on scopolamine. F. M. G. M.

**Derivatives of Triketopyrrolidine and their Conversion into Trimethylparamide.** OTTO MUMM and CLEMENS BERGELL (*Ber.*, 1912, 45, 3149—3155).—By the action of potassium oxalate on the additive product of methyl sulphate and  $\alpha$ -methylisooxazole an *N*-oxalyl compound,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NMe}\cdot\text{CO}\cdot\text{CO}_2\text{K}$ , is obtained, which immediately loses water, forming *triketo-3-acetyl-1-methylpyrrolidine*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}\begin{smallmatrix} \text{CO}\cdot\text{NMe} \\ \text{CO}\cdot\text{CO} \end{smallmatrix}$ . The *potassium* salt at first formed is readily hydrolysed by acids. The corresponding *benzoyl* derivative is prepared in a similar manner from 2-phenylisooxazole. Both acyl compounds have acid properties; they are colourless, but form yellow salts. With phenylhydrazine, the benzoyl derivative forms an additive compound, which is converted into the phenylhydrazone when boiled with alcoholic hydrogen chloride.

The benzoyl compound is not affected by boiling with water, but the acetyl derivative loses acetic acid, forming a polymeride of the methyl-imide of acetylenedicarboxylic acid, namely, *trimethylparamide*, which may be regarded as the trimethylimide of mellitic acid (annexed formula).

It is assumed that in the acyl compounds the oxalic acid residue is attached to nitrogen. Proof of this is afforded by the formation of 3-methyl-2-acetonyl-4-quinazolone,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}\cdot\text{NMe} \\ \text{N}=\text{C}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3 \end{smallmatrix}$ , when sodium anthranilate acts on the methyl sulphate additive product of  $\alpha$ -methylisooxazole. When boiled with dilute hydrochloric acid, acetic acid is eliminated and 2:3-dimethylquinazolone,  $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CO}\cdot\text{NMe} \\ \text{N}=\text{CMe} \end{smallmatrix}$ , is obtained.

The *potassium* salt of *triketo-3-benzoyl-1-methylpyrrolidine* crystallises in yellow, interlaced needles, m. p. 175°, and yields when acidified the *triketopyrrolidine* itself, m. p. 107°. The *additive product* with phenylhydrazine has m. p. 143°; the *phenylhydrazone* forms yellow prisms, m. p. 165°.

*Triketo-3-acetyl-1-methylpyrrolidine* separates in almost colourless prisms, m. p. 120—124°; the *potassium* salt is yellow.

*Trimethylparamide* crystallises in slender, colourless needles, subliming at about 400°.

3-Methyl-2-acetonyl-4-quinazolone crystallises in colourless rods, m. p. 198°. E. F. A.

**The Blood Pigment.** X. J. GRABOWSKI and LEON MARCHLEWSKI (*Zeitsch. physiol. Chem.*, 1912, 81, 86—89).—It is probable that methyl ethylpyrrole is a constituent of hæmopyrrole.

3-Methyl-4-*n*-propylpyrrole, prepared from methyl-*n*-propylmaleic anhydride, distils in oily drops. In aqueous solution it gives a red coloration with Ehrlich's reagent, and a white precipitate with mercuric chloride. In ethereal solution it reacts with diazonium chloride; the product consists of dark blue crystals with a coppery lustre, m. p. 253°, and slender needles, m. p. 225°. The corresponding compounds from 3-methyl-4-ethylpyrrole have m. p. 264° and 233°, whereas similar compounds from hæmopyrrole show m. p. 268° and 233°. E. F. A.

**Action of Sodium Alkylloxides on Esters of Pyrrole-carboxylic Acids. II. and III.** U. COLACICCHI and C. BERTONI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 450—454, 518—523. Compare this vol., i, 647).—II. When sodium ethoxide (10%) and ethyl 3-acetyl-2:4-dimethylpyrrole-5-carboxylate are heated for fourteen to sixteen hours at 220°, it is possible to separate from the reaction product by extraction with ether and fractional distillation, a dimethyldiethylpyrrole, which yields a picrate, m. p. 88—89°, identical with that of Fischer and Bartholomäus (this vol., i, 384). The *dimethyldiethylpyrrole* obtained from this picrate is an almost colourless oil, b. p. 112—114°/22 mm. It has an odour resembling that of thymol; it does not give the pine-splinter or Ehrlich reactions. The picrate prepared from it has m. p. 92°.

The action of sodium ethoxide on 3-acetyl-2:4-dimethylpyrrole (twelve hours at 150—170°) also yields among other substances the tetra-substitution product, which was isolated as picrate.

III. When ethyl 2:5-dimethylpyrrole-3:4-dicarboxylate is heated with sodium ethoxide (10%) for fourteen hours at 220—230°, a *dimethyldiethylpyrrole* is formed. Its *picrate*,  $C_{16}H_{20}O_7N_4$ , crystallises in yellow prisms, m. p. 102—103°.

When an ethereal solution of benzoyl chloride is added to the product of the reaction between magnesium methyl iodide and 2:3:5-trimethylpyrrole, 3-*benzoyl*-2:4:5-*trimethylpyrrole*,  $C_{14}H_{15}ON$ , is obtained. It crystallises in somewhat red needles, m. p. 172—173°, and is identical with the substance prepared from oximinomethyl ethyl ketone and benzoylacetone by Knorr's method. R. V. S.

**Some Acyl Derivatives of 2- and 3-Aminopyridines.** F. CARLO PALAZZO and G. MAROGNA (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 512—518. Compare Palazzo and Tamburini, *Abstr.*, 1911, i, 327).—When 3-aminopyridine is treated with ethyl acetoacetate under the same conditions as were employed by Palazzo and Tamburini, 3-*acetoacetylaminopyridine* is obtained, m. p. 134—135° (previously softening). It is soluble in acids and alkalis, gives a green precipitate with ammoniacal copper acetate, and an intense reddish-violet coloration with ferric chloride. 3-*Benzoylacetylaminopyridine* has m. p. 100—101° (softening at 96°), and has properties similar to those of the aceto-derivative.

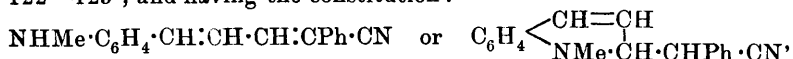
2-Aminopyridine reacts with  $\omega$ -bromoacetophenone (preferably in alcoholic solution), forming the *compound*,  $C_5H_4N \cdot NH \cdot CH_2 \cdot C(=O)Ph$ , which crystallises in silky needles, m. p. 135°. R. V. S.

**Preparation of the Hydrochlorides of Quinoline- and Pyridine-Iodochlorides.** MORITZ KOHN and ARTUR KLEIN (*Monatsh.*, 1912, 33, 967—970).—When a mixture of quinoline with diluted nitric acid and iodine is heated to boiling and concentrated hydrochloric acid added gradually, the brown colour of the iodine disappears, and an oil separates which crystallises on cooling; this substance is the hydrochloride of quinoline, iodochloride,  $C_9H_7N, ICl, HCl$ , m. p. 118—120° (compare Dittmar, *Abstr.*, 1886, 158; Pictet and Krafft, *Abstr.*, 1892, 1356); the substance is readily hydrolysed by water with the formation of the free quinoline iodochloride, m. p. 156—157°.

In a similar manner, pyridine yields the hydrochloride of pyridine iodochloride, m. p. 183°.

D. F. T.

**Preparation of Condensation Products of Cyclic Ammonium Bases.** A. KAUFMANN (D.R.-P. 250154).—Compounds of therapeutic value are obtained by the action of an alkali hydroxide or ethoxide on quaternary salts of quinoline in the presence of ethyl acetoacetate, phenylacetoneitrile, or indoxyl. The *compound*,  $C_{18}H_{16}N_2$ , m. p. 122—125°, and having the constitution :



is prepared from phenylacetoneitrile, quinoline, methyl sulphate, and sodium ethoxide.

The *compound*,  $C_{10}H_6N \cdot CH_2 \cdot NO_2$ , brownish-yellow needles, is obtained from quinoline, methyl sulphate, and nitromethane, whilst quinoline methiodide and ethyl acetoacetate furnish the *compound*,  $C_{20}H_{28}O_3N_2$ , leaf-like aggregates, m. p. 146—147°, and nitromethane with *iso*-quinoline methiodide, a *product* with m. p. 99°.

F. M. G. M.

**4-Quinolyl Ketones.** ADOLF KAUFMANN, HEINRICH PEYER, and MAX KUNKLER (*Ber.*, 1912, 45, 3090—3098).—The authors suggest that the specific action of quinine in cases of malaria is connected with the presence of the  $-CH(OH) \cdot \dot{C}H \cdot N:$  group in the 4-position of the quinoline nucleus, and in support of this view mention that adrenaline contains the same grouping, and that the physiological properties of quinine are essentially modified by the disappearance of the hydroxyl group from the molecule.

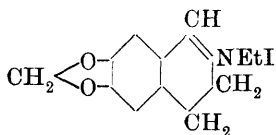
The synthesis of quinoline derivatives containing the above group in the 4-position is being undertaken; in the present paper a number of 4-quinolyl ketones are described. These form well crystallised salts, and resemble in their chemical behaviour and constitution the cinchotoxins of Miller and Rohde (*Abstr.*, 1893, i, 434).

**4-Quinolyl methyl ketone**,  $C_9H_6N \cdot COMe$ , prepared by the interaction of 4-cyanoquinoline and magnesium methyl iodide, and purified by means of its *picrate*, which forms soft, yellow needles, m. p. 165—170° (decomp.), or its *acetate* (long, white needles, m. p. 70°), is a pale yellow oil, b. p. 138°/2 mm., m. p. below  $-20^\circ$ ; the *hydrochloride* forms colourless prisms, m. p. 200—214° (decomp.); the *methiodide*, dark red crystals, m. p. 172° (decomp.); the yellow *phenylhydrazone* forms a *picrate*, which crystallises from acetic acid in cinnabar-red granules, m. p. 224° (decomp.).

**4-Quinolyl phenyl ketone**, prepared from 4-cyanoquinoline and magnesium phenyl bromide, distils at  $155^{\circ}/0.5$  mm., as a viscid, pale yellow oil, which solidifies to an opal-like mass, m. p.  $58-59^{\circ}$ ; it crystallises from water in long, white needles, and yields a *picrate*, crystallising in brownish-yellow leaflets, m. p.  $214^{\circ}$  (decomp.), and a *phenylhydrazone*, which forms a yellow, crystalline powder, m. p.  $239-240^{\circ}$ . It is not identical with the compound, m. p.  $294^{\circ}$ , described under the same name by Remfry and Decker (Abstr., 1908, i, 364), and obtained by the action of magnesium phenyl bromide on ethyl cinchonate.

**6-Methoxy-4-quinolyl methyl ketone**,  $\text{OMe} \cdot \text{C}_9\text{H}_5\text{N} \cdot \text{COMe}$ , obtained from quinonitrile (4-cyano-6-methoxyquinoline), crystallises in thin, golden-yellow platelets, m. p.  $92^{\circ}$ , and give solutions having a yellowish-green fluorescence. F. B.

**Preparation of Dihydroisoquinoline Derivatives.** HERMAN DECKER (D.R.-P. 249723. Compare this vol., i, 581).—It is found that the physiological action of 6:7-methylenedioxy-3:4-dihydroisoquinoline (Abstr., 1911, i, 906) is increased by alkylation; the *ethiodide* (annexed formula) forms yellow leaflets, m. p.  $220^{\circ}$ , and the corresponding *benzyl chloride* is a pale yellow, hygroscopic, crystalline powder, m. p.  $215^{\circ}$ .



F. M. G. M.

**Preparation of Compounds from 2-Phenylquinoline-4-carboxylic Acid or its Homologues with Glycine.** CHEMISCHE FABRIK AUF ACTIEN (VORM. E. SCHERING) (D.R.-P. 249766).—When 2-phenylquinoline-4-carboxylic acid or its homologues react with the alkyl esters of glycine the corresponding salts are formed: *Ethylglycyl 2-phenylquinoline-4-carboxylate* forms pale yellow needles, m. p.  $135^{\circ}$ , whilst the corresponding *ester* of 2-phenyl-6-methylquinoline-4-carboxylic acid is a colourless, crystalline powder, m. p.  $126-127^{\circ}$ .

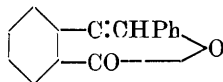
F. M. G. M.

**Preparation of Substituted 2:3-Diphenylquinoline-4-carboxylic Acid.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 249765).—When isatin derivatives are condensed with deoxybenzoin they yield 2:3-diphenylquinoline-4-carboxylic acids, which are colourless, crystalline, tasteless, and of therapeutic value.

**2:3-Diphenyl-6:8-dimethylquinoline-4-carboxylic acid**, colourless needles, m. p.  $245^{\circ}$ , is obtained when dimethylisatin (60 parts) in boiling 30% potassium hydroxide solution (5 parts KOH) is slowly treated with an alcoholic solution of deoxybenzoin (80 parts).

**2:3-Diphenyl-6-methylquinoline-4-carboxylic acid**, m. p.  $319^{\circ}$ , is prepared in a similar manner from deoxybenzoin with *p*-methylisatin; **3-phenyl-2-*p*-tolylquinoline-4-carboxylic acid**, m. p.  $304^{\circ}$ , from isatin with *p*-methyldeoxybenzoin, whilst isatin with *p*-methoxydeoxybenzoin furnishes **3-phenyl-2-*p*-anisylquinoline-4-carboxylic acid**, colourless leaflets, m. p.  $291^{\circ}$ .

3-Phenyl-2-o-carboxyphenylquinoline-4-carboxylic acid, colourless leaflets, m. p. 78°, is obtained by the condensation of isatin with the anhydride of deoxybenzoincarboxylic acid (annexed formula), whilst 2:4-dibromoisatin with deoxybenzoin furnishes 6:8-dibromo-2:3-diphenylquinoline-4-carboxylic acid, colourless needles, m. p. 250°, and 3-phenyl-2-p-tolyl-6-methylquinoline-4-carboxylic acid, colourless needles, m. p. 290°, is obtained from p-methylisatin with p-methyldeoxybenzoin.



F. M. G. M.

**New Derivatives of Phenylisooxazolone.** ANDRÉ MEYER (*Compt. rend.*, 1912, 155, 841—844).—With a view to a study of the relations between colour and constitution, the author has prepared a number of derivatives of phenylisooxazolone by condensation with cyclic aldehydes according to a method previously described (compare Wahl and Meyer, *Abstr.*, 1908, i, 368). The following condensation products (substituted 3-phenyl-4-benzylideneisooxazolones) were prepared.

3-Phenyl-4-p-tolylideneisooxazolone,  $C_3O_2NPh:CH:C_6H_4Me$ , yellow needles, m. p. 177—178°, giving a deep yellow solution in sulphuric acid.

3-Phenyl-4-p-isopropylbenzylideneisooxazolone,  
 $C_3O_2NPh:CH:C_6H_4Pr^i$ ,  
 golden-yellow scales, m. p. 147—148°.

3-Phenyl-4-o-nitrobenzylideneisooxazolone,  $C_3O_2NPh:CH:C_6H_4NO_2$ , yellow needles, m. p. 132—133°. The meta-isomeride forms deep yellow crystals, m. p. 138—139°, and the para-isomeride, tufts of yellow needles, m. p. 179—180°.

3-Phenyl-4-o-anisylideneisooxazolone,  $C_3O_2NPh:CH:C_6H_4OMe$ , deep yellow prisms, m. p. 165—166°.

3-Phenyl-4-vanillylideneisooxazolone,  $C_3O_2NPh:CH:C_6H_3(OH)OMe$ , long, pale yellow needles, m. p. 180—181°.

3-Phenyl-4-op-dihydroxybenzylideneisooxazolone,  
 $C_3O_2NPh:CH:C_6H_3(OH)_2$ ,  
 deep yellow needles, m. p. 280°, only very slightly soluble in the usual solvents, giving an orange-yellow solution in alkalis.

3-Phenyl-4-mp-dihydroxybenzylideneisooxazolone, brown leaflets, m. p. 202—203°, giving a reddish-violet solution in alkalis.

isoPhthalylidene-bis-3-phenylisooxazolone,  $C_6H_4(CH:C_3O_2NPh)_2$ , bright yellow needles, m. p. 212—213°.

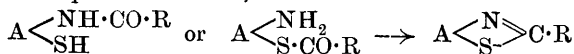
3-Phenyl-4-salicylideneisooxazolone gives an *acetyl* derivative, small, yellow crystals, m. p. 142—143°.

The colour of the compounds containing a free hydroxyl group is deeper than their ethers. Acetylation diminishes the depth of colour more than methylation. The position of the hydroxyl group has an influence on the colour, ortho-derivatives being generally less coloured than para-derivatives, the former, however, yielding more deeply coloured solutions in alkalis or sulphuric acid than the latter. Of the nitro-derivatives the meta possesses most colour and the ortho least. The colour is attributed to the complex  $CO:C:C$ , the group CO being part of a pentatomic heterocyclic ring.

The author proposes the name "*isooxazole-indogenides*" for these derivatives, and points out their resemblance to the corresponding pyrazole derivatives, the colour of the latter being less pronounced than that of the former.

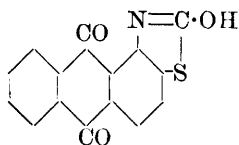
W. G.

**Preparation of Anthraquinone Derivatives.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 250090).—The condensation of acyl derivatives of *o*-diaminoanthraquinones has previously been described (this vol., i, 140); it is now found that if *o*-aminoanthraquinone mercaptans are employed, the following reaction takes place, yielding anthraquinonethiazoles,



(A = anthraquinone).

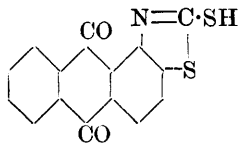
The *thiazole*, obtained when sodium 1-aminoanthraquinone-2-mercaptan (1 part) is boiled with acetic anhydride (5 parts), separates in pale yellow needles.



(I.)

The *hydroxythiazole* (formula I.), small needles, m. p. 255°, is prepared from sodium-1-aminoanthraquinone-2-mercaptan with ethyl chlorocarbonate in alcoholic solution.

The *thiazolmercaptole* (formula II.), orange-yellow needles, is prepared in a similar manner in the presence of carbon disulphide, whilst 1:4-diaminoanthraquinone-2-mercaptol when boiled with benzoyl chloride in nitrobenzene solution furnishes 4-benzylaminoanthraquinone-1:2-thiazole, brown prisms.

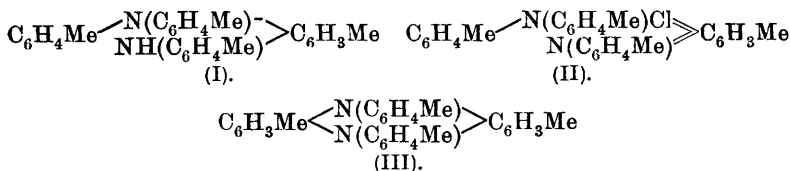


(II.)

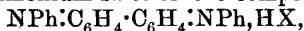
F. M. G. M.

**Cause of the Blue Colour Produced by Nitrous Acid and Other Oxidising Agents in Sulphuric Acid Solutions of Diphenylamine.** FRIEDRICH KEHMAN and ST. MICEWICZ (*Ber.*, 1912, 45, 2641—2653).—By boiling tetraphenylhydrazine in toluene solution, Wieland (*Abstr.*, 1911, i, 569) obtained a yellow substance, which dissolved in sulphuric acid in the presence of oxidising agents with a blue coloration, and was considered by him to be a diphenyldihydrophenazine. The blue coloration produced in the diphenylamine reaction was referred by Wieland to the intermediate formation of this substance. The authors point out, however, that the properties of the substance differ very considerably from those of the homologous di-*p*-tolylidihydrotolazine, and thus render it improbable that the compound has the structure assigned to it by Wieland. Further, the explanations given by Wieland of the transformation of tetra-arylhydrazines into phenazonium derivatives are not in accord with the results obtained by Jacobson, who has shown that, under the influence of acids, symmetrical diarylamines containing substituents in the para-position undergo the semidine transformation, whilst unsubstituted diarylhydrazines are converted into benzidine derivatives. The

action of sulphuric acid on tetra-*p*-tolylhydrazine would thus lead to the formation of a semidine (I), which is then converted by oxidation into the *o*-indamine (II), and finally by loss of hydrogen chloride into di-*p*-tolylldihydrotolazine (III):



Tetraphenylhydrazine, on the other hand, undergoes the benzidine transformation, yielding *NN'*-diphenylbenzidine, which cannot be further converted into diphenyldihydrophenazine. In order to determine the cause of the blue coloration in the diphenylamine reaction, the authors have examined the action of nitrous acid and other oxidising agents on diphenylamine and *NN'*-diphenylbenzidine, and come to the conclusion that the blue coloration is due to the formation of quinoneimonium salts of the composition

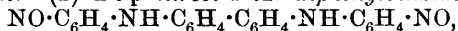


produced by the oxidation of *NN'*-diphenylbenzidine, the latter compound being formed by the action of sulphuric acid on diphenylamine (compare Kadiera, Abstr., 1905, i, 934).

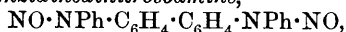
The green salt obtained by Wieland by the action of ethereal hydrogen chloride on di-*p*-tolylldihydrotolazine is more readily prepared by the oxidation of di-*p*-tolylamine with sodium dichromate in acetic acid solution and treating the product with hydrochloric acid. It has the composition  $\text{C}_{56}\text{H}_{54}\text{N}_4\text{Cl}_4$  and is a *N*-quinhydrone, consisting of di-*p*-tolyltolazonium dichloride (1 mol.) combined with di-*p*-tolylldihydrotolazine dihydrochloride (1 mol.); on crystallisation from water it loses 2HCl, yielding the normal salt,  $\text{C}_{56}\text{H}_{52}\text{N}_4\text{Cl}_2$ . The quinhydrone salts are converted by aqueous ferric chloride into the *holo* quinonoid salt, which was isolated in the form of its dark brown *platinichloride*,  $\text{C}_{28}\text{H}_{26}\text{N}_2\text{PtCl}_6$ .

Oxidation of diphenylamine by means of potassium persulphate and sulphuric acid in glacial acetic acid solution at the ordinary temperature yields the *N*-quinhydrone sulphate of *NN'*-diphenylbenzidine. This is a dark olive-green, microcrystalline substance, which is oxidised by excess of potassium persulphate, or better by sodium dichromate and sulphuric acid, to the corresponding *holo*-quinonoid sulphate.

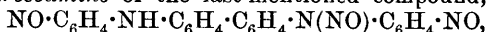
When decomposed by water, the dark blue liquid formed by the addition of sodium nitrite to a solution of diphenylamine in strong sulphuric acid yields an olive-green precipitate, which contains the following substances: (1) the *N*-quinhydrone sulphate of *NN'*-diphenylbenzidine. (2) *Di-p-nitroso-N:N'*-diphenylbenzidine,



which forms yellowish-red granules (decomp. 290°), gives a violet-red coloration with sulphuric acid, and is often accompanied by *NN'*-diphenylbenzidine, from which it is separated only with difficulty.

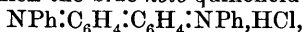
(3) *NN'*-Diphenylbenzidinedinitrosoamine,

which forms microscopic, yellowish-white needles, m. p.  $124^\circ$ , and dissolves in strong sulphuric acid with a blue coloration and evolution of nitric oxide. From the instability of the dinitrosoamine in sulphuric acid, the authors draw the conclusion that the original blue solution, obtained by the addition of sodium nitrite to diphenylamine in sulphuric acid, contains *NN'*-diphenylbenzidine, and that the formation of the dinitrosoamine takes place during the subsequent dilution with water. The addition of sodium nitrite to a solution of *NN'*-diphenylbenzidine in glacial acetic acid, containing a little sulphuric acid at the ordinary temperature, yields the above-mentioned dinitrosoamine; if the mixture is warmed, di-*p*-nitroso-*NN'*-diphenylbenzidine is produced; in one instance, using an excess of sodium nitrite, a *nitrosoamine* of the last-mentioned compound,

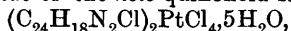


was obtained.

Oxidation with ferric chloride and a mixture of acetic and sulphuric acids converts *NN'*-diphenylbenzidine into a dark green *N*-quinhydrone salt, from which the blue *holo*-quinonoid salt,



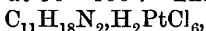
is obtained by oxidation with chromic acid. The dark violet crystalline *platinichloride* of the *holo*-quinonoid salt,



was analysed.

F. B.

$\delta$ -Phenyl- $\alpha$ -methyltetramethylenediamine. [ $\alpha\delta$ -Diamino- $\alpha$ -phenylpentane.] CESARE FINZI (*Gazzetta*, 1912, 42, ii, 364—367).—Acetophenoneacetonedioxime is best obtained by the action of hydroxylamine hydrochloride on an excess of the monoxime (compare this vol., i, 995) in alkaline solution. When the dioxime is reduced with sodium and alcohol,  $\alpha\delta$ -diamino- $\alpha$ -phenylpentane is obtained. It is a dense, yellow oil, which absorbs carbon dioxide from the air, and gives the reactions and precipitates characteristic of alkaloids. Its *carbonate* (or *carbamate*) decomposes at  $90$ — $100^\circ$ . The *platinichloride*,

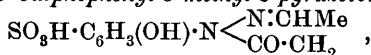


crystallises in tufts of yellow needles, which become brown at  $245^\circ$  and melt at  $249^\circ$  (decomp.). The *dibenzoyl* derivative,  $\text{C}_{25}\text{H}_{26}\text{O}_2\text{N}_2$ , has m. p.  $224^\circ$ .

R. V. S.

**Preparation of Pyrazolone Derivatives in the Benzene Series Containing a Free Hydroxyl Group.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 249626).—Pyrazolones containing a free hydroxyl group are of technical importance for the preparation of dyes and pharmaceutical products, and can be prepared by the action of acetoacetic ester on the hydrazines of aminophenols.

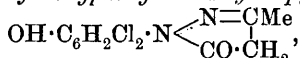
1 : 2'-Hydroxy-5'-sulphophenyl-3-methyl-5-pyrazolone,



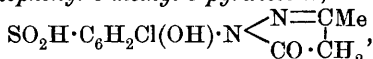
colourless crystals, is obtained as follows: 2-amino-*p*-phenolsulphonic acid is diazotised, reduced to 2-hydrazino-*p*-phenolsulphonic acid, which

is then treated with ethyl acetoacetate in concentrated aqueous solution, when, after prolonged stirring at 60°, the ring closes and furnishes the foregoing compound.

1 : 3' : 5'-Dichloro-2'-hydroxyphenyl-3-methyl-5-pyrazolone,



is prepared in a similar manner from 4 : 6-dichloro-*o*-aminophenol, whilst 4-chloro-2-amino-*o*-phenolsulphonic acid furnishes 1 : 5'-chloro-2'-hydroxy-3'-sulphophenyl-3-methyl-5-pyrazolone,



when the intermediate *hydrazine* is treated with acetoacetate, or if ethyl-oxalacetate is employed it yields 1 : 5'-chloro-3'-sulpho-2'-hydroxyphenyl-

5-pyrazolone-3-carboxylic acid,  $\text{SO}_3\text{H} \cdot \text{C}_6\text{H}_2\text{Cl}(\text{OH}) \cdot \text{N} \begin{array}{l} \text{N}=\text{C} \cdot \text{CO}_2\text{H} \\ \text{CO} \cdot \text{CH}_2 \end{array},$

or with sodium dioxytartrate it furnishes a red tartrazine dye.

Other aminophenols and their derivatives (Abstr., 1908, i, 785) can be employed in this reaction.

F. M. G. M.

**Derivatives of 5-Benzylpyrimidine.** HERMANN KAST (*Ber.*, 1912, 45, 3124—3135).—Benzylbarbituric acid is best prepared by condensing ethyl benzylmalonate with carbamide by means of sodium ethoxide in alcoholic solution. It is converted by phosphoryl chloride at 120° into 2 : 4 : 6-trichloro-5-benzylpyrimidine, which crystallises in colourless needles, m. p. 66·5°, and when warmed with hydriodic acid and phosphonium iodide yields 2(or 6)-iodo-4-hydroxy-5-benzylpyrimidine. This forms long, colourless needles, m. p. 208°, dissolves in both acids and alkalis, and has also been prepared by the action of hydriodic acid on 2 : 6-dichloro-4-methoxy-5-benzylpyrimidine, which crystallises in colourless prisms, m. p. 74°, and is readily obtained by the interaction of 2 : 4 : 6-trichloro-5-benzylpyrimidine and sodium methoxide in methyl-alcoholic solution.

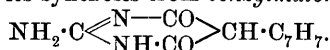
2 : 6-Dichloro-4-methoxy-5-benzylpyrimidine reacts with alcoholic ammonia, yielding 6-chloro-2-amino-4-methoxy-5-benzylpyrimidine, colourless platelets, m. p. 162°, and with methyl-alcoholic sodium methoxide to form 6-chloro-2 : 4-dimethoxy-5-benzylpyrimidine, which separates from alcohol in rhombohedral crystals, m. p. 48°, belonging to the triclinic system, and, on reduction with zinc and hydrochloric acid in alcoholic solution, is converted into 2 : 4-dihydroxy-5-benzylpyrimidine (*phenylthymine*). This forms small, prismatic crystals, m. p. 285—286°, and may be obtained directly from benzylbarbituric acid by reduction with phosphorus and hydriodic acid at 150—160°.

2 : 4 : 6-Trimethoxy-5-benzylpyrimidine, prepared from 2 : 4 : 6-trichloro-5-benzylpyrimidine and excess of sodium methoxide, has m. p. 99·5°.

The trichloro-compound reacts with ammonia at the ordinary temperature, yielding 4 : 6-dichloro-2-amino-5-benzylpyrimidine, which crystallises in needles, m. p. 204·5°, and is accompanied by 2 : 4-dichloro-6-amino-5-benzylpyrimidine. The last-mentioned compound

crystallises with benzene ( $\frac{1}{2}$  mol.), which is lost at  $100^\circ$ ; from alcohol it separates in long, slender, lustrous, silky needles.

The constitution of 4:6-dichloro-2-amino-5-benzylpyrimidine has been established by its synthesis from *benzylmalonylguanidine*,



This crystallises with  $1\text{H}_2\text{O}$ , and is prepared by the condensation of ethyl benzylmalonate and guanidine thiocyanate with sodium ethoxide in alcoholic solution; when heated at  $120$ — $125^\circ$  with phosphoryl chloride, it yields 4:6-dichloro-2-amino-5-benzylpyrimidine, which is reduced by zinc dust and aqueous alcohol to 2-amino-5-benzylpyrimidine, crystallising in lustrous scales, m. p.  $133.5^\circ$  (*aurichloride*, yellow needles; *platinichloride*, orange-red needles).

The action of methyl-alcoholic ammonia on 4:6-dichloro-2-amino-5-benzylpyrimidine leads to the formation of 6-chloro-2-amino-4-methoxy-5-benzylpyrimidine.

2- or 6-Iodo-4-amino-5-benzylpyrimidine, prepared by reducing 2:6-dichloro-4-amino-5-benzylpyrimidine with hydriodic acid and phosphonium iodide, crystallises in columns, m. p.  $201^\circ$ ; the *hydrochloride*, rhombohedra, *hydriodide*, *aurichloride*, and *platinichloride* are described. On reduction with zinc dust and aqueous alcohol, it yields 4-amino-5-benzylpyrimidine, which crystallises in lustrous, colourless platelets, m. p.  $156^\circ$ , and forms a *zinci-iodide* crystallising in short, flat needles, m. p. about  $240^\circ$ .

2:4:6-Trichloro-5-benzylpyrimidine reacts with alcoholic ammonia at  $150$ — $160^\circ$  to form 6-chloro-2:4-diamino-5-benzylpyrimidine. This crystallises in white needles, m. p.  $163^\circ$ , and has also been obtained by the reaction of 4:6-dichloro-2-amino-5-benzylpyrimidine with ammonia in alcoholic solution. When reduced with zinc and hydrochloric acid in aqueous solution, 6-chloro-2:4-diamino-5-benzylpyrimidine is converted into 2:4-diamino-5-benzylpyrimidine, which forms small, felted needles, melting at  $145$ — $146^\circ$ , to a turbid liquid.

Reduction with hydriodic acid and phosphonium iodide yields 6-iodo-2:4-diamino-5-benzylpyrimidine *hydriodide*, pale yellow, pointed needles, m. p.  $246$ — $250^\circ$  (decomp.), from which the free base is liberated by aqueous alkalis. This crystallises in clusters of needles, which become brown and have m. p.  $191$ — $192^\circ$ ; the *hydrochloride* is mentioned. On reduction with zinc and aqueous alcohol, it gives rise to 2:4-diamino-5-benzylpyrimidine. F. B.

**Preparation of Derivatives of Barbituric Acid.** FARBEFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 247952. Compare Trans., 1909, 95, 979).—5-Phenyl-5-ethylbarbituric acid,  $\text{CO} \begin{array}{c} \text{NH} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{NH} \cdot \text{CO} \end{array} \text{C} \text{EtPh}$ , leaflets, m. p.  $170^\circ$ , is prepared by boiling 264 parts of *ethyl phenyl-ethylmalonate* (b. p.  $166^\circ/12$  mm.) with sodium (69 parts) and carbamide (90 parts) in absolute alcoholic solution during six hours and evaporating the filtered solution in a vacuum with the addition of dilute hydrochloric acid until the liquid is only feebly alkaline; it furnishes crystalline *calcium* and *sodium* salts.

5-Phenyl-5-benzylbarbituric acid, m. p. 235°; 5-phenyl-5-methylbarbituric acid, m. p. 220°; 5-phenyl-5-propylbarbituric acid, m. p. 190°; and 5-p-methoxyphenyl-5-ethylbarbituric acid, m. p. 202°, are also described in the original. F. M. G. M.

**Preparation of Derivatives of Barbituric Acid.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D R.-P. 249722. Compare following abstract).—Phenylethylmalonyl chloride, b. p. 50—60°/15 mm., is prepared from phenylethylmalonyl ester by hydrolysis with alcoholic sodium hydroxide at the ordinary temperature; the phenylethylmalonic acid (m. p. 155°) so obtained is then converted into its chloride by the usual method; when the foregoing chloride is condensed with methylisocarbamide hydrochloride in benzene solution, it furnishes 2-methoxy-5-phenyl-5-ethylbarbituric acid,  $\text{OMe} \cdot \text{C} \begin{smallmatrix} \text{N} \text{---} \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{C} \text{EtPh}$ , m. p. 152°; this when warmed with 30% hydrochloric acid evolves methyl chloride and yields phenylethylbarbituric acid,  $\text{OMe} \cdot \text{C} \begin{smallmatrix} \text{N} \text{---} \text{CO} \cdot \text{C} \text{EtPh} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$ , m. p. 170°.

Benzylmalonyl chloride has b. p. 141°/15 mm., and when condensed with ethylisocarbamide hydrochloride furnishes 2-ethoxy-5-benzylbarbituric acid,  $\text{OEt} \cdot \text{C} \begin{smallmatrix} \text{N} \text{---} \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{C} \cdot \text{CH}_2\text{Ph}$ , m. p. 202°, which when treated with 45% hydrobromic acid yields benzylbarbituric acid, m. p. 206°.

2-Ethoxy-5-phenylbarbituric acid,  $\text{OEt} \cdot \text{C} \begin{smallmatrix} \text{N} \text{---} \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{CHPh}$ , m. p. 218°, is prepared in a similar manner from phenylmalonyl chloride, b. p. 122°/15 mm., and on treatment with concentrated sulphuric acid furnishes 5-phenylbarbituric acid, m. p. 250°. F. M. G. M.

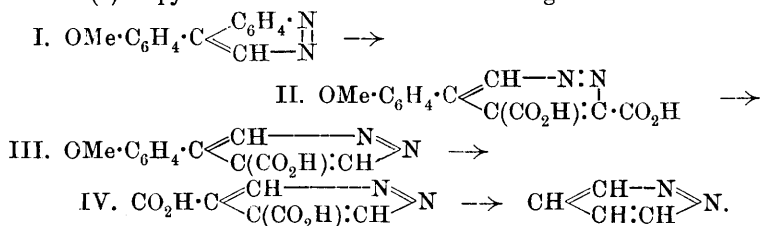
**Preparation of Mono- and Di-alkylbarbituric Acids.** FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 249907. Compare Abstr., 1900, i, 340, 431, and preceding abstract).—The action of mono- or di-alkylmalonyl haloids on isocarbamide ethers furnishes barbituric acids of general formula  $\text{OR} \cdot \text{C} \begin{smallmatrix} \text{N} \text{---} \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{CR}^1\text{R}^2$  (where R is alkyl, R<sup>1</sup> hydrogen or alkyl, and R<sup>2</sup> alkyl), which when treated with mineral acids yield alkylbarbituric acids.

2-Methoxy-5:5-diethylbarbituric acid,  $\text{OMe} \cdot \text{C} \begin{smallmatrix} \text{N} \text{---} \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{C} \text{Et}_2$ , m. p. 131°, is prepared from diethylmalonyl chloride and methylisocarbamide hydrochloride,  $\text{OMe} \cdot \text{C} \cdot \text{NH}(\text{NH}_2)$ , in aqueous-benzene solution in the presence of sodium hydroxide; when warmed with 30% hydrochloric acid it furnishes 5:5-diethylbarbituric acid and methyl chloride.

2-Ethoxy-5-ethylbarbituric acid,  $\text{OEt} \cdot \text{C} \begin{smallmatrix} \text{N} \text{---} \text{CO} \\ \text{NH} \cdot \text{CO} \end{smallmatrix} \text{CH} \text{Et}$ , m. p. 211°, is obtained from ethylisocarbamide hydrochloride and ethylmalonyl chloride; it is decomposed by boiling hydrobromic acid into 5:5-ethylbarbituric acid. F. M. G. M.

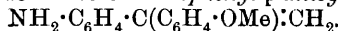
**Cinnoline Syntheses.** 4-Anisylcinnoline. RICHARD STOERMER and O. GAUS (Ber., 1912, 45, 3104—3113).—That the synthesis of

cinnoline derivatives from *o*-amino-*as*-diarylethylenes takes place according to the scheme given previously (Abstr., 1909, i, 841) has already been rendered probable by the transformation of 4-phenylcinnoline into 4-phenylpyridazine. All doubt as to the constitution of the cinnolines has now been removed by the degradation of 4-*p*-anisylcinnoline (I) to pyridazine as shown in the following scheme :



Further, the results obtained with 4-anisylcinnoline confirm the assumption made by Stoermer and Fincke (*loc. cit.*), that the removal of carbon dioxide from the cinnolinic acids takes place in the same manner as in the case of the dibasic acids of the pyridine series, namely, from the carboxyl adjacent to the nitrogen atom.

2-Amino-4'-hydroxybenzophenone, prepared by heating 2-amino-4'-methoxybenzophenone (Ullmann and Bleier, Abstr., 1903, i, 176) with hydrobromic acid, crystallises in colourless needles, m. p. 165°, dissolves in both acids and bases with a yellow colour, and reacts with magnesium methyl bromide, yielding *o*-aminophenyl-*p*-anisylethyl alcohol,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CMe}(\text{OH}) \cdot \text{C}_6\text{H}_4 \cdot \text{OMe}$ , which forms large, light yellow crystals, m. p. 99°, and is converted by boiling for one hour with 10% sulphuric acid into *o*-aminophenyl-*p*-anisylethylene,



This crystallises in colourless needles, m. p. 49°, and forms a light yellow *platinichloride*, m. p. 190°. Its solution in hydrochloric acid on treatment with sodium nitrite yields 4-*p*-anisylcinnoline (I), long, pale yellow needles, m. p. 85°, from which the following derivatives were prepared: *hydrochloride*,  $\text{B} \cdot \text{HCl} \cdot \text{H}_2\text{O}$ , yellow crystals, m. p. 215°; *picrate*, m. p. 150°; *nitrate*, which crystallises in slender, dark yellow needles, m. p. 151—152°, and reacts with silver nitrate in nitric acid or alcoholic solution to form the compound,  $\text{C}_{15}\text{H}_{12}\text{O}_2\text{N}_2 \cdot \text{AgNO}_3$ , golden-yellow needles, m. p. 250° (decomp.); *sulphate*,  $\text{B} \cdot \text{H}_2\text{SO}_4$ , m. p. 211° (decomp.); *methiodide*, long, dark reddish-brown needles (decomp. 220°); *methochloride*, which is light yellow, m. p. 190° (decomp.); *platinichloride*, brownish-yellow crystals (decomp. 200°). It forms with auric chloride in alcoholic solution the *aurichloride*,  $2\text{B} \cdot 2\text{HCl} \cdot \text{AuCl}_3$ , slender, golden-yellow needles (decomp. about 100°); in aqueous hydrochloric acid solution the *normal aurichloride*,  $\text{B} \cdot \text{HCl} \cdot \text{AuCl}_3$ , m. p. 120° (decomp.), is produced.

4-*p*-Hydroxyphenylcinnoline,  $\text{C}_{14}\text{H}_{10}\text{ON}_2$ , prepared by heating the anisyl compound with hydrobromic acid, crystallises in pale yellow leaflets, m. p. 230°, and forms a *sulphate*,  $\text{B} \cdot \text{H}_2\text{SO}_4$ , light red leaflets, m. p. 210°, and a reddish-yellow *platinichloride* (decomp. 252°); its solutions in aqueous sodium hydroxide have an intensely dark yellow colour, and deposit a canary-yellow, crystalline *sodium salt*, m. p. 85°.

4-Anisylcinnoline is oxidised by potassium permanganate in aqueous solution to 4-*p*-anisylcinnolinic (4-anisylpyridazine-5:6-dicarboxylic acid (II)). This crystallises in slender, white needles, m. p. 205°, containing 1H<sub>2</sub>O, which cannot be removed without simultaneous loss of carbon dioxide and transformation into 4-*p*-anisylpyridazine-5-carboxylic acid; it forms an *acid silver* salt,

$$\text{C}_{13}\text{H}_8\text{O}_5\text{N}_2\text{Ag}_2, \text{C}_{13}\text{H}_9\text{O}_5\text{N}_2\text{Ag},$$
a *normal silver* salt,  $\text{C}_{13}\text{H}_8\text{O}_5\text{N}_2\text{Ag}_2, \text{H}_2\text{O}$ , and a *barium* salt crystallising in lustrous, white leaflets.

4-*p*-Anisylpyridazine-5-carboxylic acid (III), prepared by heating the preceding compound, forms long, pale yellow needles, m. p. 205°, and yields a *platinichloride*.

When warmed with dilute nitric acid, 4-anisylcinnolinic acid is converted into a *nitro*-derivative of 4-*p*-anisylpyridazine-5-carboxylic acid,  $\text{C}_{12}\text{H}_9\text{O}_5\text{N}_2$ , which crystallises in slender, felted, light yellow needles, m. p. 230° (decomp.), and probably contains the nitro-group in the anisyl residue. On reduction with ferrous sulphate and ammonia, the nitro-compound yields *amino-p*-anisylpyridazine-5-carboxylic acid, slender, pale brown needles, m. p. 225° (decomp.).

4-*p*-Anisylpyridazine,  $\text{N} \begin{smallmatrix} \text{CH}:\text{CH} \\ \text{N}-\text{CH} \end{smallmatrix} \text{C}_6\text{H}_4\cdot\text{OMe}$ , obtained by the distillation of 4-*p*-anisylpyridazine-5-carboxylic acid with soda-lime under diminished pressure, forms almost colourless, long needles, m. p. 85°, and when heated with hydrobromic acid is transformed into 4-*p*-hydroxyphenylpyridazine, long, colourless needles, m. p. 242°.

4-*p*-Hydroxyphenylpyridazine-5-carboxylic acid,  $\text{N} \begin{smallmatrix} \text{CH}:\text{C}\cdot\text{CO}_2\text{H} \\ \text{N}\cdot\text{CH}:\text{C}\cdot\text{C}_6\text{H}_4\cdot\text{OH}' \end{smallmatrix}$ , prepared by heating 4-*p*-anisylcinnolinic acid with hydrobromic acid, crystallises in dark yellow needles, m. p. 225° (decomp.), containing 1H<sub>2</sub>O, which is lost at 120°; the anhydrous acid forms long, citron-yellow needles, m. p. 240°, and is best obtained by heating 4-*p*-anisylpyridazine-5-carboxylic acid with hydrobromic acid; the *silver* salt is a yellow powder.

When oxidised with potassium permanganate in alkaline solution, the preceding compound yields pyridazine-4:5-dicarboxylic acid (IV), which becomes brown at 208° (decomp. 209—210°) (compare Täuber, Abstr., 1895, i, 301; Gabriel, Abstr., 1904, i, 103), and is converted by loss of carbon dioxide into pyridazine; the *platinichloride* of the latter base forms slender, yellow needles (decomp. 180°). F. B.

**A Red Indigotin, 5:5'-Dichloro-4:4'-dimethylindigotin.** FRANZ KUNCKELL and RICHARD LILLIG (*J. pr. Chem.*, 1912, [ii], 86, 517—518).—2-*Chloroaceto-p*-toluidide forms snow-white needles, m. p. 104°, and reacts with chloroacetyl chloride and aluminium chloride in carbon disulphide solution, yielding  $\omega$ :4-dichloro-6-acetylamino-3-methylacetophenone,  $\text{NHAc}\cdot\text{C}_6\text{H}_2\text{MeCl}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ , which forms yellow crystals, m. p. 163°, and is converted by boiling with 5% aqueous sodium hydroxide and simultaneous atmospheric oxidation into a red or reddish-violet 5:5-dichloro-4:4'-dimethylindigotin.  $\omega$ :4-Dichloro-6-amino-3-methylacetophenone crystallises in yellow needles, m. p. 118°.

F. B.

**Behaviour of Phenylazoimide with Aniline and with *p*-Toluidine.** LUDWIG WOLFF (*Annalen*, 1912, 394, 59—68).—Although a diazoketone and phenylazoimide react in an analogous manner with potassium cyanide, their behaviour with aniline is quite dissimilar. Whilst the diazoketone yields an anilide (next page), phenylazoimide and aniline at about 150° yield a substance,  $C_{12}H_{12}N_2$ , m. p. 151°, colourless needles, which is called *dibenzamil*,

and to which the constitution  $\begin{array}{c} CH:CH \cdot CH \cdot NH \\ | \\ CH:CH \cdot CH \cdot NPh \end{array}$  is provisionally

ascribed. It forms an *aurichloride*, m. p. 148° (decomp.), yellow prisms, reacts with phenylcarbimide at the ordinary temperature to form a *phenylcarbamide*,  $C_{19}H_{17}ON_3$ , m. p. 127—128°, glistening prisms, and yields with acetic anhydride at the ordinary temperature an oily *acetyl* derivative, which is converted by heating into *acetyl-o-aminodiphenylamine*,  $C_{14}H_{14}ON_2$ , m. p. 121°, colourless needles. The latter, which is also obtained by acetylating *o*-aminodiphenylamine, is converted by boiling alcoholic sodium hydroxide or by cold hydrochloric acid into 1-phenyl-2-methylbenziminazole,  $C_6H_4 \begin{array}{c} \nwarrow NPh \\ \nearrow N \end{array} CMe$ , m. p. 72—73°, colourless prisms. By benzylation with benzoyl chloride and cold 10% sodium hydroxide, dibenzamil yields a brown, viscous substance and *benzoyl-o-aminodiphenylamine*,  $NHBz \cdot C_6H_4 \cdot NHPh$ , m. p. 136°; from the latter, 1:2-diphenylbenziminazole, m. p. 111° (*hydrochloride*, m. p. 260° [decomp.]), can be obtained.

[With F. KOLASIUS.]—Phenylazoimide and *p*-toluidine at 140° yield a substance,  $C_{13}H_{14}N_2$ , m. p. 116°, colourless needles, by the benzylation of which a brown viscous mass is produced, from which benzo-*p*-toluidide is obtained by treatment with alcohol and hydrochloric acid.

C. S.

**Preparation of Anthraquinone Derivatives.** FRANZ ULLMANN (D.R.-P. 248998. Compare Abstr., 1911, i, 165504).—It is found that the halogenated pyridazoneanthrones condense readily with aromatic amines to form arylaminopyridazoneanthrones.

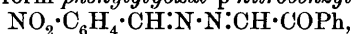
4-Anilinopyridazoneanthrone, orange-red needles, is prepared by boiling pyridazone-4-chloroanthrone (obtained from hydrazine and 1:4-chloroanthraquinonecarbonyl chloride), with aniline (6 parts), potassium acetate (0.4 part), and copper acetate (0.1 part).

4-*p*-Toluidinophenylpyridazoneanthrone, orange needles, m. p. 290°, is obtained in a similar manner from *p*-toluidine and phenylpyridazone-4-chloroanthrone. These compounds can be readily sulphonated, yielding soluble compounds, which dye wool yellow shades.

F. M. G. M.

**Diazoanhydrides (1:2:3-Oxadiazoles or Diazo-oxides) and Diazoketones.** LUDWIG WOLFF (*Annalen*, 1912, 394, 23—59).—Phenylglyoxalhydrazone,  $NH_2 \cdot N:CH \cdot COPh$ , m. p. 120—121°, colourless needles, obtained by passing hydrogen sulphide into a concentrated alcoholic solution of diazoacetophenone containing a few drops of ammonium sulphide, is easily decomposed into acetophenone and nitrogen by heating above its m. p., or by warming with aqueous

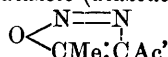
sodium hydroxide, reduces Fehling's solution, ferric chloride, and mercuric chloride, and is oxidised quantitatively to diazoacetophenone by potassium permanganate. It condenses with *p*-nitrobenzaldehyde in warm alcohol to form *phenylglyoxal-p-nitrobenzylideneazine*,



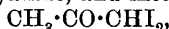
m. p. 138°, yellow prisms, and reacts with hot acetic anhydride to form the *acetyl* derivative,  $\text{NHAc}\cdot\text{N:CH}\cdot\text{COPh}$ , m. p. 145—146°, which, unlike the parent substance, has feeble acid properties.

Phenylglyoxalhydrazone instantly reduces an ammoniacal solution of silver oxide, and is itself thereby converted into phenylacetamide. This transformation is due to the conversion of the initially formed diazoacetophenone into the amide by the ammonia, the transformation being catalytically accelerated by the silver oxide. Diazoacetophenone is converted into nitrogen and benzoylcarbinol by boiling water, into phenylacetic acid by a solution of silver oxide in aqueous sodium thiosulphate at 50—60°, into phenylacetamide by a little silver oxide in aqueous ammonia, and into phenylacetanilide by boiling aniline. Similarly, diazoacetone is converted into propionamide by aqueous ammonia containing silver oxide, and into propionanilide by hot aniline.

[With R. GREULICH.]—By reduction to aminoacetylacetone and subsequent diazotisation, oximinoacetylacetone is converted into 4-acetyl-5-methyl-1:2:3-oxadiazole (*diazoacetylacetone anhydride*),

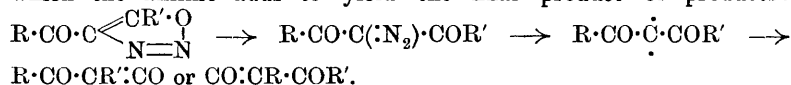


a yellow oil, which yields *diazoacetone*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH:N}_2$ , b. p. 4—47°/15 mm., by treatment with dilute sodium hydroxide at 0°. Diazoacetone is a pale yellow, not unpleasantly odorous liquid, D<sup>20</sup> 1·0864, which is converted into acetylcarbinol and nitrogen by water at 70—80°, into *diazoacetone cyanide*,  $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{N:N}\cdot\text{CN}$  (*semicarbazone*, m. p. about 210° [decomp.], yellow, crystalline powder), by concentrated aqueous potassium cyanide, and into *di-iodoacetone*,



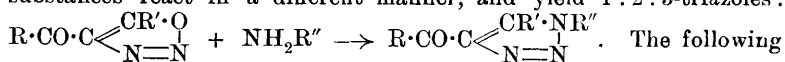
by iodine in chloroform at 30°. A concentrated solution of di-iodoacetone in chloroform yields iodine and methylglyoxal by prolonged exposure to air in diffused daylight.

The diazoanhydride of ethyl acetoacetate and boiling aniline yield ethyl *isosuccinanilate*; the diazo-anhydride of acetylacetone and aniline at 100° yield methylacetoacetanilide; the 4-benzoyl-5-methyl-1:2:3-oxadiazole and aniline at 85—100° yield *α-benzoylpropionanilide*,  $\text{CHMeBz}\cdot\text{CO}\cdot\text{NHPh}$ , m. p. 137—138°, colourless prisms, and *α-acetylphenylacetanilide*,  $\text{CHPhAc}\cdot\text{CO}\cdot\text{NHPh}$ , m. p. 97°, colourless needles. The preceding reactions can be explained by assuming that the diazo-anhydride changes to the diazo-ketone; this loses nitrogen and leaves a complex which yields by migration of a radicle a keten to which the aniline adds to yield the final product or products:



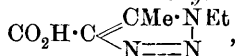
[With R. KRÜCHE.]—In the presence of acetic acid, the preceding

substances react in a different manner, and yield 1:2:3-triazoles:



The following substances have been obtained by the interaction of a primary base and the diazo-anhydride of ethylacetoacetate in acetic acid at 80—100°, and hydrolysis and decomposition of the product.

*5-Methyl-1-ethyl-1:2:3-triazole-4-carboxylic acid*,

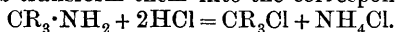


m. p. 184°, colourless prisms, yields by heating *5-methyl-1-ethyltriazole*, b. p. 251°/741 mm.; by oxidation by potassium permanganate, the latter is converted into *1-ethyltriazole-5-carboxylic acid*, m. p. 178—182° (decomp.), from which *1-ethyltriazole*, b. p. 238—239°, is obtained at its m. p. *1-Ethyltriazole-4:5-dicarboxylic acid*, m. p. about 108—110° (decomp.), obtained by oxidising *5-methyl-1-ethyltriazole-4-carboxylic acid*, forms crystals containing H<sub>2</sub>O. *1:5-Dimethyl-1:2:3-triazole-4-carboxylic acid*, C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>N<sub>3</sub>·H<sub>2</sub>O, m. p. about 203° (decomp.), colourless leaflets, yields *1:5-dimethyltriazole*, b. p. 255°, by heating; the base forms a deliquescent *methiodide* and an *aurichloride*, m. p. 149—150°, yellow needles, and yields *1-methyltriazole-5-carboxylic acid*, decomp. 188°, colourless plates, by oxidation with alkaline potassium permanganate at 90°. *1-Methyltriazole* has m. p. 15—16°, and b. p. 228°.

*1-Benzyl-5-methyl-1:2:3-triazole-4-carboxylic acid*, C<sub>11</sub>H<sub>11</sub>O<sub>2</sub>N<sub>3</sub>·H<sub>2</sub>O, colourless leaflets, forms an *ethyl ester*, m. p. 79—80°. At its m. p., 168—169°, the anhydrous acid is converted into *1-benzyl-5-methyltriazole*, m. p. 84°, b. p. 325—330°/750 mm.. *1-Benzyltriazole-5-carboxylic acid* has m. p. 196—197° (decomp.).

The decomposition of the acetylmethyloxadiazole by ammonia yields, in addition to diazoacetone, *4-acetyl-5-methyl-1:2:3-triazole*, m. p. 172°, which is readily soluble in aqueous sodium carbonate. C. S.

**Colour Bases of the Triphenylmethane Group.** VICTOR VILLIGER and EDUARD KOPETSCHNI (*Ber.*, 1912, 45, 2910—2922).—The employment of ammonia for the purpose of liberating the colour bases from salts of the triphenylmethane series leads to the production of amines instead of carbinols. These amine bases are colourless, generally well-crystallised compounds which in solubility and m. p. closely resemble the corresponding carbinols. They can be boiled for a short time with alcoholic sodium hydroxide without losing ammonia. Acids transform them into the corresponding dyes:



The readiest method of estimating the ammonia removable by acids consists in treating the amine with boiling methyl or ethyl alcohol, whereby the ammonia is quantitatively removed, alkyl ethers of the corresponding carbinols being formed. Perfectly neutral alcohol is, however, incapable of bringing about the change, the presence of a trace of acid being essential.

*Tetramethyldi-p-aminotriphenylmethylamine* is best obtained by extracting a solution of Victoria-green in aqueous hydrochloric acid

with chloroform and subsequent treatment of the dry chloroform extract with gaseous ammonia. The use of aqueous ammonia results in admixture of the amine with more or less carbinol. It has m. p. 138°. When heated for some time at about 110°, it decomposes with evolution of ammonia and methylamine. Boiling, faintly acid ethyl alcohol transforms it quantitatively into the corresponding ethyl ether, m. p. 162—163°.

*Phenyltetramethyl-di-p-aminotriphenylmethylamine*, prisms, m. p. 187—195° (decomp.) according to the rate of heating, may be prepared by treating a solution of Victoria-green in pyridine with excess of aniline, or, better, by heating the methyl ether of tetramethyl-*p*-diaminotriphenylcarbinol with aniline during two to three hours at 135—145°. The aniline removable by acid may be estimated by boiling the substance in feebly acid alcoholic solution, and subsequent distillation of the aniline in steam and titration of it by means of *N*/10-sodium nitrite.

Tetramethyl-di-*p*-aminotriphenylcarbinol is obtained by the gradual addition of sodium hydroxide to an aqueous solution of Victoria-green. It separates from light petroleum in indistinct crystals, m. p. 120—122°, and from ether in microscopic cubes, m. p. 109—110°. Solutions of it in toluene or xylene deposit large quadratic plates or cubes, m. p. about 109°, which, however, obstinately retain traces of the solvent. Apparently, this is a case of dimorphism, since the crystals of m. p. 120—122° can be transformed into those of m. p. 109—110° by crystallisation from ether, whilst the m. p. of the latter can be raised to 120—122° by crystallisation from light petroleum. The compounds described by O. Fischer (Abstr., 1881, 587) and by Doebner (Abstr., 1883, 861) appear to have been impure.

*Hexamethyltri-p-aminotriphenylmethylamine*, leaflets, m. p. 190—195° (decomp.), is obtained by treating a solution of crystal-violet in chloroform with gaseous ammonia. Feebly acid ethyl alcohol transforms it into the corresponding ethyl ether, m. p. 143° (compare Rosenstiehl, Abstr., 1895, i, 377). The carbinol decomposes at 205—210° (compare Wichelhaus, Abstr., 1886, 362).

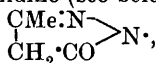
*Tri-p-aminotriphenylmethylamine*, which does not melt, is prepared by grinding para-magenta with aqueous ammonia (20%), or, better, by pouring a concentrated solution of the same substance in methyl alcohol into saturated methyl-alcoholic ammonia. Weakly acid methyl alcohol converts it into the corresponding methyl ether (compare Baeyer and Villiger, Abstr., 1904, i, 786).

The amine bases of the triphenylmethane dyes show a close analogy to leucoauramine; thus, the latter when heated with weakly acid ethyl alcohol evolves ammonia, and leaves an oil which is transformed by dilute hydrochloric acid into tetramethyldiaminobenzhydrol, m. p. 102°. When ethyl alcohol is replaced by methyl alcohol, methoxytetramethyldiaminodiphenylmethane, m. p. 71—72°, is produced. The reverse transformation of the hydrol into the amine was also attempted. Tetramethyldiaminobenzhydrol picrate when treated with ammonia in aqueous or methyl-alcoholic solution

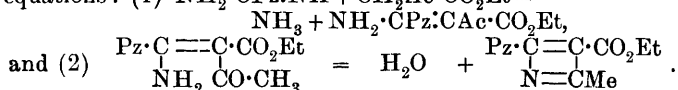
yielded, however, the imine,  $\text{NH}[\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2]_2$ , m. p.  $188^\circ$  (Weil, Abstr., 1894, i, 419 gives  $185^\circ$ ). H. W.

**Pyrimidines and the Reactions of Amidines with Ethyl Acetoacetate.** PETER J. SCHESTAKOFF and N. KAZAKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1312—1320).—According to Pinner (Abstr., 1893, i, 735), the synthesis of pyrimidines by the interaction of amidines and ethers of  $\beta$ -ketonic acids (or, in general,  $\beta$ -diketones) fails in the case of formamidine, in which the amidine group is united, not with carbon, but with hydrogen; the compound formed in the latter instance was regarded by Pinner as ethyl  $\beta$ -cyanocrotonate.

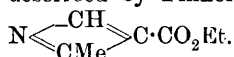
Guanidine also reacts with  $\beta$ -diketones, yielding pyrimidine derivatives, but it has not been established whether the two amino-groups or one amino- and one imino-group of the guanidine molecule take part in the ring-formation. In order to settle this point, the authors have investigated the interaction of ethyl acetoacetate and 3-methylpyrazolone-1-carbamidine (see below). If the residue,



is indicated by Pz, the course of this reaction is expressed by the equations: (1)  $\text{NH}_2\cdot\text{CPz:NH} + \text{CH}_2\text{Ac}\cdot\text{CO}_2\text{Et} =$



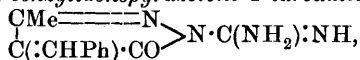
(compare Dains, Abstr., 1902, i, 602). The interaction of formamidine and ethyl acetoacetate probably proceeds similarly, the compound described by Pinner as ethyl  $\beta$ -cyanocrotonate having the structure



Hence,  $\beta$ -keto-acids react to form pyrimidines only with amidines containing in the molecule the complex  $\text{C}-\text{C}(\text{NH}_2):\text{NH}$ , amidines in which the carbon atom of the amidine group is united, not with carbon, but with hydrogen or nitrogen, giving derivatives containing the ring  $-\text{C} \begin{array}{c} \diagup \quad \diagdown \\ \text{C} \\ \text{N} \end{array} \text{C}-$ .

Further, the above results indicate that the  $\alpha$ -modification of 2-amino-6-hydroxy-4-phenylpyrimidine obtained by Warmington (Abstr., 1893, i, 369) from ethyl benzoylacetate and guanidine has the structure:  $\text{NH}\cdot\text{C} \begin{array}{c} \diagup \quad \diagdown \\ \text{NH}\cdot\text{C}(\text{OH}) \\ \text{N}=\text{CPh} \end{array} \text{CH}$ , the  $\beta$ -modification being the tautomeric form  $\text{NH}_2\cdot\text{C} \begin{array}{c} \diagup \quad \diagdown \\ \text{N}\cdot\text{C}(\text{OH}) \\ \text{N}=\text{CPh} \end{array} \text{CH}$ .

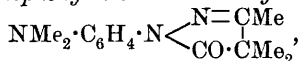
3-Methylpyrazolone-1-carbamidine,  $\begin{array}{c} \text{CMe=N} \\ \diagup \quad \diagdown \\ \text{CH}_2\cdot\text{CO} \end{array} \text{N}\cdot\text{C}(\text{NH}_2):\text{NH}$ , prepared by the action of aminoguanidine on ethyl acetoacetate, forms long, colourless needles, m. p.  $235^\circ$  (decomp.), and reduces neither Fehling's solution nor ammoniacal silver solution. With benzaldehyde it yields 3-methyl-4-benzylidenepyrazolone-1-carbamidine,



which forms orange crystals, m. p.  $210^{\circ}$  (decomp.). The *oximino*-derivative,  $\begin{array}{c} \text{CMe}=\text{N} \\ | \\ \text{C}(\text{NOH})\cdot\text{CO} \end{array} \text{N}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}$ , forms pale green crystals, m. p.  $222^{\circ}$ .

With ethyl acetate, 3-methylpyrazolone-1-carbamidine gives the compound,  $\begin{array}{c} \text{CMe}=\text{N} \\ | \\ \text{CH}_2\cdot\text{CO} \end{array} \text{N}\cdot\text{C} \begin{array}{c} \text{C}(\text{CO}_2\text{Et}) \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{N} \begin{array}{c} \text{CMe} \\ \diagdown \quad \diagup \\ \text{N} \end{array}$ , which forms colourless or faintly yellow crystals, m. p.  $180^{\circ}$ , has the normal molecular weight in freezing phenol, gives an intense green coloration, changing to brown on heating, with ferric chloride, and when heated with hydrochloric acid yields carbon dioxide and a colourless compound, m. p.  $155^{\circ}$ . T. H. P.

**Preparation of 1-p-Dimethylaminophenyl-3:4:4-trimethyl-5-pyrazolone.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 248887).—When 1-phenyl-3:4:4-trimethyl-5-pyrazolone is nitrated at  $0-5^{\circ}$  in concentrated sulphuric acid solution, it yields 1-p-nitrophenyl-3:4:4-trimethyl-5-pyrazolone, spear-shaped crystals, m. p.  $126^{\circ}$ ; this on reduction with tin and hydrochloric acid furnishes 1-p-amino-phenyl-3:4:4-trimethyl-5-pyrazolone, colourless needles, m. p.  $116^{\circ}$ , which forms a crystalline *hydrochloride*, and on alkylation is converted into 1-p-dimethylaminophenyl-3:4:4-trimethyl-5-pyrazolone,



m. p.  $58-59^{\circ}$ .

F. M. G. M.

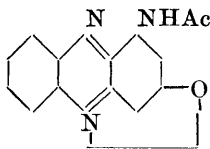
**Preparation of Indophenols of the Benziminazole Group and their Leuco-derivatives.** ACTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 248091. Compare Abstr., 1893, i, 433).—When benziminazoles containing an amino-group in the para-position to the imino-group are oxidised together with phenols containing a free para-position they furnish a new series of indophenols.

5-Amino-2-methylbenziminazole (Abstr., 1898, i, 44) when oxidised in the presence of phenol by means of sodium hypochlorite yields an *indophenol* which separates in brownish-red flakes; the leuco-compound obtained by its reduction with sodium sulphide is isolated as a yellow powder.

The analogous compound from *o*-cresol is described, and those from other iminazoles and phenolic compounds discussed in the original.

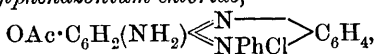
F. M. G. M.

**Action of Acetic Anhydride on 1-Aminoaposafranone.** FRIEDRICH KEHRMANN and A. MASSLENIKOFF (*Ber.*, 1912, 45, 2891—2895).—The following behaviour of 1-aminoaposafranone is in complete harmony with the conception of *aposafranone* as a phenol-betaine. When 1-aminoaposafranone sulphate is heated with 10 parts of acetic anhydride on the water-bath until the colour has changed to ponceau-red, and the solution is diluted with water and basified with



aqueous ammonia, 1-acetyl*aposafranone* (annexed formula), greenish-black crystals with blue reflex, is obtained.

When the preceding sulphate is shaken with acetic anhydride (10 parts) and anhydrous sodium acetate (1 part) at the ordinary temperature until the solution has a magenta colour, and the solution is treated with water and sodium chloride, 1-amino-3-acetoxy-10-phenylphenazonium chloride,

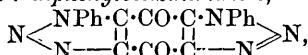


is obtained as a brownish-violet, crystalline powder, from which 1-aminoaposafranone is regenerated by aqueous ammonia at the ordinary temperature. By heating 1-acetylaminoposafranone with acetic anhydride and sodium acetate on the water-bath until an orange-red solution is obtained, and diluting with water and adding sodium chloride, 1-acetylamino-3-acetoxy-10-phenylphenazonium chloride is obtained as a brick-red, crystalline powder; its platinichloride is also a brick-red, crystalline powder.

C. S.

**Addition of Phenylazoimide to Quinones.** LUDWIG WOLFF (*Annalen*, 1912, 394, 68—85) [with G. K. GRAU].—Approximately equal quantities of *p*-benzoquinone and phenylazoimide react in benzene at 60—65° to yield after twenty-four hours quinhydrone, 4 : 7-diketo-

1-phenyl-1 : 2 : 3-benztriazole,  $\begin{array}{c} \text{CH} \cdot \text{CO} \cdot \text{C} \cdot \text{NPh} \\ \text{CH} \cdot \text{CO} \cdot \text{C} \cdot \text{N} \end{array} \gg \text{N}$ , m. p. 180—184° (decomp.), golden-yellow leaflets; 4 : 8-diketo-1 : 5-diphenylbenzditriazole,  $\text{N} \llcorner \text{NPh} \cdot \text{C} \cdot \text{CO} \cdot \text{C} \cdot \text{N} \begin{array}{c} \text{---} \\ \text{N} \end{array} \text{---} \text{C} \cdot \text{CO} \cdot \text{C} \cdot \text{NPh} \gg \text{N}$ , decomp. about 340°, colourless plates; 4 : 8-diketo-1 : 7-diphenylbenzditriazole,



m. p. 280—285° (decomp.), yellow needles, and a yellow substance,  $\text{C}_{18}\text{H}_{14}\text{O}_2\text{N}_4$ , m. p. 157°; the last has not been examined further.

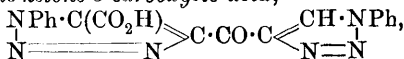
4 : 7-Diketo-1-phenyl-1 : 2 : 3-benztriazole is reduced to the corresponding quinol,  $\text{C}_{12}\text{H}_9\text{O}_2\text{N}_3 \cdot \text{H}_2\text{O}$ , m. p. 203° (decomp.), colourless needles, by zinc dust and acetic acid, yields 1-phenyl-1 : 2 : 3-triazole-4 : 5-dicarboxylic acid by oxidation with sodium hypobromite, forms a semicarbazone,  $\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_6$ , m. p. 247—248° (decomp.), brown needles, and reacts with aniline in warm alcohol to form the anilino-derivative,  $\text{NHPh} \cdot \text{C}_6\text{H}_4\text{O}_2 \llcorner \text{NPh} \begin{array}{c} \text{---} \\ \text{N} \end{array} \text{---} \text{N}$ , m. p. 235° decomp.), reddish-brown needles.

The anilino-derivative is converted into 6-hydroxy-4 : 7-diketo-1-phenyl-1 : 2 : 3-benztriazole,  $\text{OH} \cdot \text{C}_6\text{H}_3\text{O}_2 \llcorner \text{NPh} \begin{array}{c} \text{---} \\ \text{N} \end{array} \text{---} \text{N}$ ,  $\text{H}_2\text{O}$ , yellow needles, m. p. about 165—168° (decomp.) when anhydrous, by warm 2% sodium hydroxide, whilst the semicarbazone is converted by boiling 3% sodium hydroxide into ammonia, carbon dioxide, nitrogen, and 7-hydroxy-1-phenyl-1 : 2 : 3-benztriazole,  $\text{OH} \cdot \text{C}_6\text{H}_3 \llcorner \text{NPh} \begin{array}{c} \text{---} \\ \text{N} \end{array} \text{---} \text{N}$ , m. p. 234°, almost colourless needles.

4:8-Diketo-1:5-diphenylbenzditriazole is converted into 1-phenyl-1:2:3-triazole-4-carboxylic acid by hot 5% sodium hydroxide. 4:8-Diketo-1:7-diphenylbenzditriazole forms a *semicarbazone*,

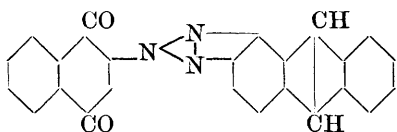


m. p. about 265° (decomp.), yellow needles, and is converted by hot aqueous sodium carbonate, ammonia, or sodium hydroxide into *diphenylditriazole-ketone-5-carboxylic acid*,



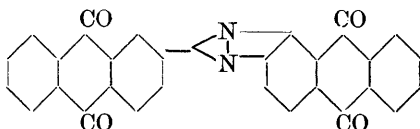
m. p. 230°, colourless needles (*semicarbazone*,  $\text{C}_{19}\text{H}_{15}\text{O}_3\text{N}_9$ , m. p. 234°, colourless needles; *oxime*,  $\text{C}_{18}\text{H}_{13}\text{O}_3\text{N}_7$ , m. p. about 175° [decomp.]), which yields 1-phenyl-1:2:3-triazole-4:5-dicarboxylic acid by oxidation with warm alkaline potassium permanganate, and is converted at 200–230° into *diphenylditriazole ketone*,  $\text{C}_{17}\text{H}_{12}\text{ON}_6$ , m. p. 231°, colourless needles (*oxime*, m. p. 247° [decomp.]). C. S.

[Preparation of Anthraquinone Derivatives.] CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 250274).—When the *azo*-



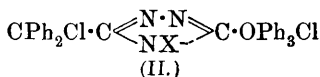
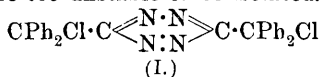
compound (a dark blue powder) obtained by coupling diazotised 2-aminoanthraquinone with 2-aminoanthracene is oxidised with sodium dichromate in acetic acid solution it furnishes the *compound* (annexed formula), orange-yellow

crystals, and on further oxidation in sulphuric acid solution the *compound*:



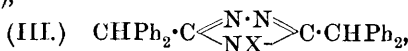
F. M. G. M.

Preparation of Azo-compounds by Removal of Halogen in the 1:6- and 1:10-Positions. ROBERT STOLLÉ and FR. SCHMIDT (*Ber.*, 1912, 45, 3116–3123).—The previous work (*Abstr.*, 1911, i, 508) on the formation of azo-compounds by the removal of halogen from the  $\alpha$ : $\zeta$ -positions has been extended to di- $\omega$ -chloro-3:6-dibenzhydryl-1:2:4:5-tetrazine (I) and di- $\omega$ -chloro-2:5-dibenzhydryl-1:3:4-triazoles of the constitution II (where X = H,  $p\text{-C}_6\text{H}_4\cdot\text{OH}$ , and  $p\text{-C}_6\text{H}_4\cdot\text{NMe}_2$ ), but in the latter case the azo-compounds thus produced were too unstable to be isolated.



An example of the formation of an azo-compound by the removal of halogen in the  $\alpha$ : $\kappa$ -positions is also recorded.

1-*p*-Hydroxyphenyl-2:5-dibenzhydryl-1:3:4-triazole (formula III, X =  $p\text{-C}_6\text{H}_4\cdot\text{OH}$ ),



prepared by heating bis-diphenylacetylhydrazide chloride with *p*-aminophenol, forms stout crystals, m. p. 283°, and on chlorination yields a *chloro*-derivative, which gives an intense violet coloration when shaken with mercury in benzene solution.

1-*p*-Dimethylamino-2:5-dibenzhydryl-1:3:4-triazole (III, X =  $p\text{-C}_6\text{H}_4\cdot\text{NMe}_2$ ), obtained in a similar manner from *p*-aminodimethylaniline, forms colourless crystals, m. p. 249°, and yields a *chloro*-derivative, m. p. 204° (not sharp) which also gives a violet coloration when its benzene solution is shaken with mercury.

1-Amino-2:5-dibenzhydryl-1:3:4-triazole (III, X =  $\text{NH}_2$ ) is obtained by heating 3:6-dibenzhydryl-1:2-dihydro-1:2:4:5-tetrazine (*loc. cit.*) with alcoholic hydrogen chloride. It crystallises in colourless, felted needles, m. p. 239°, and is accompanied by *s*-bi-diphenylacetylhydrazide.

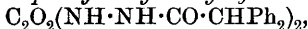
2:5-Dibenzhydryl-1:3:4-triazole (III, X = H), prepared by the addition of sodium nitrite to a solution of the preceding compound in alcoholic hydrogen chloride, forms colourless prisms, m. p. 197°, and is also produced, together with a substance, m. p. 212°, by heating bi-diphenylacetylhydrazide chloride with alcoholic ammonia at 80°.

The interaction of diphenylacetyl chloride and 1-amino-2:5-dibenzhydryl-1:3:5-triazole in benzene solution in the presence of pyridine yields 1-diphenylacetyl-amino-2:5-dibenzhydryl-1:3:5-triazole (III, X =  $\text{NH}\cdot\text{CO}\cdot\text{CHPh}_2$ ), prisms, m. p. 285°, and the corresponding 1-*bi*-diphenylacetyl-amino-derivative [III, X =  $\text{N}(\text{CO}\cdot\text{CHPh}_2)_2$ ], stout prisms, m. p. 186°.

1-Diphenylacetyl-amino-3:6-dibenzhydryl-1:2-dihydro-1:2:4:5-tetrazine,  $\begin{array}{c} \text{C}(\text{CHPh}_2)_2\cdot\text{N}=\text{N} \\ \text{NH}\cdot\text{N}(\text{CO}\cdot\text{CHPh}_2) \end{array} > \text{C}\cdot\text{CHPh}_2$ , obtained from diphenylacetyl chloride and 3:6-dibenzhydryl-1:2-dihydro-1:2:4:5-tetrazine in a similar manner, crystallises in leaflets, m. p. 185°.

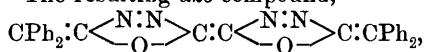
*Di- $\omega$ -chloro*-3:6-dibenzhydryl-1:2:4:5-tetrazine (formula I), prepared by chlorinating 3:6-dibenzhydryl-1:2:4:5-tetrazine in boiling carbon tetrachloride solution, forms stout, violet-red crystals, m. p. 162° (decomp.), and is slowly converted by boiling in ethyl acetate solution into tetraphenylsuccinonitrile. When shaken with mercury in benzene solution it forms 3:6-*bi*-diphenylmethylene-3:6-dihydro-1:2:4:5-tetrazine,  $\text{CPh}_2\cdot\text{C} \begin{array}{c} \text{N}\cdot\text{N} \\ \text{N}\cdot\text{N} \end{array} > \text{C}\cdot\text{CPh}_2$ . The latter compound crystallises in black prisms, having a metallic lustre, and explodes at about 170° when rapidly heated. On reduction with zinc and acetic acid it yields 3:6-dibenzhydryldihydro-1:2:4:5-tetrazine. It combines with chlorine to form the original dichlorotetrazine, and with bromine, yielding *di- $\omega$ -bromo*-3:6-dibenzhydryl-1:2:4:5-tetrazine, m. p. 162°. When heated either alone at 170° or in benzene solution, it loses nitrogen with the formation of tetraphenylsuccinonitrile.

Diphenylacetylhydrazide,  $\text{CHPh}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2$ , prepared by heating ethyl diphenylacetate with hydrazine hydrate, crystallises in prisms, m. p. 135°, and is converted by the action of ethyl oxalate at 140—170° into  $\beta\beta'$ -*bi*-diphenylacetyloxalylhydrazide,

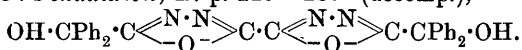


which crystallises in slender needles, m. p. 315°, and when heated with

phosphoryl chloride yields 5:5'-dibenzhydryl-2:2'-bis-1:3:4-oxadiazole,  $\text{CPh}_2 \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C} \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C} \cdot \text{CPh}_2$ , colourless needles, m. p. 235°. On chlorination in boiling carbon tetrachloride solution, this gives rise to *di- $\omega$ -chloro-5:5'-dibenzhydryl-2:2'-bis-1:3:4-oxadiazole*,  $\text{CPh}_2\text{Cl} \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C} \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{O} \end{smallmatrix} \text{C} \cdot \text{CPh}_2\text{Cl}$ , m. p. 249°, from which the halogen in the  $\alpha$ k-positions is removed by shaking with mercury in hot xylene solution. The resulting *azo*-compound,



could not be isolated in a state of purity. Its solutions in xylene have an intense emerald-green colour, which disappears when the solutions are exposed to the simultaneous action of air and moisture. Addition of alcohol to the decolorised solutions yields *di- $\omega$ -hydroxy-5:5'-dibenzhydryl-2:2'-bis-1:3:4-oxadiazole*, m. p. 225–235° (decomp.),



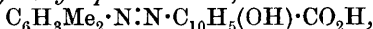
F. B.

### Azo-salicylic Acid and Azo-hydroxynaphthoic Acid Dyes.

ANUKUL C. SIRCAR and EDWIN R. WATSON (*J. Soc. Chem. Ind.*, 1912, 31, 968–971).—In a previous paper (*ibid.*, 1911, 30, 6) it has been shown that benzeneazosalicylic acid when dyed with a chrome mordant is characterised by a fastness towards light, alkali, and acid, superior to that of any other simple monoazo-dye. Attempts to prepare similar dyes having the same all-round fastness, but of a deeper colour, by replacing the phenyl group with heavier hydrocarbon residues or with other groups containing chromophores, and also by substituting the *o*-hydroxynaphthoic acid residue for that of salicylic acid, met with only partial success. Brown and claret-brown shades on chrome-mordanted wool were obtained, but only by the introduction of such groups as are prejudicial to fastness towards milling and light.

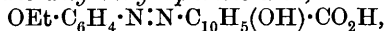
*m*-Xyleneazosalicylic acid,  $\text{C}_6\text{H}_3\text{Me}_2 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CO}_2\text{H}$ , prepared from diazotised *m*-xylidine and salicylic acid, crystallises in orange-yellow needles, m. p. 201°, and forms a sodium salt, crystallising in slender, yellow needles.

*m*-Xyleneazo- $\alpha$ -hydroxynaphthoic acid,



forms yellowish-brown needles, m. p. 180°; its sodium salt crystallises in brownish-yellow needles.

*p*-Ethoxybenzeneazo- $\alpha$ -hydroxynaphthoic acid,



prepared by coupling *p*-phenetidine with  $\alpha$ -hydroxynaphthoic acid, forms yellowish-brown needles, m. p. 198.5°. Diazotised *p*-aminoazobenzene combines with salicylic acid, yielding benzeneazobenzene-*p*-azosalicylic acid,  $\text{NPh} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CO}_2\text{H}$ , a yellowish-brown powder, m. p. 248–250°, and with  $\alpha$ -hydroxynaphthoic acid to form benzeneazobenzene-*p*-azo- $\alpha$ -hydroxynaphthoic acid, m. p. 200–205°.

Benzeneazobenzene-*p*-diazonium chloride (Hewitt and Thole, *Trans.*,

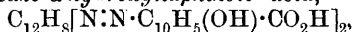
1910, 97, 514) is obtained in orange prisms by passing nitrous acid into a solution of *p*-aminoazobenzene in alcoholic hydrogen chloride.

Attempts to couple naphthaleneazo- $\alpha$ -naphthalene-4-diazonium sulphate and benzeneazo- $\alpha$ -naphthalene-4-diazonium sulphate with salicylic acid proved unsuccessful.

Diazotised 6:8-disulphonaphthalene-2-azo- $\alpha$ -naphthylamine combines with salicylic acid to form 6:8-disulphonaphthalene-2-azo- $\alpha$ -naphthalene-4-azosalicyclic acid,  $C_{10}H_5(SO_3H)_2 \cdot N:N \cdot C_{10}H_6 \cdot N:N \cdot C_6H_3(OH) \cdot CO_2H$ , and with  $\alpha$ -hydroxynaphthoic acid, yielding 6:8-disulphonaphthalene-2-azo- $\alpha$ -naphthalene-4-azo- $\alpha$ -hydroxynaphthoic acid,

$C_{10}H_5(SO_3H)_2 \cdot N:N \cdot C_{10}H_6 \cdot N:N \cdot C_{10}H_5(OH) \cdot CO_2H$ , which forms a hygroscopic, reddish-brown powder.

*Diphenyl-4:4'-bisazo- $\alpha$ -hydroxynaphthoic acid*,



prepared by coupling diazotised benzidine with  $\alpha$ -hydroxynaphthoic acid is a brownish-black powder, which does not melt below 275°.

The colorations produced by dissolving the dyes in alkalis and also in strong sulphuric acid together with the shades obtained on unmordanted and chrome-mordanted wool are described. F. B.

**The Formation of Lakes between *p*-Nitrobenzeneazo- $\beta$ -naphthol and Aluminium and Antimony Compounds.** ROBERT STREBINGER (*Zeitsch. angew. Chem.*, 1912, 25, 2196—2200).—In alkaline solutions of aluminium sulphate the formation of a lake with *p*-nitrobenzeneazo- $\beta$ -naphthol, either at room temperatures or at high temperatures, or in the presence of tartaric acid, takes place to such a slight extent, if at all, that it is of no technical importance. There is also practically no lake formation when the above azo-compound is made from a diazotised solution of *p*-nitroaniline and alkaline  $\beta$ -naphthol in the presence of aluminium sulphate. The same results hold when tartar emetic is used in place of aluminium sulphate.

All the preparations obtained in the presence of aluminium sulphate contained traces of  $SO_4$ -anion. T. S. P.

**Constitution of Dyes Containing Negative Substituents Derived from Sulphonic Acids of  $\alpha$ -Naphthylamine and of  $\alpha$ -Naphthol.** LUDWIG GATTERMANN and HANS LIEBERMANN (*Annalen*, 1912, 393, 198—214).—Diazotised *p*-chloroaniline, 2:5-dichloroaniline, 2:4:5-trichloroaniline, *o*-, *m*- and *p*-nitroaniline, 4-chloro-3-nitroaniline, 2:4-dinitroaniline, sulphanilic acid, and *o*-nitroaniline-*p*-sulphonic acid have been condensed with  $\alpha$ -naphthylamine-3- and -5-sulphonic acid in acetic acid solution and with  $\alpha$ -naphthol-3- and -5-sulphonic acid in aqueous sodium hydroxide in order to ascertain how the relative amounts of *o*- and *p*-azo-dyes produced in each case are influenced by the presence of the negative substituents.

Those of the preceding amines which are difficultly diazotised by the usual methods are treated as follows. Sodium nitrite (10.6 grams) is added gradually to 180 grams of well cooled, concentrated sulphuric acid, and the mixture is heated at 80° for three to four hours. Eighteen grams of the nitrososulphuric acid (= 1 gram of sodium nitrite), cooled in ice, are stirred and treated rapidly with rather more than the

calculated amount of the amine. If a drop of the solution poured on ice contains nitrous acid, the solution is heated at about  $60^{\circ}$  for a short time. It is then poured on to ice, the solution of the diazo-sulphate is diluted to about 250 c.c., and filtered from the excess of amine.

The azo-dyes obtained are examined as follows: The washed and dried crude product is decolorised by stannous chloride and hydrochloric acid on the water-bath, the solution is diluted with water, and the naphthylenediaminesulphonic acids or aminonaphtholsulphonic acids are collected and washed, when necessary, with ether to remove the accompanying primary amine.

The solubilities of 1:2- and 1:4-naphthylenediaminesulphonic acids in aqueous sodium sulphite are so different that they can be quantitatively separated in a mixture of both, and hence the amounts of the ortho- and para-isomerides in the original azo-dye can be calculated. The presence of the 1:2-naphthylenediaminesulphonic acid in the mixture of acids obtained can be detected: (i) by the intense green coloration produced by aqueous ferric chloride, and (ii) by the yellow precipitate of sodium naphthaphenanthrazinesulphonate produced by the addition of the sodium hydrogen sulphite compound of phenanthraquinone to a solution of the acids in aqueous sodium acetate faintly acidified with acetic acid. The orientation of the amino-groups in the naphthylenediaminesulphonic acids is determined by replacing the sulphonic acid group by hydrogen by reduction with sodium amalgam and sulphurous acid, and isolating and characterising the resulting naphthylenediamines.

The position of the amino-group in the aminonaphthol-5-sulphonic acids is determined by eliminating the sulpho-group as above. In the case of the aminonaphthol-3-sulphonic acids, however, it is necessary to heat the acids with stannous chloride and concentrated hydrochloric acid at  $110^{\circ}$  in a sealed tube, whereby 2-amino-1-naphthol-3-sulphonic acid is converted into 2-amino-1-naphthol.

The results of the experiments show that, although a sharp generalisation cannot be made, the presence of the negative substituents in the diazotised amine facilitates in general the formation of the para-azo-dye; thus  $\alpha$ -naphthylamine-5-sulphonic acid usually yields a mixture of the ortho- and the para-azo-dyes, the amount of the latter being greater the larger the number and the more strongly negative the character of the substituents in the diazotised amine. The presence of a sulpho-group in the diazotised amine causes abnormal results; thus  $\alpha$ -naphthylamine-5-sulphonic acid forms exclusively the ortho-azo-dye with diazotised sulphanilic acid, and exclusively the para-azo-dye with diazotised *o*-nitroaniline-*p*-sulphonic acid.

In general, the naphtholsulphonic acids have a greater tendency than the naphthylaminesulphonic acids to form para-azo-dyes, and the 3-sulphonic acids have a greater tendency than the 5-sulphonic acids to form ortho-azo-dyes.

C. S.

Existence of Primary Arylnitrosoamines as well as the Isomeric *anti*-Diazohydrates. ARTHUR HANTZSCH (*Ber.*, 1912, 45, 3036—3040).—Bamberger (this vol., i, 733) has stated that primary

arylnitrosoamines do not exist. The reasons are now summarised for the existence of the primary nitrosoamines as the pseudo-acids corresponding with the *anti*-diazohydrates. They afford the first example of structural isomerism within a purely inorganic complex ( $N_2OH$ ).

In particular, proof of this individuality is afforded by the fact that the compound  $NO_2 \cdot C_6H_4 \cdot N_2 \cdot OH$  shows selective absorption in ethereal solution as the diazohydrate,  $NO_2 \cdot C_6H_4 \cdot N:N \cdot OH$ , whereas it absorbs generally in chloroform solution as the nitrosoamine,  $NO_2 \cdot C_6H_4 \cdot NH \cdot NO$ . Bamberger now accepts this interpretation. E. F. A.

**Behaviour of Iron Salts, in the Presence of Albumins and Other Organic Substances, towards Certain Reagents.** HENRY J. M. CREIGHTON (*Trans. Nova Scotia Inst. Sci.*, 1912, 13, 61—75).—It has been found that egg-albumin, serum-albumin, and gelatin tend to prevent certain reactions which are exhibited by ferric chloride, potassium ferricyanide, and soluble Prussian-blue under normal circumstances. The same proteins, however, appear to be without influence on the reactions of ferrous ammonium sulphate and potassium ferrocyanide. The activity of the proteins would therefore seem to be confined to tervalent iron.

In regard to the mechanism of inhibition, it is supposed that the tervalent iron salts are adsorbed by the colloidal proteins, and that definite chemical compounds are formed. The complex substances formed are readily decomposed by hydrochloric acid, but are fairly stable towards a rise of temperature. In the case of those which are formed with soluble Prussian-blue, the temperature may be raised to 100° without decomposition setting in.

Apart from the prevention of precipitation on the addition of ammonia or alkali hydroxide to ferric chloride solutions, it has been found that sucrose, glycerol, and tartaric acid have no influence on the behaviour of either ferrous or ferric iron towards different reagents.

H. M. D.

**The Intimate Associations of Inorganic Ions with Native and Derived Proteins.** DAVID F. HARRIS (*Trans. Nova Scotia Inst. Sci.*, 1912, 13, 76—86. Compare Creighton, preceding abstract).—A number of observations are referred to which show that the functional activity of protoplasm is dependent on the association of the proteins with inorganic substances in a particular and intimate form.

H. M. D.

**The Influence of the Physical Condition of Proteins on the Rapidity of their Cleavage by Enzymes. The Importance of Peptic Digestion on the Further Cleavage of Proteins by Trypsin. The Degree of Cleavage of Proteins by Enzymes.** EMIL ABDERHALDEN and CHAUNCEY J. VALLETTE PETTIBONE (*Zeitsch. physiol. Chem.*, 1912, 81, 458—472).—The bulk of the paper relates to the methods (optical method, estimation of amino-nitrogen, etc.) which may be employed. Coagulated egg is digested more rapidly

than the fresh material. Pancreatic digestion occurs more rapidly after the preliminary digestion by pepsin has taken place.

W. D. H.

**The Free Amino-groups of the Proteins.** ALBRECHT KOSSEL and N. GAWRILOW (*Zeitsch. physiol. Chem.*, 1912, 81, 274—279).—Those proteins which lack lysine in their molecule contain no nitrogen which can be titrated in presence of formaldehyde. Proteins containing lysine become acid in presence of formaldehyde. This is confirmed by the titration of a number of proteins with and without lysine. Free proline, which contains an imine-group, can be titrated in presence of formaldehyde, but proteins containing a large proportion of proline show no reaction in presence of formaldehyde. This affords evidence that the nitrogen of proline takes part in the peptide formation, and that the proline nitrogen in these proteins is tertiary.

E. F. A.

**Condition which Phosphorus and Calcium Affect in Milk Casein.** LÉON LINDET (*Compt. rend.*, 1912, 155, 923—924\*).—About one-half of the phosphorus contained in casein, precipitated from milk by rennet, is present as calcium phosphate, the other half being in combination as an organic phosphate, which is easily hydrolysed by weak alkalis in the cold. Three-fifths of the calcium is present as phosphate, and the remaining two-fifths is combined with the acid groups of the casein.

W. G.

**Oxyprotosulphonic Acids. II.** JOSEF BURACZEWSKI and L. KRAUZE (*Bull. Acad. Sci. Cracow*, 1912, 7 A, 698—704. Compare this vol., i, 58).—Attempts have been made to purify and characterise the various fractions of the oxyprotosulphonic acids described previously (this vol., i, 58). Measurements of basicity and of optical activity show little difference, and the same is true of the total sulphur and the amount of sulphur eliminated by lead acetate. The fractions yield iodine derivatives of varying colour and iodine content, but the latter did not exhibit any regularities. The oxidation product obtained on treating the  $\alpha$ -fraction with potassium permanganate could be divided into a number of fractions.

E. F. A.

**Oxyprotosulphonic Acid from Casein.** (Mlle.) M. SCHUBERT-HÓWNA (*Bull. Acad. sci. Cracow*, 1912, 7 A, 705—713. Compare Buraczewski and Krauze, this vol., i, 58).—The oxyprotosulphonic acids from casein are divisible only into four fractions, the  $\beta$ -fraction crystallising from acetic acid solution in the cold usually failing.

On further oxidation of the  $\alpha$ -fraction with potassium permanganate an  $\alpha'$ -fraction insoluble in acetic acid was obtained. This is characteristically colourless, whereas the  $\alpha$ -fraction from casein is somewhat yellow. It contains about the same proportion of carbon and hydrogen as the  $\alpha$ -fraction, but lacks any loosely combined sulphur, and contains less total sulphur. It is also unable to absorb iodine.

No difference in the basicity of the six fractions obtained from casein could be measured, and their optical behaviour was alike. They all contain phosphorus.

E. F. A.

\* and *Bull. Soc. chim.*, 1912, [iv], 11, 950—952.

**The Influence of Temperature on the Activity of Nuclease.** E. C. TEODORESCO (*Compt. rend.*, 1912, 155, 554—557).—The behaviour of nuclease contained in a fern (*Pteris aquilina*), a lichen (*Avernia prunastri*), and a basidiomycete (*Pholliota mutabilis*) was studied. Equal portions of the fresh material were heated for half an hour to temperatures from 36° to 100°. A solution of sodium nucleate was then added, and the whole incubated at 36° for several days. Temperatures above 66° cause a rapid decrease in activity of the enzyme, whilst 90—100° destroys it. The optimum temperature for the nuclease of *Pholliota* was found to be about 34°. H. B. H.

**Preparation of "Lipase Powder" Acting in Neutral Medium and its Technical Application.** YOSHIO TANAKA (*J. Coll. Eng. Imp. Univ. Tokyo*, 1912, 5, 125—136).—"Lipase powder" is an active lipolytic substance, prepared by treating pressed castor seed with acid and completely washing out with water all the soluble matter. The optimum temperature of the digestion in which the zymogen of lipase is most favourably developed is 30—35°. The activity of the liberated lipase depends on the amount and not on the concentration of the acid employed. The length of time of the digestion has little effect on the activity.

Lipase powder is odourless and tasteless. It hydrolyses fats and fatty oils rapidly in absence of any soluble acid, and may be kept for a long time without undergoing appreciable change. N. H. J. M.

**Influence of the Products of Change on the Action of Lipase.** YOSHIO TANAKA (*J. Coll. Eng. Imp. Univ. Tokyo*, 1912, 5, 137—141).—The activity of lipase is inhibited by glycerol, and the retardation of the hydrolysis of oils is chiefly due to the glycerol produced, although the reversible action of the lipase is also partly responsible. To obtain the maximum hydrolysis, it is desirable to use the maximum amount of water which does not prevent the production of a good emulsion, or to remove the glycerol and again treat with lipase powder.

Fatty acids are almost without effect on the activity of lipase.

N. H. J. M.

**Influence of Some Neutral Salts, Nitrogenous Matters, and Castor Seed Extract on Lipase.** YOSHIO TANAKA (*J. Coll. Eng. Imp. Univ. Tokyo*, 1912, 5, 142—151).—The activity of lipase is much increased by the addition of neutral salts of the alkali metals, and is not retarded in solutions containing as much as 10%. Salts of magnesium, calcium, and especially copper retard the activity of lipase, even in small amounts.

The stimulating effect of salts of the alkali metals and of manganese is only manifested in the first phase of the hydrolysis.

The hydrolysing power of lipase is also increased by adding an extract of castor seed. This is attributed to salts of alkali metals and proteose present in the extract; globulin and other coagulable proteins do not seem to have any effect.

Leucine and asparagine have a distinct stimulating effect on the action of lipase.

N. H. J. M.

**Action of Lipase on Oxidised and Polymerised Oils.** YOSHIO TANAKA (*J. Coll. Eng. Imp. Univ. Tokyo*, 1912, 5, 152—161).—Lipase acts less rapidly on oil oxidised by insolation, or by air alone, than on the original oil, owing probably to the production of substances of greater mol. weight. Rancid oil is also only slowly hydrolysed, owing to the presence of oxidised substances, less readily hydrolysed, and to the retarding effect of the aldehydic substances it contains. Light without air has no effect. Oil which has been heated in an atmosphere of nitrogen is less readily hydrolysed by lipase than the original oil; the polymerised products of glycerides are evidently attacked with difficulty. N. H. J. M.

**Paralysis and Stimulation of Zymase and Catalase.** HENRI VAN LAER (*Centr. Bakt. Par.*, 1912, ii, 34, 481—484).—The author claims that Lebedeff's maceration method of extracting zymase gives a juice of greater fermentative power than that obtained by Buchner's method. The latter produces a liquid rich in coagulable albumins, and the rate of auto-digestion in such juice has been studied. It was found that an extract of malt retarded auto-digestion, whilst the addition of a solution of papain accelerated the change.

Comparative experiments in which yeast was extracted with water, malt extract, and papain solution show that malt extract increases the activity of zymase and catalase; papain destroys the action of zymase and diminishes that of catalase. H. B. H.

**Asymmetric Phosphorus. I.** EDGAR WEDEKIND (*Ber.*, 1912, 45, 2933—2940. Compare Pope and Gibson, *Trans.*, 1912, 101, 735).—Experiments have been undertaken in the hope of effecting a resolution of an asymmetric phosphonium base into its optically active components. The behaviour of quaternary phosphonium salts towards different solvents has also been examined.

*p*-Tolyldichlorophosphine was prepared by the action of phosphorus trichloride on toluene in the presence of aluminium chloride (compare Michaelis and Panek, *Abstr.*, 1882, 958), and was transformed by mercury diphenyl into phenyl-*p*-tolylchlorophosphine. The yields are unsatisfactory, but the best results are obtained by use of an excess of the dichloride. An ethereal solution of magnesium ethyl bromide transformed phenyl-*p*-tolylchlorophosphine into phenyl-*p*-tolylethylphosphine (compare Michaelis, *Abstr.*, 1901, i, 300), which, on treatment with methyl iodide, yielded phenyl-*p*-tolylmethylethylphosphonium iodide, m. p. 150° (Michaelis, *loc. cit.*, gives 138°). By treatment with silver *d*-camphorsulphonate in dilute alcoholic solution, the latter substance was converted into phenyl-*p*-tolylmethylethylphosphonium *d*-camphorsulphonate, which separated from ethyl acetate in colourless needles, m. p. 128°. Aqueous solutions of this substance rapidly become cloudy, so that for polarimetric observations the addition of a certain amount of alcohol was necessary. In these circumstances, the value  $[M]_D + 101.6^\circ$  was observed, whilst in alcohol alone the value  $[M]_D + 103.85^\circ$  was obtained. On the supposition that the sulphonate is sufficiently dissociated in dilute aqueous-alcoholic solution, this gives  $[M]_D + 52.15^\circ$  for the phosphonium ion. When, however,

the above aqueous-alcoholic solution (10 c.c.) was diluted with water (25 c.c.) and filtered, the molecular rotation diminished from  $+103.85^\circ$  to  $+59.89^\circ$ .

*Phenyl-p-tolylbenzylethylphosphonium iodide*, m. p.  $192^\circ$ , prepared by the union of phenyl-*p*-tolylethylphosphine with benzyl iodide, was converted into the corresponding *d*-camphorsulphonate. The latter formed a hard, amorphous, glassy mass, which could not be obtained in the crystalline form. The *bromocamphorsulphonate* was also unsuitable for purposes of resolution. *Phenyl-p-tolylbenzylethylphosphonium bromide* crystallised in colourless needles, m. p.  $215.5^\circ$ .

Phenyl-*p*-tolylbenzylethylphosphonium iodide was found to be associated in boiling chloroform solution (mol. wt. 728.6, 730. Cal. 416), and also, in contrast to many ammonium and sulphonium salts, to be stable in solution in this reagent. An attempt to electrolyse the fused salt with platinum electrodes was also made. Iodine was formed at the anode. Decomposition occurred at the cathode. Finally, a brown oily residue was obtained, from which hydrochloric acid dissolved a phosphine base which yielded a solid platinichloride.

H. W.

**Preparation of 2:5-Diaminophenyl-1-arsinic Acid.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 248047).—When 5-nitro-2-aminophenyl-1-arsinic acid, m. p.  $235-236^\circ$  (prepared from *p*-nitroaniline and arsenic acid), is reduced under the following conditions only the nitro-group is attacked, and the  $-\text{AsO}(\text{OH})_2$  group remains intact, yielding 2:5-diaminophenyl-1-arsinic acid, needles, decomp.  $210^\circ$ .

5-Nitro-2-aminophenyl-1-arsinic acid (13 parts) is dissolved in 80 parts of 10*N*-sodium hydroxide with 320 parts of water, treated at the ordinary temperature with 110 parts of ferrous chloride solution (18.9% iron), and allowed to remain until the reduction is complete; the solution is filtered, and acidified with sulphuric acid, when the product slowly separates in crystalline form.

F. M. G. M.

**Preparation of Neutral Readily Soluble Derivatives of 4:4'-Dihydroxy-3:3'-diaminoarsenobenzene.** FARBERWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 249726).—When the therapeutically active diaminodihydroxyarsenobenzenes are treated with formaldehyde bisulphite, they furnish compounds which contain the group  $\text{CH}_2\cdot\text{SO}_3\text{H}$ , and form neutral alkali and ammonium salts.

3:3'-Diamino-4:4'-dihydroxyarsenobenzene is suspended in water (3 parts), gently warmed with 40% formaldehyde solution (0.3 part) and 1 part of sodium hydrogen sulphite solution (40%), and the product isolated by the addition of hydrochloric acid; the free *o*-methyl-acid is a yellowish-red powder, soluble in sodium carbonate, and decomposing when heated without fusion; the sodium salt is a reddish-brown mass precipitable by alcohol.

F. M. G. M.

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN  
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PART II.

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General and Physical Chemistry.

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**The Refractive Index of Binary Mixtures.** F. SCHWERS (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 510—518).—A reply to the criticisms of Mazzucchelli (*Abstr.*, 1911, ii, 781) on the author's work (*Abstr.*, 1910, ii, 913, 1039; 1911, ii, 92).  
C. H. D.

**The Ratio of the Intensities of the Series Lines of Hydrogen in the Canal Ray Spectrum.** JOHANNES STARK (*Ann. Physik*, 1911, [iv], 36, 861—865).—The experiments of Lunkenheimer (*Abstr.*, 1911, ii, 950) are considered to be inconclusive, and the author has no grounds for doubting the correctness of the results obtained by Stark and Steubing (*Abstr.*, 1908, ii, 546), which show that the intensity distribution is dependent on the cathode fall of potential.  
H. M. D.

**Spark Spectrum of Indium.** OTTO SCHULEMANN (*Zeitsch. wiss. Photochem.*, 1911, 10, 263—279).—The spectrum was generated by means of sparks passing between an upper carbon electrode and a lower electrode of indium contained in a small porcelain capsule, and the requisite dispersion obtained by a Rowland concave grating of 3.15 metres radius of curvature. Wave-lengths of lines are recorded from 200 to 760 $\mu\mu$ , and the data compared with the much less complete measurements of previous observers.  
H. M. D.

**Wave length Measurements for Some of the Platinum Metals in the Short-waved Ultra-violet Spectrum.** A. MIETHE and B. SEEGER (*Zeitsch. wiss. Photochem.*, 1911, 10, 245—249).—The wave-lengths of lines in the ultra-violet region between  $\lambda=190$  and  $224\mu$  have been measured for platinum, rhodium, and iridium. The spectra were obtained by means of gratings, and the wave-lengths, referred to copper lines as standards, are compared with the data recorded by Exner and Haschek. H. M. D.

**The Alteration of Absorption Lines by Foreign Gases.** EVA VON BAHR (*Physikal. Zeitsch.*, 1911, 12, 1167—1169).—The changes which have been observed in the absorption of ultra-red rays by certain gases (Abstr., 1909, ii, 630; 1910, ii, 914) when the total pressure on the absorbing gas is increased cannot be satisfactorily explained on the assumption that the absorption changes in quality in consequence of a broadening of the absorption bands. Although this broadening undoubtedly takes place, it is shown that changes in the intensity of the absorption also occur to a marked extent.

The fact that different gases exert the same effect on the absorption of ultra-red radiation is inconsistent with the view that the absorption is determined by the frequency of the molecular collisions, and the essential factor involved appears to be the total gas pressure.

H. M. D.

**Absorption Spectra of Complex Inorganic Salts.** ELENA VALLA (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 406—411).—Tables are given showing the absorption spectra at various dilutions of solutions of the following salts:  $\{\text{Co}(\text{NH}_3)_4\text{CO}_3\}\text{Cl}$ ,  $\{\text{Co}(\text{NH}_3)_4(\text{OH})_2\}\text{Cl}_2$ ,  $\{\text{Co}(\text{NH}_3)_5(\text{OH}_2)\}\text{Cl}_2$ ,  $\{\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3\}$ ,  $\{\text{Co}(\text{NH}_3)_4\text{NO}_2\}\text{Cl}$ ,  $\{\text{Co}(\text{NH}_3)_5\text{Cl}\}\text{Cl}_2$ ,  $\{\text{Co}(\text{NH}_3)_5\text{NO}_3\}\{\text{NO}_3\}_2$ ,  $\{\text{Co}(\text{NH}_3)_2(\text{NO}_2)_4\}\text{K}$ .

R. V. S.

**Spectro-chemistry of Auxiliary Valency.** FRITZ EISENLOHR (*Ber.*, 1911, 44, 3188—3208).—In the case of elements which occur in more than one degree of valency, the auxiliary valencies have an influence on the optical properties. It is due to the magnitude of their influence that one and the same element can have several equivalents, for example, ether and hydroxyl oxygen: primary, secondary, and tertiary amine nitrogen.

The unsaturated character of these auxiliary valencies is shown by the optical exaltation produced when they are in a conjugated position to a double bond. The magnitude of this exaltation is usually not large and is considerably less than that caused by conjugated double bond systems; it varies according to the extent to which the element in question is saturated.

Disturbing substituted groups introduced into such conjugations depress the exaltation, and when two or more disturbing groups are introduced the exaltation becomes a depression.

Crossed conjugations in which auxiliary valencies take part do not behave optically in an analogous manner to the corresponding double bond systems. In the former case there is a considerable lessening of the exaltation.

Optical depression is not restricted to aromatic heterocyclic compounds; as a result of disturbance it may appear in both acyclic and alicyclic compounds.

The optical influence of the auxiliary valencies in an incompletely saturated atom is most marked in the refraction value, less so in the dispersion value.

The original should be consulted for the details of the argument: the following physical constants of crotonic acid derivatives have been determined.

Ethyl  $\beta$ -aminocrotonate, b. p. 105.4—107°/14.5 mm.,  $D_4^{18.8}$  1.0219,  $n_D$  1.50067.

Ethyl  $\beta$ -amino- $\alpha$ -ethylcrotonate, m. p. 59—60°,  $D_4^{55.2}$  0.9526,  $n_D$  1.47557.

Methyl  $\alpha$ -chlorocrotonate, b. p. 161.5—161.7°/762 mm.,  $D_4^{26.6}$  1.1537,  $n_D$  1.45634.

Ethyl  $\alpha$ -chlorocrotonate, b. p. 175—175.5°,  $D_4^{19.8}$  1.1133,  $n_D$  1.45378.

Ethyl  $\beta$ -chloroisocrotonate, b. p. 159—161°,  $D_4^{18.7}$  1.0924,  $n_D$  1.45423.

E. F. A.

**Observations on Valency-Isomeric Ammonium Salts.** ARTHUR HANTZSCH (*Ber.*, 1911, 44, 3290—3293. Compare Abstr., 1911, i, 673).—The author has investigated the ultra-violet absorption of a number of aliphatic ammonium salts in order to determine whether these exist in valency-isomeric forms. The existence of such valency-isomerides is indicated by two modifications of dimethylammonium platinichloride (Schryver, *Proc.*, 1891, 7, 39). In all solvents the molecular absorption of the alkylammonium salts is independent of the concentration, so that no evidence of the existence of valency-isomerides was obtained.

From the independence of the absorption and concentration, the conclusion is drawn that neither association nor dissociation has any appreciable influence on the absorption. F. B.

**Spectrochemistry of Enols and Enolic Derivatives.** KARL AUWERS (*Ber.*, 1911, 44, 3514—3524).—As a rule, the exaltation of the molecular refraction and dispersion of a substance, due to the presence of a conjugated system, is more or less diminished by a substituent in the system, the substituent exerting the greatest depressing influence when it is attached to one of the internal carbon atoms; the exaltation, therefore, is greatest in the first, and least in the last, of the three systems:  $>\dot{C}:\dot{C}:\dot{C}:C<$ ,  $\cdot CR:\dot{C}:\dot{C}:C<$ ,  $>C:CR:\dot{C}:C<$ . Hitherto, only substances have been examined in which R is an alkyl or aryl group, but for the purpose of applying the property under discussion to the solution of problems connected with keto-enol tautomerism it is necessary to know what will be the effect when R is OH, OR', or OAc. The molecular refractions and dispersions of the  $\alpha$ - and  $\beta$ -alkyloxystyrenes and of the  $\alpha$ - and  $\beta$ -alkyloxyacrylic esters show that the presence of OR at the terminal carbon of the conjugated system causes marked exaltation, but at one of the inner carbon atoms it may produce little or no exaltation, or even cause a depression of the molecular refraction. However, attention is called to the fact that the influence of other factors must be determined before the exalta-

tion of the molecular refraction or dispersion can be safely used as a criterion of enolic structure. C. S.

**Spectrochemical Behaviour and Constitution of Ethyl Acetoacetate.** KARL AUWERS (*Ber.*, 1911, 44, 3525—3542).—A severe criticism of Hantzsch's work on the molecular refractions and the absorption spectra of ethyl acetoacetate and its derivatives (*Abstr.*, 1910, i, 811). The paper also contains a discussion of the methods and data available for the estimation of the percentage of the enol modification in ethyl acetoacetate. C. S.

**The Ultra-violet Fluorescence of Benzene and Some of its Derivatives.** ERNEST DICKSON (*Zeitsch. wiss. Photochem.*, 1911, 10, 166—180, 181—199).—Photographic records of the fluorescence spectrum of a number of aromatic compounds have been obtained. The spark discharge between zinc electrodes was used as a source of light. The wave-lengths of the edges of the fluorescence bands are recorded and compared with wave-length measurements in the corresponding absorption spectra.

The substances examined were benzene, toluene, *o*-, *m*- and *p*-xylene, mesitylene, diphenyl, diphenylmethane, triphenylmethane, naphthalene, phenanthrene, anthracene, and anthranol, which exhibit several fluorescence bands, and also aniline, quinoline, diphenylamine, quinol, phenol,  $\alpha$ - and  $\beta$ -naphthol,  $\alpha$ - and  $\beta$ -naphthylamine, and quinine sulphate, which show a single band. In some cases the bands show equal frequency differences, whilst in others the relationship between the separate bands can be best represented by means of a Deslandres's formula of the type  $1/\lambda = A - Bn^2$ . H. M. D.

**Photochemical Studies. III. Progressive Light Reactions.** JOH. PLOTNIKOFF (*Zeitsch. physikal. Chem.*, 1911, 78, 293—298).—If a system sensitive to light absorbs light very strongly and becomes bleached as a result of the chemical change, thus allowing the light to act on deeper layers, it should be possible to follow the rate of the reaction from the rate of bleaching of the solution. This is realised in the combination of bromine with cinnamic acid in benzene solution. A glass tube is filled with the solution, and the end closed with a glass plate. The tube is placed horizontally, and light from a uviolet lamp allowed to enter from the end through the glass cover, access of light to the sides and the other end being carefully guarded against. In these circumstances bleaching proceeds gradually from the illuminated end until the solution is completely decolorised. So far, only qualitative measurements have been made. G. S.

**Theory of Colour Sensitiveness. II.** CHR. WINTHER (*Zeitsch. wiss. Photochem.*, 1911, 10, 209—211. Compare *Abstr.*, 1911, ii, 239).—An explanation is given of certain terms used by the author in his previous paper. The assumption of a primary separation of electrons is not inconsistent with Weigert's theory of reaction nuclei. H. M. D.

**The Actions of Very Short-waved Ultra-violet Light on Gases.** C. RAMSAUER (*Ber. Deut. physikal. Ges.*, 1911, 13, 899—902).—In a summary of results obtained in the investigation of the action of ultra-violet light on gases, it is necessary to differentiate between (1) purely chemical action, (2) formation of fog nuclei, and (3) formation of carriers of electricity. Pure chemical changes, such as the transformation of oxygen into ozone, are brought about by light which is not at all readily absorbed. Such changes are quite independent of the formation of fog nuclei or ions. The formation of fog nuclei is also due to chemical action in the first instance, and only differs from changes of the first type in that the end-products are solid or liquid particles. These changes are also independent of the liberation of electrons. The third kind of action differs from the other two in that it is determined by ultra-violet rays which are selectively absorbed. The rays which are mainly responsible for this type of change correspond with wave-lengths in the extreme ultra-violet region.

H. M. D.

**Photo-electric Effects of Certain Compounds.** A. LL. HUGHES (*Proc. Camb. Phil. Soc.*, 1911, 16, 376—383).—In order to ascertain whether certain gases or vapours can be ionised at the ordinary temperature by ultra-violet light of moderately long wave-length, experiments have been made with carbon disulphide, carbon dioxide, stannic chloride, and zinc ethyl. In no case could ionisation be detected, although for the same amount of light energy, the leak from a zinc or carbon surface would have been about  $10^6$  times that of the smallest effect which was measurable with the arrangement of apparatus employed.

Solid compounds of zinc and tin are found to be photo-electrically active.

H. M. D.

**A Relationship between the Selective Photo-electric Effect and Phosphorescence.** ROBERT POHL (*Ber. Deut. physikal. Ges.*, 1911, 13, 961—966).—The emission of electrons which accompanies the excitation of a phosphorescent substance is considered as an indication that the phosphorescence affords an instance of selective photo-electric action.

The wave-lengths of the three exciting bands in the case of twenty-four phosphorescent alkaline earth metal or zinc sulphides examined by Lenard are shown to have a mean ratio of 100 : 81.5 : 66.7. These are approximately the numbers corresponding with the ratio  $1/\sqrt{2} : 1/\sqrt{3} : 1/\sqrt{4}$ , and this agreement is, by reference to Lindemann's formula for the wave-lengths of the photo-electrically active rays, considered to furnish evidence of phosphorescence being a selective photo-electric effect.

H. M. D.

**The Photo-electric Behaviour of Solutions.** HEINRICH NIENHAUS (*Zeitsch. wiss. Photochem.*, 1911, 10, 250—263).—The question as to whether solutions exhibit photo-electric activity has been examined by experiments with aqueous solutions of potassium nitrate, potassium nitrite, copper nitrate, nitric acid, copper sulphate,

and sodium sulphate. Two different methods were employed, but no evidence of a photo-electric effect was obtained even at very high potentials.

H. M. D.

**The Probability Distribution of the Time Intervals of  $\alpha$ -Particles with Application to the Number of  $\alpha$ -Particles Emitted by Uranium.** E. MARSDEN and T. BARRATT (*Proc. London Phys. Soc.*, 1911, 23, 367—373).—The great preponderance of short intervals between the  $\alpha$ -particles in scintillation experiments is theoretically to be expected, for the theory of probability leads to the result that, in a large number,  $N$ , of intervals, the probable number of intervals larger than  $t$  and smaller than  $t + \delta t$  is  $N\mu e^{-\mu t} \delta t$ , where  $1/\mu$  is the average time interval. This formula has been tested by experiments on the  $\alpha$ -particles of polonium and uranium by the method previously employed (Geiger and Marsden, *Abstr.*, 1910, ii, 92), in which a film of the radioactive substance is placed between two zinc sulphide screens, with only thin aluminium foil between, and opposite portions of the two screens are examined simultaneously by two observers. In this way practically all the  $\alpha$ -particles produce scintillations, and double scintillations can be observed if they occur. If the two  $\alpha$ -particles known to be emitted per atom of uranium disintegrating were simultaneously expelled, or if the product producing the second had a period of only a few seconds or less, there should be a larger proportion of shorter intervals than the theory indicates. The results, however, both with uranium and polonium agreed within the probable limits of error with the theory given. Hence the two  $\alpha$ -particles from uranium are not expelled simultaneously, and the period between the first and the second must be greater than a few seconds, a view which is supported by the short range of both particles. Certain of the records obtained by Rutherford and Geiger on the probability distribution of the time-intervals of the  $\alpha$ -particles of polonium have been re-examined, and found to be in excellent agreement with the theory given, so that the possibility that particles are expelled in groups, the groups being distributed in time according to probability, is excluded.

F. S.

**The Chemical Action of the  $\alpha$ - and  $\beta$ -Rays, Individually and Jointly.** FRANCIS L. USHER (*Jahrb. Radioaktiv. Electronik*, 1911, 8, 323—336).—The action of  $\beta$ -rays alone on water was determined in an apparatus consisting of a capillary tube, of wall-thickness 0.17 mm., containing radium emanation, sealed into a wider tube containing water which had been previously freed from dissolved gas by means of a mercury pump. One curie of emanation was calculated to give 6.486 cm.<sup>3</sup> of electrolytic gas during its complete disintegration. In another experiment the emanation was dissolved in gas-free water kept under slight pressure, so that all the gases produced remained dissolved. The total chemical effect corresponded with the production of 136.66 cm.<sup>3</sup> of electrolytic gas per curie. The view is taken that the chemical action is primarily not mechanical, that is, due to the collision of the radiant particles with the molecules decomposed, but that the electric charges on the radiant particles are the principal

factor in the chemical action. The efficiency of the emanation in decomposing water is calculated to be 2.7%, which is nearly three times greater than its efficiency in decomposing ammonia. F. S.

**Magnetic Spectrum of  $\beta$ -Rays of Radium.** OTTO VON BAEYER, OTTO HAHN, and LISE MEITNER (*Physikal. Zeitsch.*, 1911, 12, 1099—1101. Compare Danysz, *Abstr.*, 1911, ii, 840).—The magnetic spectrum of radium-*B* and -*C*, deposited on a silver wire, 1 cm. long and 0.2 mm. thick, and covered with tin foil, 0.007 mm. thick, to prevent scattering of the material by recoil, showed in addition to the strong  $\alpha$ -rays, seven distinct lines due to  $\beta$ -rays capable of being accurately measured. Separate measurements were made with uncovered wires and with weaker fields to give the velocity of the less penetrating  $\beta$ -rays more accurately. In these experiments two other lines, due to very low velocity rays, were observed, making nine in all. Experiments with pure radium-*C* deposited on a nickel wire gave only the four least deflected lines, so that the other five lines, all due to low velocity rays, belong to radium-*B*. The velocities calculated, according to the Lorentz-Einstein formula, with  $e/m_0 = 1.77 \times 10^7$ , are for radium-*C*, 0.98, 0.94, 0.86, 0.80, and for radium-*B*, 0.74, 0.69, 0.63, 0.41, and 0.36 in terms of that of light as unity. The  $\beta$ -rays of radium itself were examined. For the purpose a solution of radium was long boiled to remove the emanation, precipitated as a carbonate, and the precipitate filled into a small glass groove. Only one experiment and a provisional measurement of the velocity of the  $\beta$ -rays were possible. Two lines were observed, one strong, due to rays of velocity 0.65, and one weak, due to rays of velocity 0.52. Corrected values for the velocities of the  $\beta$ -rays of radium-*D* are 0.39 and 0.33, and for thorium-*B* and -*D* (new nomenclature) 0.36 and 0.29 (compare *Abstr.*, 1911, ii, 567, 569). F. S.

**The Scattered Röntgen Radiation from Different Radiators.** J. A. CROWTHER (*Proc. Camb. Phil. Soc.*, 1911, 16, 365—369).—Experiments are described in which the author has measured the proportion of a primary Röntgen ray-beam which is scattered by different radiators. From observations with filter-paper, aluminium, nickel, copper, and tin, it appears that the intensity of the radiation scattered from equal masses of different materials is not independent of the nature of the radiator, but increases very considerably as the atomic weight of the radiator increases. Since the scattered radiation from hydrogen is appreciably greater than that from an equal mass of air, it would seem that the scattered radiation is a minimum for elements in the neighbourhood of carbon and oxygen, and increases both for elements of smaller and larger atomic weight.

In the case of aluminium, the distribution of the scattered radiation was examined in some detail. The distribution is dependent on the thickness of the radiator, but, in a direction at right angles to the primary, the intensity of the scattered radiation is directly proportional to the thickness of the radiator. H. M. D.

**Production of Canal Rays in Potassium, Rubidium, and Cæsium.** EUGEN GOLDSTEIN (*Ber. Deut. physikal. Ges.*, 1911, 13, 972—973).—A form of discharge tube is described, suitable for the production of canal rays in the vapours of the alkali metals. The colour of the rays in potassium is reddish-yellow, in rubidium yellowish-red, and in cæsium greenish-white with a blue tinge. The canal-ray spectra show the brightest lines of the fundamental spectra, together with some of the series lines.

The discharge tubes can be employed for long periods without interference from blackening of the walls. H. M. D.

**The Emission of Electrons ( $\delta$ -Rays) by Metals under the Influence of  $\alpha$ -Rays.** HENRY A. BUMSTEAD (*Phil. Mag.*, 1911, [vi], 22, 907—922).—Previous results point to the conclusion that all atoms are less effective in retarding swift  $\alpha$ -rays than slow ones, but heavy atoms are relatively more effective than light atoms in stopping swift  $\alpha$ -rays. The emission of  $\delta$ -rays from metals struck by  $\alpha$ -rays is probably analogous in every way to the ionisation of a gas, and measurements have been made of the number of  $\delta$ -rays escaping from a thin metal foil struck by  $\alpha$ -rays at different points in the range. Curves connecting this emission with the range have all the characteristics of the Bragg ionisation curve. The emission first increases and then rapidly decreases, as the  $\alpha$ -rays near the end of their range, showing the characteristic "knee." The  $\alpha$ -rays of polonium were for the most part employed, but one set of measurements with the thorium active deposit showed clearly the two "knees," corresponding with the two sets of  $\alpha$ -rays of different ranges. In comparing aluminium and gold with air, the metals showed, as was to be expected, less pronounced "knees" than the gas, but the close similarity of the curves for these two metals, differing so widely in density and atomic weight, gives rise to a suspicion that the  $\delta$ -rays result, not from the metal, but from a layer of adsorbed gas of the same nature in each case. F. S.

**Nature and Velocity of an Ion in a Gas.** RICHARD D. KLEEMAN (*Proc. Camb. Phil. Soc.*, 1911, 16, 285—298).—The nature of an ion in a gas must be subjected to continual change, the formation and disintegration of the various ion clusters being governed by the same laws as those which regulate the formation and dissociation of neutral gas molecules. On the basis of this hypothesis, an expression is deduced for the average velocity of an ion in a gas subjected to the influence of an electric field. According to this, it follows that the velocity of an ion is nearly independent of its mass, when this is greater than the mass of the molecules of gas through which it moves. Different observers have obtained results which agree with this deduction. When the mass of the ion is small in comparison with that of the gas molecules, the author's formula indicates that the variation of the velocity with the mass of the ion should be much greater. No experiments are available to test this conclusion.

H. M. D.

**The Positive Ionisation Produced by Phosphates when Heated.** FRANK HORTON (*Proc. Camb. Phil. Soc.*, 1911, 16, 318—320).—An investigation has been made of the rate at which

positive ions are emitted by lithium phosphate when heated at  $800^{\circ}$  in air, oxygen, carbon monoxide, and hydrogen at pressures up to 30 mm. of mercury. The rate of leakage under a saturation voltage of 40 volts is about the same as for sodium phosphate (Abstr., 1911, ii, 246) under similar conditions. In oxygen and air the rates of leakage are nearly equal, but the ionisation current is considerably greater in carbon monoxide and still greater in hydrogen. From observations at gradually diminishing pressures, a maximum rate of leakage was found at a pressure between 0.1 and 0.3 mm. of mercury. A similar maximum was observed in observations at gradually increasing pressures, but in these circumstances the corresponding pressure is higher. It is probable that this hysteresis effect is due to the phosphate requiring an appreciable time before a condition of equilibrium is attained between it and the surrounding gas.

H. M. D.

**An Absolute Determination of the Minimum Ionising Energy of an Electron and the Application of the Theory of Ionisation by Collision to Mixtures of Gases.** EDWIN S. BISHOP (*Physikal. Zeitsch.*, 1911, 12, 1148—1157).—The ionisation produced in hydrogen, air, and carbon dioxide by the action of ultra-violet rays from the spark discharge between zinc electrodes has been investigated in reference to Townsend's theory. The experimental data obtained are in agreement with this theory for gas pressures as high as 40 cm. of mercury. For each gas, the minimum energy, which an electron must have to bring about ionisation, has been determined, and this corresponds with 9.66, 10.21, and 6.21 volts for hydrogen, air, and carbon dioxide respectively. This minimal ionisation energy is independent of the gas pressure and of the intensity of the electrical field. Experiments were also made on the ionisation in mixtures of hydrogen and air and of hydrogen and carbon dioxide, and a theory of the action in mixtures of gases is developed which accords satisfactorily with the observations.

H. M. D.

**Rays of Positive Electricity from the Wehnelt Cathode.** CHARLES T. KNIPP (*Phil. Mag.*, 1911, [vi], 22, 926—933).—The nature of the carriers of positive electricity emitted by a hot lime cathode has been examined by means of the records obtained on a photographic plate inserted in the discharge tube. The velocity with which the positive ions are emitted is not large enough to affect a photographic plate, but by the introduction of an accelerating condenser, photographic records are readily obtained. The minimum potential difference required for this is about 500 volts per centimetre, but the photographs become more clearly cut and well defined as the acceleration of the slowly-moving carriers is increased. The values of  $e/m$ , which are indicated by the photographs obtained in experiments with residual air, are the same as those found by Thomson in the case of the positive rays emitted by the ordinary perforated cathode with high potential discharge.

H. M. D.

**The Chemical Action of Penetrating Radium Rays. I. The Influence of Penetrating Rays on Hydrogen Peroxide in Neutral Solution.** ANTON KAILAN (*Monatsh.*, 1911, 32, 1019—1034).—The influence of the penetrating rays from radium preparations of various strengths on the decomposition of hydrogen peroxide has been investigated in paraffined and non-paraffined glass vessels at 25° in a thermostat, and also at 13—15°. The reaction proceeds approximately according to the law for a reaction of the first order, the coefficient of velocity being increased by the action of the rays, although, with increasing quantities of radium, less rapidly than it would be if the effect were proportional to the quantity of radium. The temperature-coefficient of the action of the rays is about 1.2, which corresponds with the value for photochemical reactions, whereas the temperature-coefficient of the reaction occurring in absence of the rays is much greater. Blank tests were performed throughout, and the results are expressed in terms of the coefficient of velocity of the unassisted reaction. The effect of the rays on the glass produces substances which increase the velocity of the unassisted reaction. The production of the peroxide from water by the penetrating rays has been confirmed. F. S.

**Solubility of the Radium Emanation. Application of Henry's Law at Low Partial Pressures.** R. W. BOYLE (*Phil. Mag.*, 1911, [vi], 22, 840—854. Compare Ramstedt, *Abstr.*, 1911, ii, 842).—The emanation mixed with air or other gas was shaken with a known volume of the absorbing liquid in a mixing bulb immersed in a thermostat. When equilibrium was obtained either a portion of the liquid phase or a portion of the gas was withdrawn by opening a tap in connexion with an exhausted sampling bulb of known volume. The two bulbs were separated, kept four hours for radium-C to come into equilibrium, and the quantity of emanation in each measured by means of the  $\gamma$ -rays in a  $\gamma$ -ray electroscope, standardised by the  $\gamma$ -rays from a known amount of radium placed at the same distance. An accuracy of about 1.5% was attained. Henry's law was found to be valid, and the emanation is rather more soluble in water at 14° than nitric oxide, about one-quarter remaining with the liquid and three-quarters with the gas when equal volumes of each are used. The solubility is 0.303 at 14°, and decreases from 0.507 at 0° to 0.153 at 40°. Sea-water at 14° of D 1.022 absorbs 0.84 times as much as pure water, and mercury is not able to absorb the emanation. At 14° absolute ethyl alcohol absorbs twenty-four times, amyl alcohol thirty-one times, and toluene forty-five times as strongly as water. F. S.

**Some Simple Methods of Preparing Radioactive Disintegration Products.** LISE MEITNER (*Physikal. Zeitsch.*, 1911, 12, 1094—1099).—An examination has been made of two of the common methods of separating radioactive products from solution, the first by depositing it on a less "noble" metal, and the second by electrolysis. In electrolysis a silver wire as cathode and platinum wire as anode, about a millimetre apart, connected with a 220 volt circuit

through a 25 c.p. carbon lamp arranged to burn brightly, and small volumes of solutions, at most a few c.c., are the conditions recommended. The solutions were kept boiling rapidly during electrolysis. The radium active deposit solution in hydrochloric acid gave after fifteen to twenty minutes' electrolysis with a silver wire cathode, 0.8 mm. diameter and 10 to 15 mm. long, almost the whole of the radium-*B* and -*C* to the cathode. Other cathodes of platinum, gold, and nickel were less satisfactory. In strongly acid solutions less was deposited, and the radium-*C* was in excess in the deposit, whilst in alkaline solutions no active matter was deposited. The anode remained always inactive. Radium-*C* was best deposited on nickel foil or wire, immersed in the boiling, and only slightly acid, solution of as small a bulk as possible. No separation of radium-*C*<sub>1</sub> from radium-*C*<sub>2</sub> was obtained by this method. These two methods on a hydrochloric acid solution of radium-*D*, -*E*, and -*F*, obtained by allowing the radium emanation to decay in a closed vessel, give deposits of radium-*E* containing some radium-*F*. From lead chloride, separated from uranium minerals, the radium-*E* and -*F* may be concentrated in the solution after the greater part of the salt has crystallised out, and from this solution the radium-*E* is deposited on nickel foil. The deposit may be then dissolved in hydrochloric acid and electrolysed for thirty minutes to obtain the radium-*E* on a very small surface. If the presence of radium-*F* interferes, it may be first removed by placing a bismuth plate in the solution. The decay curve of radium-*E* over a period of forty-six days was perfectly exponential with the half-period of five days (compare Antonoff, Abstr., 1910, ii, 251).

Mesothorium-2 containing small proportions of the thorium active deposit is separated from a mesothorium solution by precipitating iron in the solution by ammonia. After the first few precipitations at daily intervals, the radiothorium and thorium-*X* are removed, and then the precipitates, obtained by a trace only of iron, consist of mesothorium-2 and a little thorium-*B*. By electrolysis of the hydrochloric acid solution with platinum cathode, the iron and the thorium-*B* are deposited. The solution is nearly neutralised, boiled vigorously and electrolysed with a silver cathode, and the mesothorium-2 is deposited.

The active deposit of thorium on tin foil is dissolved in dilute hydrochloric acid and electrolysed with gold or platinum cathode. Thorium-*B* is deposited comparatively pure, and thorium-*C* and -*D* remain in solution usually, although sometimes some thorium-*C* is also deposited. Thorium-*C* may be quantitatively separated by immersing nickel in the solution, which, if then electrolysed for some minutes with gold or platinum cathode, yields pure thorium-*B*. Silver, without electrolysis, precipitates thorium-*B* and -*C*, the latter in great excess. Thorium-*D* is most easily prepared by recoil. A nickel plate immersed for one or two minutes in the boiling, feebly acid solution of the actinium active deposit separates actinium-*C* in a state of extraordinary purity, the  $\alpha$ -rays of which decay exponentially over a period of twelve minutes, with the half-period 2.15 minutes. The solution electrolysed with silver cathode deposits actinium-*B*, -*C*, and -*D*, the

former in excess. The separation of actinium-*C* by nickel is recommended as a delicate test of the presence of actinium. [Throughout the altered nomenclature has been employed (compare Abstr., 1911, ii, 955)]. F. S.

**The Amount of the Radioactive Products Present in the Atmosphere.** S. KINOSHITA, S. NISHIKAWA, and S. ONO (*Phil. Mag.*, 1911, [vi], 22, 821—840).—Measurements have been made of the proportion of the active deposit on negatively charged wires due to radium and thorium respectively at heights 6.5 and 1.5 metres above the ground at the Physical Laboratory of the University of Tōkyō. The ratio of the amounts of radium-*C* on the upper and lower wires was nearly constant and equal to 0.95, and that of the thorium active deposit on the two wires about 0.5. The latter ratio varied with the velocity of the wind. From a mathematical investigation of the number of molecules of radium-*A* that should be deposited on the wire, assuming their mobility to be 1.3 as found by Rutherford, it is calculated that the amount of radium emanation per cubic metre of the atmosphere at Tōkyō is only  $5 \times 10^{-12}$  curie, which is from twelve to twenty-one times less than that found at Montreal, Chicago, and Cambridge (Eng.). No direct measurements at Tōkyō have been made, but the discrepancy may be due to the charged molecules of radium-*A* attracting dust particles, with consequent great diminution of mobility, before they become transformed into radium-*B*. The range of variation of the amount of emanation in the air was practically the same as that observed by Satterly at Cambridge, and a fall in atmospheric pressure caused an increase in the amount of emanation. F. S.

**The Radioactivity of the Waters of Valles-Bains,** CHASPOUL and JAUBERT DE BEAUJEU (*Compt. rend.*, 1911, 153, 944—946).—The radioactivity of the various springs of the Valles-Bains has been determined in E.S.U. per litre, and found to lie between 2.21 and 0.115 ( $\times 10^{-3}$ ) for the water, and between 10.7 and 0.737 ( $\times 10^{-3}$ ) for the gas collected from the spring. Exceptionally, the radioactivity of these springs is proportional to the quantity of carbon dioxide liberated. In all cases the activity is due to radium emanation. F. S.

**Contact Electrification.** ALBERT GRUMBACH (*Ann. Chim. Phys.*, 1911, [viii], 24, 433—501. Compare Abstr., 1910, ii, 93).—Measurements have been made of the changes which occur in the contact electrification at the surface separating a solid dielectric from a solution of an electrolyte, when the water in the solution is partly replaced by equal weights of certain organic substances. The actual method of procedure consisted in measuring the potential differences set up when solutions of potassium chloride are filtered under different pressures through dielectric porous media. In parallel series of experiments, the water was partly replaced by methyl, ethyl, and isobutyl alcohols and by phenol, and in all cases the magnitude of the contact potential difference was found to be diminished by this

substitution. The diminution can be quantitatively represented by the equation:  $1 - (M/M_0)^2 = \lambda x^p$ , in which  $M_0$  and  $M$  are the electric moments in the case of the aqueous and mixed solutions,  $x$  the concentration of the substituted solvent in mols. per 1000 grams of solution,  $\lambda$  and  $p$  constants characteristic of the added solvent.

On the basis of the results obtained, it is shown that the phenomenon of contact electrification is intimately connected with that of adsorption.

H. M. D.

**Oil Emulsions. I. The Electric Charge.** RIDSDALE ELLIS (*Zeitsch. physikal. Chem.*, 1911, 78, 321—352).—The rate of movement of the minute particles in an oil-water emulsion under the influence of an electric field and the effect of electrolytes on the rate and direction of the movement have been determined. The straight tube method of Whitney and Blake and the U-tube method of Burton were found unsatisfactory, and the majority of the measurements were made by direct microscopic observation of the speed of the particles. The velocity of the particles depends on their distance from the lower surface of the cover-glass. A method by which the speed of the particles relative to water can be obtained by observation of their velocity at varying distances from the lower surface of the cover-glass is described in detail. From the observations the differences of potential water | glass and oil | water are calculated by known formulæ.

The contact-potential at the oil-water surface is of the same order for oils of different kinds, and is not much influenced by the purity of the oil. The potential oil | water is also of the same order as that at the surface of contact of glass and water, and at the surface of suspended particles of colloidal metals, lycopodium, quartz, etc.; it varies from 0.02 to about 0.05 volt.

The contact potential at the oil-water and glass-water boundaries reaches a maximum in a neutral or slightly alkaline medium. The addition of hydrochloric acid diminishes the contact potential very rapidly for small concentrations, and only gradually for relatively high concentrations. The addition of sodium hydroxide at first increases the contact potential at the oil-water surface, but when the concentration exceeds  $N/1000$  the potential diminishes, at first rapidly, then slowly, as the concentration is gradually increased. This diminution of the contact potential is probably due to a kind of electric adsorption.

The measurement of the effect of electrolytes on the contact potential presented great experimental difficulties on account of the disturbances due to bubbles of gas liberated at the electrodes, but these difficulties were overcome by the use of depolarisers and by special mechanical devices which are fully described.

G. S.

**Variation of the Electromotive Force of Voltaic Cells with the Temperature.** BEDEAU (*Ann. Chim. Phys.*, 1911, [viii], 24, 553—563).—The variation with temperature of the *E.M.F.* of the following galvanic combinations has been measured:

Cu | 1 molar  $\text{Cu}(\text{NO}_3)_2$  | 1 molar  $\text{AgNO}_3$  | Ag;

Cu |  $\text{Cu}(\text{NO}_3)_2, 100\text{H}_2\text{O}$  |  $2\text{AgNO}_3, 100\text{H}_2\text{O}$  | Ag;

$\text{Cu} \mid 1 \text{ molar } \text{Cu}(\text{ClO}_3)_2 \mid 1 \text{ molar } \text{AgClO}_3 \mid \text{Ag}$ . By taking Berthelot's value (35,300 cal.) for the heat of the reaction:  $\text{Cu} + 2\text{AgNO}_3 = \text{Cu}(\text{NO}_3)_2 + 2\text{Ag}$ , constant values are obtained for the temperature-coefficient in agreement with the experimental observations, whereas Jahn's value (30,040 cal.) leads to a variable temperature-coefficient.

By a suitable arrangement of the electrodes and solutions it has been found that the seat of the variation of the *E.M.F.* with the temperature is at the contact surfaces between the metals and the solutions, and not at the surface of separation of the two solutions.

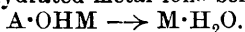
H. M. D.

**Thermodynamics of the Clark Cell.** F. POLLITZER (*Zeitsch. physikal. Chem.*, 1911, 78, 374—383).—Cohen (Abstr., 1911, ii, 180), from a comparison of the heat of reaction in the Clark cell as obtained from the thermochemical data and from the change of *E.M.F.* with temperature, has drawn the conclusion that the temperature formula of Jaeger and Kahle is unsuitable for thermodynamic calculations. The author shows that this conclusion is not justified. In calculating the heat of reaction from thermochemical data, Cohen has neglected the change of the heat of formation and heat of solution with the temperature. When allowance is made for these there is an approximately constant difference from 0° to 30° between the heats of reaction as obtained by the two methods. The possible causes of this discrepancy are discussed. One factor which has been neglected is the heat of amalgamation of zinc.

G. S.

**Chemical Theory of Galvanic Cells of the Daniell Type.** PAUL PFEIFFER (*Zeitsch. Elektrochem.*, 1911, 17, 990—994).—On the basis of Werner's views as to the nature of acids, bases, and salts, a new theory of the origin of the *E.M.F.* in a galvanic cell is developed, which accounts for the fact that there is a distinct parallelism between the heat of oxidation of the metals and their *E.M.F.*

According to Werner's theory, in salt solutions there are  $\text{OH}'$  ions mainly in association with the acid, A, as  $\text{A}\cdot\text{OH}'$ . The metal is oxidised by this complex ion, the negative electron being liberated, thus:  $\text{A}\cdot\text{OH}' + \text{M} = \text{A}\cdot\text{OHM} + \ominus$ . The resulting compound then establishes an equilibrium with the other ions and complexes in the solution, among others hydrated metal ions being formed:



The greater the affinity of the metal for oxygen, the greater the energy of the liberated electrons, and therefore the higher the *E.M.F.* of the combination metal | metallic salt. On similar lines it may be shown that the electromotive activity of negative ions such as the halogens is a reduction process, and as a matter of fact there is an evident relationship between the normal discharge potential of the halogens and their heat of reduction.

It is shown that these views are in quantitative accord with the results of *E.M.F.* measurements; for instance, they lead to a deduction of the simple Nernst formula, and are in accord with Abegg and Bodländer's views on electro-affinity.

G. S.

**Piezo-chemical Studies. VIII. Influence of Pressure on Affinity. II.** G. TIMOFÉEFF (*Zeitsch. physikal. Chem.*, 1911, 78, 299—320).—The influence of pressure on the *E.M.F.* of the cell lead amalgam | lead chloride solution | mercurous chloride | mercury has been investigated directly and indirectly by the methods fully described in previous papers by E. Cohen and his co-workers (compare Abstr., 1910, ii, 1029).

In the first experiments, 30% lead amalgam was used (compare Babinski, *Diss.*, Leipzig, 1906). In the indirect calculation by means of the equation  $E_{\pi} - E_0 = \pi(v_2 - v_1)$ , where  $v_1$  and  $v_2$  represent the volumes of the system before and after the passage of 96,540 coulombs, and  $\pi$  is the pressure,  $(v_1 - v_2)$  amounts to  $-3.368$  c.c., and  $E_{500} - E_0$  is  $1.77 \times 10^{-3}$  volt. Direct determinations by means of the pressure apparatus already described give in good agreement  $1.95 \times 10^{-3}$  volt at  $25^\circ$ .

The cell, lead amalgam 30% | lead chloride solution | lead, gave for the calculated and observed values of  $E_{500} - E_0$   $0.091 \times 10^{-3}$  and  $0.100 \times 10^{-3}$  volt respectively, and the cell, lead amalgam 1% | lead chloride solution | mercurous chloride | mercury,  $1.46 \times 10^{-3}$  and  $1.49 \times 10^{-3}$  volts respectively. Finally, the cell, lead amalgam 30% | lead chloride solution | lead amalgam 1%, gave  $0.31 \times 10^{-3}$  and  $0.36 \times 10^{-3}$  volt for the observed and calculated values respectively.

G. S.

**Electrolytic Corrosion of Some Metals.** GEORGE R. WHITE (*J. Physical Chem.*, 1911, 15, 723—792. Compare Schoch and Randolph, Abstr., 1911, ii, 14).—The behaviour of anodes of zinc, copper, nickel, tin, iron, and cadmium has been observed in solutions of sodium chloride, sulphate, nitrate, acetate, and tartrate. The current density was usually 1 to 2 amperes per square decimetre of anode surface, and the electrolyte contained 75 grams of salt per litre, or occasionally 25 grams. The anodes were cleaned by filing and by scouring with carborundum paper before each run.

A number of experiments with rotating anodes were run in series, with a copper voltameter of ample proportions in the circuit, and the theoretical anode loss was calculated on the assumption that the anode dissolved with its normal valency. The efficiency of corrosion was in many cases approximately 100%. Where corrosion was less than the calculated the anode was found to be protected by the formation of an oxide or hydroxide film. In some cases where the anode attained to complete passivity, oxygen was liberated, and the electrolytic efficiency was very low. On the other hand, the efficiency with copper, tin, and cadmium was frequently much more than 100%, and even attained 200% in a few cases. When these abnormal results were corrected for the chemical (local current) dissolution of the anode by the electrolyte and for loss of unoxidised metal by disintegration of the anode surface, there still remained a large excess of corrosion unaccounted for. With copper when the efficiency was abnormally high, as for example, with sodium chloride, cuprous salts were always in evidence. The author suggests that in the parallel cases tin and

cadmium dissolve in a univalent form. This applies particularly to the corrosion in sodium nitrate.

In the electrolysis of nitrate solutions, nitrite is always formed by cathodic reduction. With cadmium, reduction to nitrite also occurs at the anode, and is attributed to the interaction of cadmium suboxide and sodium nitrate.

When an anode became passive, anodic oxidation of the electrolyte could occur. This was observed with copper anodes in sodium tartrate, where formic acid was produced, which in turn reduced cupric compounds to cuprous hydroxide. The metals exhibited a greater tendency to be rendered passive in the more dilute electrolytes and at the lower temperatures, but the relation of current density to corrosion efficiency is subject to no general rule.

The filtered electrolyte was almost invariably alkaline after electrolysis, and in some cases metal was deposited at the cathode.

The paper records a large number of interesting observations on the colour and appearance of the anodic deposits. The suboxides of tin and cadmium appear to be greyish-white.

R. J. C.

**The Decomposition of Nitrogen Peroxide in the Electrical Glow.** J. ZENNECK (*Ber. Deut. physikal. Ges.*, 1911, 13, 953—954).—When a current from an induction coil is passed through a long, narrow discharge tube, through which a current of nitrogen peroxide is drawn by means of a pump, it is found that the colour of the glow varies from one part of the tube to another. The succession of colours in the direction of the gas current is orange-yellow, bluish-violet, greenish-yellow, and bright red. When the long, narrow tube is replaced by a spherical bulb, these colours are not simultaneously observed, but when the current is started, the glow is at first reddish-yellow, and then changes successively to bluish-violet, greenish-yellow, and bright red.

It is supposed that the different colours are due to the successive stages in the decomposition of the nitrogen peroxide.

H. M. D.

**Electrical Theory of Dyeing.** WILLIAM HARRISON (*J. Soc. Dyers*, 1911, 27, 279—289).—In reference to the electrical theory of dyeing suggested by Perrin, measurements have been made of the potential differences which are set up at the surface of contact between cotton and aqueous solutions when these are filtered through the cotton by application of mechanical pressure. Dilute solutions of sodium hydroxide, hydrochloric acid, aluminium sulphate, croceine-scarlet, diamine-blue, and sodium oleate of varying concentration, together with certain other electrolytes, were examined. The observed potential differences, which are independent of the surface of the fibre and of the rate of flow of the solution, vary for *N*/1000 solutions from 0.0306 volt for sodium hydroxide to 0.0036 volt for aluminium sulphate.

In connexion with these measurements, various observations relating to the absorption of dyes and mordants are described, and it is shown that a parallelism exists between this absorption and the contact differences of potential. In the application of the electrical theory,

for which evidence is thus obtained, it is necessary to take into account (1) the electrical charge on the particles of the dye, (2) the charge on the fibre, (3) the size of the particles of dye, and (4) the extent of the surface of the fibre, including that within its pores.

H. M. D.

**Magnetisation of Nickel, Cobalt, and of Alloys of Nickel and Cobalt.** PIERRE WEISS and O. BLOCH (*Compt. rend.*, 1911, 153, 941—943).—The coefficient expressing the atomic magnetic moment of cobalt, or of alloys of this metal with nickel containing 80—90% of cobalt, cannot be experimentally determined owing to the impossibility of realising saturation. Alloys containing less cobalt show a linear variation of the coefficient with the percentage composition.

By extrapolation from values obtained at the temperature of liquid air, it is found that the coefficient for pure cobalt corresponds with the existence of nine magnetons per atom.

At temperatures equal to three-quarters of those of the Curie points, the saturation admits of investigation with alloys containing over 80% of cobalt. By plotting the values for the Curie points and extrapolating, the number of magnetons per atom of cobalt and nickel above these temperatures are found to approximate to fifteen and eight respectively.

W. O. W.

**Influence of Oxide Formation and of Thermal Treatment on the Magnetism of Copper.** FEODOR BEHNSEN (*Physikal. Zeitsch.*, 1911, 12, 1157—1160).—The results of experiments on the magnetisability of copper are described. According to these, electrolytic copper, cupric and cuprous oxides cannot be permanently magnetised, whereas commercial copper oxide can. Moreover, the metal obtained from this oxide by reduction exhibits a more strongly developed permanent magnetism than the oxide itself.

In reference to induced magnetism, it is found that electrolytic copper is diamagnetic, whereas the pure oxides are paramagnetic. The metal reduced from commercial oxide is more strongly paramagnetic than the oxide from which it is derived. It is supposed that the commercial oxide contains minute traces of ferric oxide, the quantity of which is too small for detection by chemical tests, and that on reduction this oxide is converted into the more strongly magnetic metal.

H. M. D.

**Dependence of the Thermal Conductivity of Certain Gases on the Temperature.** ARNOLD EUCKEN (*Physikal. Zeitsch.*, 1911, 12, 1101—1107).—By a modification of Schleiermacher's method, the thermal conductivity of helium, argon, hydrogen, nitrogen, oxygen, air, and carbon dioxide has been measured at temperatures between  $-190^{\circ}$  and  $+100^{\circ}$  and at a pressure of 30—40 cms. of mercury. The experimental data are applied to the calculation of the value of  $K$  in the equation  $k = K.c_v.\eta$ , in which  $k$  is the thermal conductivity,  $c_v$  the specific heat at constant volume, and  $\eta$  the coefficient of viscosity. For helium, argon, nitrogen, oxygen, and air, the product  $K.c_v$  is nearly independent of the temperature, whereas it varies appreciably in the

case of hydrogen and carbon dioxide. The variation observed with hydrogen appears to be due to a diminution of  $c_v$  with falling temperature, and, in general, the observations accord with the assumption that  $K$  is independent of the temperature. H. M. D.

**Selective Absorption and Emission.** KARL SCHAUM and HEINRICH WÜSTENFELD (*Zeitsch. wiss. Photochem.*, 1911, 10, 213—237).—The emission of rays within the region of the visible spectrum has been investigated in the case of a number of substances which exhibit selective absorption, and the spectra compared with that of an approximately black body at the same temperature. To permit of a comparison of the emission at different temperatures, the authors made use of electrically heated platinum strips tapering towards the middle, one half being covered with a thin layer of the substance under examination, the other half with a layer of ferric oxide, which behaves approximately as a black substance. The reflexion spectra at different temperatures were also examined by means of similar strips, a Welsbach mantle being used as the source of radiant energy.

The oxides of zinc, uranium, thorium, cerium, neodymium and erbium, Welsbach mixture, Thénard's blue, copper and gold were investigated in this manner. From the photographic records it is found that the absorption bands become broader with rise of temperature, the broadening being more strongly developed towards the red end of the spectrum. No displacement of the absorption lines occurs when the temperature changes, and at a given temperature the emission corresponds exactly with the absorption. In the case of copper and gold, which exhibit strongly developed selective reflexion in the red and yellow regions, it is found that the visible rays which are first observed when the temperature is raised, are of a greenish-yellow colour. The behaviour of these substances shows, therefore, that the primary visible radiation may consist of other rays than red, a possibility which has been already anticipated by Schaum.

H. M. D.

**Theory of the Critical Opalescence.** WOLFGANG OSTWALD (*Ann. Physik*, 1911, [iv], 36, 848—854).—The observations of Friedländer (Abstr., 1901, ii, 643) relative to the occurrence of opalescence in mixtures of isobutyric acid and water in the neighbourhood of the critical solution temperature are examined in reference to Smoluchowski's theory. By assigning slightly different critical temperatures to mixtures containing from 36.0 to 45.4% of isobutyric acid, it is found that the intensity of the opalescence is inversely proportional in each case to the difference between the temperature of observation and the critical temperature for the particular mixture. For very small differences of temperature (less than  $0.05^\circ$ ), this relationship does not hold, however, and the calculated intensity is very much greater than that actually observed. The opalescence effect exhibited by ethylene in the neighbourhood of its critical point appears to deviate in the same way when the temperature of the substance approaches very closely to the critical temperature.

H. M. D.

**The Thermodynamics of Equilibria in One-Component Systems. I. Equilibrium of Isotropic and Anisotropic Phases.** GUSTAV TAMMANN (*Chem. Zentr.*, 1911, ii, 1091—1092; from *Nachr. k. Ges. Wiss. Göttingen*, 1911, 236—260).—It is shown by the method of the thermodynamic potential that two forms of equilibrium curves are possible in one-component systems. In one case, the point at which the differences of volume and energy between the two phases vanish lies on the curve (critical point), in the other such a point is absent. The first presents itself when both phases are isotropic, and the second when one or both are anisotropic. The second condition occurs when the compressibility of a crystal is less than that of the liquid, and when the difference of volume between crystal and liquid vanishes at a finite pressure. Observation confirms these conclusions. Critical points are never observed when one or more of the phases are anisotropic. C. H. D.

**Determination of the Transition Temperatures of Ammonium Nitrate.** KARL VOGT (*Physikal. Zeitsch.*, 1911, 12, 1129—1131).—From dilatometric observations the transition temperatures of ammonium nitrate were found to be  $32.5^\circ \pm 0.05^\circ$ ,  $82.26^\circ \pm 0.10^\circ$ , and  $125.2^\circ \pm 0.06^\circ$ . Observations of the changes in double refraction under the microscope led to the values  $32.7^\circ$ ,  $83.9^\circ$ , and  $125.4^\circ$ . For the measurement of the transition temperature below  $0^\circ$ , use was made of a thermo-element surrounded by the substance which was slowly cooled or heated, and in this way  $-16.6^\circ$  was obtained. H. M. D.

**Specific Heat,  $C_p$ , of Air at Room and Low Temperatures.** KARL SCHEEL and WILHELM HEUSE (*Ber. Deut. physikal. Ges.*, 1911, 13, 870—873 \*).—The method employed was that used by Callendar and Barnes in the determination of the specific heat of water. A current of dry air, free from carbon dioxide, was passed at a measured rate through an insulated tube, in which the gas is heated by an electric current passing through a fine platinum wire. By means of resistance thermometers the temperatures of the entering and emerging air were measured very accurately.

From the data obtained with this apparatus the specific heat of air at constant pressure is found to be 0.2408 at  $+20^\circ$ , 0.2432 at  $-78^\circ$ , and 0.2525 at  $-183^\circ$ . The value for  $20^\circ$  is in agreement with Swann's results (*Abstr.*, 1909, ii, 465), but is higher than that calculated from most of the older determinations. H. M. D.

**Melting-point Apparatus.** E. ANTHERS (*Chem. Zeit.*, 1911, 35, 1375).—The heating vessel is a combination of Thiele's and Busch's forms, being provided with a lateral loop for circulation of the heating liquid, and also with small side openings for the introduction of melting-point tubes. The ring surrounding the thermometer, for the support of the tubes, is carried by a glass tube inserted through the cork. C. H. D.

**The Constancy of the Boiling Point of Sulphur.** CHARLES W. WAIDNER and GEORGE K. BURGESS (*Bulletin of the Bureau of Standards*, 1910, 7, 127—130).—The temperature at different points within the

\* and *Ann. Physik*, 1912, [iv], 37, 79—95.

radiation shield of the standard form of apparatus for determining the boiling point of sulphur has been examined by means of a thermocouple with wires of 0.1 mm. diameter, which had been annealed and calibrated, but not used otherwise. Although couples of stouter wire, which had been used for high temperature work, indicate variations of temperature amounting to several tenths of a degree, the results obtained with the smaller couple showed that the temperature is constant to within  $0.05^{\circ}$ , and probably within  $0.03^{\circ}$  throughout the greater portion of the sulphur vapour column. H. M. D.

**Heat of Liquefaction of Colloids.** JOSEF FRANK (*Ber. Deut. physikal. Ges.*, 1911, 13, 890—898).—A sensitive method of measuring whether the liquefaction of colloids is accompanied by absorption of heat is described. This consists in determining the rate at which heat is conducted through the colloid when the vessel containing it is immersed in a bath of constant temperature higher than the liquefaction temperature. For such observations the colloid was contained in a cylindrical tube, in the centre of which was placed one of the two junctions of an iron-constantan thermocouple. The second junction was supported in a similar position in a thin-walled capillary tube connected at the lower end with the wide tube. A sensitive galvanometer in circuit with the thermocouple permitted of measurements of the difference in temperature between the two junctions, and from such readings, taken every minute, curves were constructed which afforded information as to the nature of the heat conductance. From a comparison of such curves obtained from observations at different temperatures, it is found that the liquefaction of colophony, colophony-turpentine oil mixtures, and gelatin-water mixtures is not accompanied by any appreciable absorption of heat. H. M. D.

**A Differential Micro-calorimeter for the Estimation of Heat-production in Physiological, Bacteriological, and Enzyme Actions.** A. V. HILL (*J. Physiol.*, 1911, 43, 261—285).—The experimental fluid is placed in one vacuum flask (or ordinary "refill" of a thermos bottle), and a corresponding amount of water in another; changes occurring outside affect both equally. A copper-constantan thermocouple connected to a sensitive galvanometer is arranged with one junction in each flask, so that the deflexion of the magnet gives the difference of temperature between the two. This difference is increased by the heat-producing activity of living organisms. Owing to the good insulation, experiments can be conducted over many hours. By the use of this method, it was possible to measure the heat-production in frogs, in isolated muscles, in various forms of muscle-rigor, during the souring of milk, and during the action of yeast on sugar. No heat production occurred during the action of saliva on starch. W. D. H.

**Chemical Affinity. VI. The Formation of Naphthalene Picrate.** J. N. BRÖNSTED (*Zeitsch. physikal. Chem.*, 1911, 78, 284—292. Compare Abstr., 1911, ii, 856).—The free energy of formation,  $A$ , of naphthalene picrate has been determined by *E.M.F.*

measurements on principles discussed in previous papers. In the course of the measurements the equilibria in the systems picric acid-potassium picrate-potassium chloride-hydrochloric acid-water and naphthalenepicrate-naphthalene-potassium chloride-potassium picrate-hydrochloric acid-water have been measured. The results give for the free energy at 20°, 2190 calories, and at 0°, 2150 calories.

From these results, the total change of energy,  $U$ , calculated by means of the Helmholtz equation,  $A - U = T.dA/dT$ , amounts to 1460 calories, whereas the value of  $U$ , determined directly by calorimetric measurements, is 880 calories. In the circumstances, the agreement is considered fairly satisfactory.

G. S.

**The Heat of Combustion of a Molecule and its Chemical Attraction Constant.** RICHARD D. KLEEMAN (*Proc. Camb. Phil. Soc.*, 1911, 16, 299—312).—Further investigation of the relationships between the chemical and physical properties of substances and the attraction constants of the molecules has shown that the heats of combustion are also related to the attraction constants. For the hydrocarbons, the ratio of the heat of combustion ( $H_c$ ) to the sum of the square-roots of the weights of the atoms in a molecule ( $\Sigma \sqrt{m_{ac}}$ ) is approximately constant and its mean value is 29.5.

For compounds which contain other elements in addition to carbon and hydrogen, a similar relationship holds if certain quantities representing the effects of the additional elements are added to the heats of combustion.

The term  $H_c$  then becomes  $H_c + n.a + n'.b + n''.c + \dots$ , in which  $n$ ,  $n'$ ,  $n''$  are the numbers of atoms of the elements  $A$ ,  $B$ , and  $C$  in the molecule, and  $a$ ,  $b$ , and  $c$  are the specific influences due to the different atoms. As in the case of the hydrocarbons,  $(H_c + n.a + n'.b + n''.c + \dots) / \Sigma \sqrt{m_{ac}} = 29.5$ .

For nitrogen, the value of the atomic influence depends very largely on the constitution of the compound, and this variability is also evident in the case of other elements. The values of the above ratios are tabulated for a large number of different classes of compounds, and from these tables it is evident that relationships exist between the heats of combustion and the molecular attraction constants for a number of different groups of compounds.

H. M. D.

**The Alteration of the Properties of Metals by their Mechanical Treatment.** GUSTAV TAMMANN (*Chem. Zentr.*, 1911, ii, 1110; from *Nachr. k. Ges. Wiss. Göttingen*, 1911, 181—196. Compare Faust and Tammann, *Abstr.*, 1910, ii, 1039).—The scalar properties of metals, such as the density and the energy-content, are little altered by mechanical treatment, and such changes as occur are probably due to secondary causes. Vectorial properties, on the other hand, are much influenced by deformation of the crystal grains. The change of elasticity is due to the breaking up of the grains along gliding-planes, and that of electrical resistance to the re-orientation of the lamellæ. Wire-drawing has much more influence in this respect than pressing or hammering.

The following further data are obtained: Gold has a lower elastic

limit of 49 kilog./cm.<sup>2</sup>; its temperature of recrystallisation is 750—800°. Silver has a lower elastic limit of 86 kilog./cm.<sup>2</sup>, whilst the eutectic alloy of copper and silver has a lower elastic limit, 1000 kilog./cm.<sup>2</sup>. The lower elastic limit of zinc is 117, and of cadmium, 27 kilog./cm.<sup>2</sup>; that of the alloys closely approaches that of zinc. The lower elastic limit of alloys of copper and manganese increases with the proportion of manganese, being 260 kilog./cm.<sup>2</sup> for 5% Mn and 1250 kilog./cm.<sup>2</sup> for 90% Mn, owing to the formation of solid solutions. C. H. D.

**New and Simple Method for Determining the Avogadro Number N.** H. ZANGGER (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 216—218).—The method consists in observing and measuring the movements of the smallest particles of mercury in a mercury-water emulsion by means of a microscope provided with a micrometer eye-piece, and giving a magnification of 750. In consequence of the Brownian motion, these smallest particles do not fall vertically under the influence of gravity, but execute irregular horizontal deviations from the vertical line which passes through the original position. When certain corrections are applied, the measurements of the distances traversed in a given interval of time can be utilised for the calculation of Avogadro's constant by making use of Einstein's and Stokes's formulæ. From three independent measurements the values of  $N$  obtained were 6.24, 6.19, and  $6.32 \times 10^{23}$ . H. M. D.

**Relation between the Atomic Volumes and the Spectra of Elements.** R. ROSSI (*Phil. Mag.*, 1911, [vi], 22, 922—925).—If the logarithms of the roots of the spectral series given by Ritz's equation and of the atomic volumes are plotted on two orthogonal axes, the points which represent elements of the same family are found to lie very nearly on a straight line. This is shown to be the case for the alkali metals, for magnesium, calcium, and strontium, for zinc, cadmium, and mercury, and for oxygen, sulphur, and selenium. From this it follows, that whether the fields of magnetic force in the atom are due to elementary magnets or to solids of revolution charged with electricity at the surface and in rapid rotation round their axis, there appears to be a connexion between their dimensions or configurations and the volume of the atom containing them. H. M. D.

**Hofmann's Method for the Determination of Vapour Density.** ALFRED C. EGERTON (*Chem. News*, 1911, 104, 259—260).—A description is given of a slight modification of the ordinary apparatus, designed to overcome the usual difficulties of cleaning and drying the tube, and so give a ready and simple means of determining vapour densities by Hofmann's method. A sketch of the apparatus is given, and the steps, in making a determination by means of it, are set out in detail. The chief point in the design is that the vapour can be expelled while hot, and so leave the apparatus ready for another determination. W. G.

**A New Viscometer.** GEORGE F. WHITE (*Biochem. Zeitsch.*, 1911, 37, 482—489).—See this vol., ii, 61.

**Viscosity of Gas Mixtures.** ERNST THOMSEN (*Ann. Physik*, 1911, [iv], 36, 815—833).—By analysis of Puluĵ's formula for the viscosity of mixtures of two gases, it is shown that a maximum viscosity may be expected when the molecular weights of the two gases are widely different, provided that the viscosity coefficients of the pure gases are not very unequal.

In accordance with this anticipation, it has been found that mixtures of hydrogen with carbon dioxide, ethylene, and ammonia exhibit viscosity maxima. The data for ammonia and ethylene show the same phenomenon.

On the other hand, Puluĵ's formula can only be regarded as of a qualitative character, for the calculated and observed compositions of the various gas mixtures which exhibit maximum viscosity are not in agreement.

H. M. D.

**General Relationship between the Physical Properties of Substances.** Application to Viscosity, Capillarity, Surface-tension, Heat of Vaporisation, and the Rectilinear Diameter. G. TER GAZARIAN (*Compt. rend.*, 1911, 153, 1071—1074. Compare Abstr., 1911, ii, 1066).—This paper contains only numerical data to illustrate the generalisation put forward in an earlier communication.

W. O. W.

**Relationship between the Limiting Value of the Molecular Conductivity and the Viscosity.** PAUL WALDEN (*Zeitsch. physikal. Chem.*, 1911, 78, 257—283).—The author showed some years ago (compare Abstr., 1906, ii, 335) that the product of the molecular conductivity of an electrolyte at infinite dilution,  $\lambda_{\infty}$ , and the viscosity of the solvent is constant and = 0.700. As, however, the general validity of the rule has been denied by Dutoit and Duperthuis (compare Abstr., 1909, ii, 125), the matter has been further investigated.

Dutoit and Duperthuis determined the value of  $\lambda_{\infty}$  for sodium iodide in the higher alcohols by measurements in very dilute solution. The author contends that much more accurate results are obtained by extrapolation, and shows that with the values of  $\lambda_{\infty}$  obtained in this way,  $\lambda_{\infty} \eta_{\infty}$  is constant. Further, it is shown from the available data that the rule is also valid for solutions of potassium iodide in various solvents. Finally, conductivity measurements have been made with tetrapropylammonium iodide in ten organic solvents (acetone, propionitrile, ethylene chloride, epichlorohydrin, benzonitrile, ethyl acetate, nitrobenzene, phenylacetone, *isobutyl* alcohol, and *m*-chloroaniline), and in this case also the rule is valid, the value for the constant at 25° being 0.624. When the values of  $\lambda_{\infty}$  obtained as above are used in calculating the heat of ionisation of sodium iodide, approximately the same values are obtained in different solvents, whereas the data of Dutoit and Duperthuis lead to different values in the various solvents (compare Abstr., 1909, ii, 120).

It has, however, already been shown that certain solvents with high association constants (water, glycol, glycerol, sulphuric acid) form exceptions to the above rule, and it is now pointed out, on the basis of

theoretical deductions of the rule, that such exceptions are to be expected.

G. S.

**Osmotic Pressure.** II. MAURICE PRUD'HOMME (*Bull. Soc. chim.* 1911, [iv], 9, 1015—1017).—In the previous paper (Abstr., 1911, ii, 1071) it was shown that if the attraction between the infinitely small elements of two extremely thin layers, one of sucrose solution and the other of water, separated by a semi-permeable membrane, were directly proportional to the masses taking part, and inversely proportional to the distance squared, the relation  $f = Km/v$  would hold. In this equation  $f$  is the force of attraction between the mols. of sucrose and the mols. of water,  $m$  the mass of sucrose, and  $v$  the volume of the sucrose solution, with that of the water attracted by it. If it is further supposed that a volume  $V$  of air is introduced between the sucrose solution and the mercury in the manometer, so that the water is really attracted by a force  $f$ , the equation of equilibrium becomes  $fv = p(V - v + v_1 + \epsilon)$ , where  $p$  is the pressure of the volume of air ( $V - v + v_1 + \epsilon$ ),  $v_1$  the volume of the sucrose solution, and  $\epsilon$  the volume of air corresponding with the lowering of the mercury level in the first branch of the manometer. In Pfeffer's experiments the sucrose solution filled the space between the semi-permeable wall and the surface of the mercury in the manometer, and under such conditions the volume of water attracted is  $\epsilon = v - v_1$ , whence  $f(v_1 + \epsilon) = pv_1$ . As  $p$  is the osmotic pressure due to  $v_1$ ,  $f$  will be the osmotic pressure due to  $v_1 + \epsilon$ , whence it follows that (1) the pressure exercised by the molecules of a dissolved substance, in a certain volume of a solvent, is equal to the attraction of these molecules for those of the solvent, and (2) since  $f$  in a volume of liquid  $v$  is proportional to the mass of the dissolved substance, the osmotic pressure must be similarly influenced by the mass of the substance dissolved. Further, as in the equations  $fv = Km = p(V - v + v_1 + \epsilon)$ ,  $f$  and  $v$  represent osmotic pressures, and  $p$  the pressure due to a volume of air,  $fv$  can be regarded as relating to a gas of pressure  $f$  and volume  $v$ , the number of the molecules of which would be proportional to  $m$ , it follows that  $fv = RT$ , and that osmotic pressure obeys the gas laws and increases with absolute temperature.

T. A. H.

**Application of the Theory of Chemical Potential to the Thermodynamical Theory of Solutions.** I. General Theory of Chemical Potential in a Binary System. **Osmotic Pressure and Vapour Pressure of Solutions.** SYDNEY A. SHORTER (*Phil. Mag.*, 1911, [vi], 22, 933—942).—By means of Gibbs's theory of chemical potential, the author deduces an expression connecting the vapour pressures of two solutions, and the pressures under which they co-exist in osmotic equilibrium. The theory shows that osmotic pressure cannot be regarded as a specific property of a solution, but that it represents the increase of pressure necessary to counteract the lowering effect of the addition of the solute on the chemical potential of the solvent.

H. M. D.

**Molecular State of Substances in Solution.** PIERRE GIRARD and VICTOR HENRI (*Compt. rend.*, 1911, 153, 946—948).—A polemical

paper traversing recent statements and conclusions of Colson and of Fouard (Abstr., 1911, ii, 1071).  
W. O. W.

**The Dissolecule and Van't Hoff's Formula.** ALBERT COLSON (*Compt. rend.*, 1911, 153, 1074—1076. Compare Abstr., 1911, ii, 1076).—Polemical against Girard and Henry (preceding abstract).  
W. O. W.

**Solution and Dissolecules.** ALBERT COLSON (*Bull. Soc. chim.*, 1911, [iv], 9, 1008—1015).—It is pointed out that the theory of solutions due to van't Hoff and Arrhenius is self-contradictory in certain respects, and is not in harmony with a number of well-known facts. A re-statement of the theory is given, and the properties of dissolecules are discussed.

In the equation  $\omega V = \rho T$ , in which  $\omega$  is the osmotic pressure and  $\rho$  a constant, it is assumed that  $\rho = R$  in the gas equation  $PV = RT$ . The validity of the former depends principally on observation of the behaviour of solutions of sucrose, a substance not obtainable in either the gaseous or the liquid state, so that views as to its molecular condition in solution are incapable of experimental verification. Moreover, Pfeffer's measurements of the osmotic pressures of sucrose solutions give values for  $\rho$  which differ among themselves by as much as 10%, and those found by Ponsot (Abstr., 1899, ii, 204) and Fouard (Abstr., 1911, ii, 267) show like variations. It is known that acetic acid, either in vapour or liquid form, is bimolecular, and the fact that its heat of liquefaction is nearly identical with its heat of solution indicates that it is bimolecular in solution. In this case, therefore,  $\omega$  should be equal to  $P/2$ , whereas it is in reality equal to or a little less than  $P$  (Fouard, *loc. cit.*). When hydrogen chloride dissolves in water it is known that molecules,  $\text{HCl} \cdot 2\text{H}_2\text{O}$ , are formed, and although  $\omega$  should be identical with  $P$ , it is in reality greater, and to explain this the ionic hypothesis has been introduced. The latter explains the conductivity of certain solutions, but since non-ionised solutions, for example, silver nitrate in nitrobenzene or pyridine, may exhibit conductivity, ionisation is not necessarily correlated with conductivity. If it is admitted that cryoscopic measurements may replace measurements of osmotic pressure, the equation  $\omega V = \rho T$  requires that  $\rho = 2R$  (approx.). Such a value of  $\rho$  corresponds in all cases with weights greater than those of the simple molecules.

The molecular conductivity is not the same for all substances, and is probably correlated with the number of ions in the free molecules. The hypothesis may therefore be expressed in the following form. The molecular conductivities of dissolved substances are only comparable after dissociation of particles into molecules, as the result of dilution. If the particle or dissolecule is an aggregate, it will not, as a rule, show conductivity. The molecular conductivity of dissolecules, which are dissociable into simple molecules is generally proportional to the dilution, due regard being paid to the specific molecular conductivities, which appear to be correlated with the number of ions in the free molecule.

If in a simple solution, molecules existed in the same condition as

in a gas, the latent heat of vaporisation should be identical with the heat of solution of a substance, but this is only the case for abnormal substances, such as formic and acetic acids, and the difference between these two constants may be taken as a measure of the work done in transforming gaseous molecules into polymolecular dissolecules.

T. A. H.

**Formamide as Solvent and Ionising Medium.** PAUL WALDEN (*Bull. Acad. Sci. St. Petersbourg*, 1911, 1055—1082. Compare Abstr., 1906, ii, 335).—It is shown by a comparison of their physical properties that formamide and water show an analogous behaviour in many respects. Formamide melts at  $1.6^{\circ}$  approx., and its dielectric constant,  $>84$ , rather exceeds that of water. In their solvent power the two liquids also show considerable resemblance, and the present paper contains a comparison of their ionising power.

The mean value of the cryoscopic constant of formamide is  $35.0$ . Freezing-point and conductivity determinations show that potassium iodide, tetraethylammonium iodide, and certain other alkylammonium salts are as highly ionised in formamide as in aqueous solutions of corresponding concentration. The molecular conductivities are much smaller in formamide than in water or hydrogen cyanide. The dissociating power of a solvent also depends, however, on the nature of the electrolyte, as tribromoacetic acid, which is highly ionised in water, is only very slightly ionised in formamide.

The molecular weight of starch in formamide is about 645, corresponding with the formula  $(C_6H_{10}O_5)_n$ , and the value of  $[\alpha]_D$  is  $+189^{\circ}$ , whilst  $[\alpha]_D$  in aqueous solution is about  $+195^{\circ}$ .

G. S.

**Conductivity. I. Conductivity of Ammonia in (Anhydrous) Formic Acid.** I. "Formic Acid Hydrolysis." H. I. SCHLESINGER and R. P. CALVERT (*J. Amer. Chem. Soc.*, 1911, 33, 1924—1933).—Much attention has been given recently to the ionisation of salts in non-aqueous solvents, but the behaviour of acids and bases in these solvents has not been systematically studied. An investigation of the conductivity of such solutions has therefore been undertaken, and an account is now given of the conductivity of solutions of ammonia in anhydrous formic acid at  $25^{\circ}$ . The results show that the solutions are excellent conductors, and that ammonium formate, although a highly ionised electrolyte, obeys the law of mass action in the more concentrated solutions.

Determinations have also been made of the conductivity of ammonium chloride in formic acid at  $25^{\circ}$ . Neither the dilution law nor Kohlrausch's equation represents the course of the dissociation of the salt in these solutions. This is due to the fact that in formic acid solution ammonium chloride is the salt of a strong base, ammonia (ammonium formate), and a very weak acid, hydrogen chloride, and should therefore be partly decomposed by the solvent into those two substances exactly as similarly constituted salts are hydrolysed in aqueous solutions. Potassium chloride, bromide and iodide, and sodium chloride are similarly decomposed by "formic acid hydrolysis."

E. G.

**Effect of Salts on the Solubility of Other Salts. V. Solubility of Uni-bivalent Salts in Solutions of Salts of Different Types.** WILLIAM D. HARKINS (*J. Amer. Chem. Soc.*, 1911, 33, 1807—1827. Compare Abstr., 1911, ii, 1074, 1075).—An accurate method is described for the analysis of bromates which consists in reducing the bromate to bromide with hydrazine hydrate, acidifying with nitric acid, and precipitating with silver bromide.

The following solubilities were determined at 25°: Silver sulphate in water, and in solutions of magnesium, potassium, and silver nitrates, and magnesium and potassium sulphates; barium bromate in water, and in solutions of magnesium, potassium and barium nitrates, and potassium bromate; and lead chloride in water and solution of lead nitrate. The solubilities in water, expressed in equivalents per litre, were: silver sulphate, 0.05352; barium bromate, 0.04018; lead chloride, 0.07776.

The conductivity of all the solutions was measured at 25°, and the values for the equivalent conductivity and ionisation of the salts are tabulated.

The curves obtained by plotting the solubilities of the salts as ordinates, and the equivalent concentrations of the added salts as abscissæ are of three types: (1) When a salt containing a common univalent ion is added, the solubility decreases rapidly, and the curve is of the form to be expected from the solubility-product principle; (2) when a salt containing a common bivalent ion is added, the change in solubility is entirely different from that to be expected from the solubility-principle. The solubility of moderately soluble salts at first decreases slightly and then increases with increased concentration of the added salt. With less soluble salts, such as barium bromate, there is a slight but continuous decrease up to a concentration of 0.2*N* of the added salt. With extremely soluble salts there is a continuous increase with increase in the concentration of the bivalent ion, and the curve is therefore of the same form as that obtained when a salt without a common ion is added; (3) when a salt without a common ion is added, the solubility always increases.

The solubility of silver sulphate is decreased slightly by the addition of potassium sulphate, and less by that of potassium hydrogen sulphate or magnesium sulphate. Sulphuric acid increases the solubility.

E. G.

**Effect of Salts on the Solubility of Other Salts. VI. Solubility of Difficultly Soluble Uni-bivalent Salts.** WILLIAM D. HARKINS and W. J. WINNINGHOFF (*J. Amer. Chem. Soc.*, 1911, 33, 1827—1836).—The solubilities have been determined at 25° of barium iodate in water and in solutions of potassium nitrate and iodate, and barium nitrate; and of lead iodate in water and in solutions of potassium nitrate and iodate, and lead nitrate. The solubilities of barium iodate and lead iodate in water are 0.001579 and 0.001102 equivalent per litre respectively.

When a salt with a common bivalent ion is added to solutions of these slightly soluble salts, the solubility curves are nearly of the theoretical form in the more dilute solutions. When a salt with a

common univalent ion is added, the solubility decreases with great rapidity, and when a salt without a common ion is added, the solubility rapidly increases. The solubility curves for the addition of a common ion assume practically the same form as those for the addition of a salt without a common ion in the case of very soluble salts, such as strontium nitrate.

E. G.

**Effects of Salts on the Solubility of Other Salts. VII. Discussion of the Solubility Relations of Uni-bivalent Salts.** WILLIAM D. HARKINS (*J. Amer. Chem. Soc.*, 1911, **33**, 1836—1873).—The concentrations of the ionised and non-ionised parts of the salts saturating the solution were calculated for all the mixtures studied by Harkins and by Harkins and Winninghoff (preceding abstracts). The calculations were made by the method employed by Bray (*Abstr.*, 1911, ii, 1075). The solubility product for these uni-bivalent salts increases far more rapidly than that for uni-univalent salts, and the increase is more rapid when the common ion added is univalent than when it is bivalent. The rate of increase may be expressed (for a salt  $A_2B$ ) by equations of the form  $(A)^2(B) = k(\Sigma i)^{m_i}$ . In this equation, for ion concentrations between  $0.03N$  and  $0.10N$ ,  $m_i$  has an average value about 0.45 when the common ion added is univalent and about 0.34 when it is bivalent. The solubility product remains more nearly constant the less soluble the salt.

The decrease in the concentration of the non-ionised part of a univalent salt is much more rapid than the decrease caused in the same way in the solubility of a non-electrolyte. When the salt saturating the solution is uni-bivalent, the decrease in concentration is greater when a salt with a common univalent ion is added than the similar decrease observed for uni-univalent salts. When a salt without a common ion is added, the decrease in the concentration of the non-ionised part is much less rapid, and when a salt with a common bivalent ion is added, there is an increase instead of a decrease. The increase in the concentration of the non-ionised part when a common bivalent ion is added becomes smaller, and the decrease caused by a common univalent ion becomes larger as the concentration of the solution decreases. These results are expressed by equations of the form  $(A_2B) = k_u(\Sigma i)^{m_u}$ . The values of  $m$  are very irregular, and depend greatly on the type of ion added to the solution.

The solubility effects produced by adding a common ion are also discussed by expressing the concentrations of the salt saturating the solution and of the added salt in terms of the solubility of the former salt in water. Curves have been constructed which show the change of this "fractional solubility" with the "fractional concentration" of the added salt in relation to the solubility of the salt saturating the solution and the type of the added salt, and in relation to the "theoretical limiting curve" representing the decrease in solubility on the assumption that both salts are completely ionised.

Lead chloride in its solubility relations behaves like a more soluble salt, and this is probably connected with its abnormal ionisation.

The irregular variation of the non-ionised part, the abnormal increase in the solubility product, and the abnormal form of the

solubility curve for the addition of the common bivalent ion can be explained on the assumption that all uni-bivalent salts dissociate in two stages, and thus give rise to intermediate ions of the type  $\text{KSO}_4^-$  or  $\text{BaNO}_3^+$ . From this hypothesis, several deductions are drawn, which are shown to be in complete accord with the experimental results. Methods are suggested for determining the proportion of the intermediate ion in solutions of uni-bivalent salts. E. G.

**Velocity of Crystallisation and Dissolution.** CARL L. WAGNER (*Zeitsch. Elektrochem.*, 1911, 17, 989—990).—A further criticism of Marc's results (compare this vol., ii, 265; Marc, *Abstr.*, 1910, ii, 834). G. S.

**Test of the Validity of van der Waals's Equation of Condition for Colloidal Solutions.** THE SVEDBERG (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 219—224).—Equations are deduced by means of which it has been possible to test the applicability of van der Waals's equation to colloidal solutions. From the experimental data obtained by Svedberg and Inouyi (*Abstr.*, 1911, ii, 703), it appears that the constants  $a$  and  $b$  for gold hydrosols increase with the dilution of the solution in a linear manner. In the case of gamboge suspensions, the rate of increase is less rapid.

On the basis of the linear connexion between  $a$  and  $b$  and the volume of the solution in the case of colloidal solutions of gold, values have been calculated for  $a$  and  $b$ , represented as functions of the size of the particles and the volume of the solution, and the modified van der Waals's equation is found to afford a satisfactory representation of the compressibility data which have been obtained for gold hydrosols.

H. M. D.

**The Thermodynamics of Equilibrium in One-Component Systems. II. Polymorphism.** GUSTAV TAMMANN (*Chem. Zentr.*, 1911, ii, 1092—1093; from *Nachr. k. Ges. Wiss. Göttingen*, 1911, 325—360).—A distinction must be made between "forms" or "phases" and crystallographic crystal forms. Only those crystal forms which differ in volume, heat content, and equilibrium curves are to be regarded as distinct phases. Four classes of crystals are distinguished: totally and absolutely stable, partly and absolutely stable, totally unstable, and partly unstable. The melting curve of a totally unstable form is enclosed by that of a stable form without intersection. The  $\zeta$ -surfaces of two partly stable forms intersect in a curve, the projection of which on the  $pT$ -plane is the transformation curve of the two forms. Forms the  $\zeta$ -surfaces of which do not intersect, form a "crystal group." The melting curves of the forms belonging to a crystal group do not intersect, neither do the curves of transformation of them into the same form of another group.

These principles are applied to the case of water (*Abstr.*, 1910, ii, 495). The first group contains the absolutely stable ice I and the unstable ice IV, whilst the second, denser group includes ice III, which is probably absolutely stable, and the unstable ice II. The transformation curves and triple points are enumerated and defined.

Some quantitative relations have been found between the position of the equilibrium curves and the stability of the forms. It is also found that a substance which is readily undercooled may yield many forms of the same crystal group, and that whilst liquids composed of only one kind of molecules, as shown by Eötvös' constant, yield only forms belonging to a single crystal group, associated liquids may yield forms belonging to several groups. It is assumed that the forms of any group are composed of similar molecules, and those of different groups of dissimilar molecules.

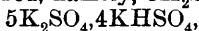
C. H. D.

**Thermal Analysis of Quaternary Systems. III.** NICOLA PARRAVANO and G. SIROVICH (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 412—417. Compare Abstr., 1911, ii, 973, 1078).—The authors continue the mathematical discussion of the interpretation of the results of the thermal analysis of quaternary systems and of their representation in a regular tetrahedron, dealing here with the information to be obtained by the study of plane sections of the tetrahedron parallel to a face.

R. V. S.

**The Equilibrium in Acid Solutions of Potassium Salts.** ALBERT J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1911, 25, 373—393).—The author has determined the constitution of the solid phase when solutions of potassium sulphate are mixed with either sulphuric, hydrochloric, or nitric acid in such proportions as to produce a solid phase. In the cases studied, the solid contained no hydrated salts. The mixtures were placed in sealed serum flasks, and kept for two months, being agitated each day. At the end of the time the composition of the liquid portion was determined, and that of the solid established by difference. The quantities used were measured in hundredths of a molecule, and two series of experiments were conducted, one at 18° and the other at 37°. The equations representing the equilibrium between the liquid and solid phases in each case are given.

In the system potassium sulphate, sulphuric acid, and water, the quantity of potassium sulphate in the liquid phase is found to diminish proportionately with the amount of sulphuric acid present. With a mixture of  $20\text{K}_2\text{SO}_4 : 10\text{H}_2\text{SO}_4$  or less, both at 18° and 37°, the solid phase consists entirely of the normal sulphate. Three new acid sulphates have been obtained, namely,  $3\text{K}_2\text{SO}_4, 2\text{KHSO}_4,$



and  $3\text{K}_2\text{SO}_4, 5\text{KHSO}_4$ .

In the system potassium sulphate, hydrochloric acid, water, with a concentration of acid equivalent to  $20\text{K}_2\text{SO}_4 : 20\text{HCl}$  or less, the presence of potassium chloride is not manifested in the solid phase at either temperature. With a concentration of 20 : 10 or less, the solid phase is entirely the normal sulphate.

In the system potassium sulphate, nitric acid, and water, the solid phase always consists of normal salts, and the limit between the production of nitrate or sulphate is found at a concentration of  $20\text{K}_2\text{SO}_4 : 20\text{HNO}_3$ .

W. G.

**Equilibrium in the System Potassium Iodide, Iodine, and Water.** CHARLES L. PARSONS and C. F. WHITTEMORE (*J. Amer. Chem. Soc.*, 1911, **33**, 1933—1936).—Parsons and Corliss (*Abstr.*, 1910, ii, 1061) have given an account of the mutual solubility of potassium iodide and iodine in dilute alcohol. A study has now been made of the solubilities in water at 25°, with reference to that part of the curve, representing complete saturation, which has not been plotted previously. The results prove conclusively that potassium polyiodides do not exist at 25°.

E. G.

**Equilibria in the System Silver Iodide, Potassium Iodide, and Water.** W. VAN DAM and A. D. DONK (*Chem. Weekblad*, 1911, **8**, 846—855).—The isothermals in the system silver iodide, potassium iodide, and water have been determined for 50°, 30°, and 0° by Schreinemaker's "residue method," and represented by his graphic method. At 0° the solid phase is  $\text{AgI}, \text{KI}$ ; at 30°,  $\text{AgI}, 2\text{KI}$ ; at 50°,  $\text{AgI}, \text{KI}$ .

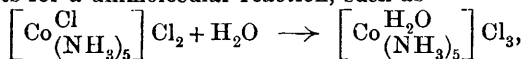
A. J. W.

**The Equilibrium in the System:  $\text{ZnSO}_4 + \text{KOH} + \text{H}_2\text{O}$ .** S. TSCHUMANOFF (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 230—233).—Varying quantities of potassium hydroxide were added to a fixed quantity of zinc sulphate, the system being then diluted with water to the same volume, and allowed to remain with frequent shaking for several days. At the end of this time, measurements were made of the electrical conductivity of the solution, and the composition of the solution and precipitate was determined. The conductivity continues to increase beyond the point corresponding with maximum precipitation, which behaviour is different from that observed in the system  $\text{ZnSO}_4 + \text{NH}_3 + \text{H}_2\text{O}$ . The deviation of the sulphate content of the precipitate from that of the solution reaches a maximum when 1.5 mols. of potassium hydroxide are added per mol. of zinc sulphate. Adsorption appears to take place, and zinc sulphate is more strongly adsorbed than potassium sulphate.

H. M. D.

**An Equilibrium in the Cobaltammines.** ARTHUR B. LAMB and JOHN W. MARDEN (*J. Amer. Chem. Soc.*, 1911, **33**, 1873—1911).—An account is given of an investigation of the mutual transformation of the purpureo-cobaltamine salts into the corresponding roseo-salts.

The velocities of transformation of the salts in dilute aqueous solution were determined. They were found to agree with the requirements for a unimolecular reaction, such as

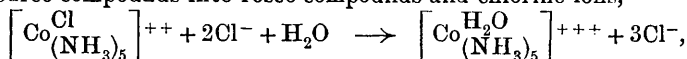


and were little affected by the acidity of the solution.

From a study of the decomposition velocities of the salts, a temperature of 70° was proved to be the best for equilibrium measurements. It was found that at this temperature a true equilibrium was established in the solution. In the case of the chlorides, the concentrations of the reacting substances and of other chlorides present were varied, and it was shown that the equilibrium is affected both

by the total concentration of the salt and by the concentration of the chlorine ion, but is independent of the acidity of the solution.

When the equilibrium was viewed as an electrolytic dissociation of purpureo-compounds into roseo-compounds and chlorine ions,



and their concentrations were substituted in the Storch-Bancroft modification of the concentration law, an approximate constant was obtained, whilst a further modification of this law gave an excellent constant. If this view is correct, the case is one of a slow electrolytic dissociation.

In the dry state, the roseo-salts have a critical aqueous vapour pressure above which only a very slow loss of water occurs; this change does not appear to be reversible. E. G.

**Chemical Equilibria in Solution.** RENÉ DUBRISAY (*Compt. rend.*, 1911, 153, 1076—1078).—If a number of substances dissolved in the same solvent are in chemical equilibrium and a chemically inert compound is added to the system, equilibrium should be displaced if the added compound is such as to diminish the solubility of any of the original components. This has been experimentally verified by examining the effect of acetone on the hydrolysis of bismuth nitrate in aqueous solution. It has been shown that acetone diminishes the solubility of the salt in dilute nitric acid, and that it diminishes the hydrolysis to an extent increasing with the amount of acetone added.

W. O. W.

**Steric Effects, Static and Dynamic.** OLIVER C. M. DAVIS (*Zeitsch. physikal. Chem.*, 1911, 78, 353—368. Compare *Trans.*, 1909, 95, 1397).—The equilibria between formic acid, a number of aromatic amines (aniline derivatives), and the resulting formanilides have been determined in a water-pyridine solution at 100°. That true equilibria were observed is shown by the fact that the same concentrations were reached by heating the components and by decomposing the anilides. The values of  $K = [\text{anilide}]/[\text{amine}][\text{acid}]$  obtained with varying concentrations of the reagents were only in moderate agreement. From the results the affinities have been calculated by the known formula:  $\text{Affinity} = 2.3026 RT \log_{10} K$ . In most cases they are positive, but are negative for the nitroanilines and for *o*-chloro- and *o*-bromo-aniline.

The relative influence of substitution in the ortho-, meta-, and para-positions depends on the nature of the substituents. The affinity is always least in the ortho-position. The affinity of aniline is lowered by ortho-substitution of the methyl and methoxy-groups, but is increased by meta- and para-substitution. The nitro-group lowers the affinity greatly in the ortho-position, and to a less extent in the meta- and para-positions. Change of temperature has very little effect on the equilibria. There is no direct connexion between the affinity of the components and the rate of decomposition of the anilides by sodium hydroxide.

A number of observations have also been made with acetic acid

in the same mixed solvent, but no true equilibria were observed, as the anilides, even on prolonged heating at  $100^\circ$ , are not as a rule decomposed by water. The equilibria of the formanilides in the absence of solvent have also been measured; most of the systems in this case are heterogeneous.

G. S.

**Possible General Relationship between the Structure of Organic Compounds and Their Equilibria.** JAMES W. MCBAIN and OLIVER C. M. DAVIS (*Zeitsch. physikal. Chem.*, 1911, **78**, 369—373. Compare preceding abstract).—It is shown that the effect of the following substituting groups: OMe, Cl, Br,  $\text{NO}_2$ , and  $\text{CO}_2\text{H}$  on the value of the equilibrium constant for the formanilides, on the dissociation constant,  $k_b$ , of the amines, and on the reciprocal of the dissociation constant,  $k_a$ , of the benzoic acids and the phenols is not only in the same direction, but there is even an approximate quantitative agreement in the influence of the substituting group on these very diverse equilibria. This result is also illustrated graphically, and its possible importance is discussed.

G. S.

**The Hypohalogenous Acids and the Hypohalogenites. V. Kinetics of the Formation of Iodate from Iodine and Hydroxyl Ion.** ANTON SKRABAL (*Monatsh.*, 1911, **32**, 815—903).—The formation of iodate according to the equation:  $3\text{IOH} + 3\text{OH}' = 2\text{I}' + \text{IO}_3 + 3\text{H}_2\text{O}$  having been previously investigated by the author (Abstr., 1911, ii, 382), an account is now given of its formation according to the equation:  $3\text{I}_3 + 6\text{OH}' = 5\text{I}' + \text{IO}_3 + 3\text{H}_2\text{O}$ . In the reaction mixtures used to determine the order of reaction, the concentration of the hydroxyl ion was kept small, but constant.

Hydroxyl ions accelerate and iodide ions retard the reaction, the velocity of which is given by the equation:  $-d[\text{I}_3]/d\theta = K[\text{I}_3]^x[\text{OH}']^y/[\text{I}']^z$ , in which  $x$ ,  $y$ , and  $z$  are positive. Electrolytes retard, and rise in temperature increases, the velocity of reaction. The values of  $x$ ,  $y$ , and  $z$  are dependent on the conditions of experiment. With relatively great  $[\text{OH}']$  and small  $[\text{I}']$ ,  $z=2$ , whilst with small  $[\text{OH}']$  and large  $[\text{I}']$ ,  $z=3$ , so that the course of the reaction depends on the experimental conditions. When the velocity of reaction is great, its course is represented by the equation:  $-d[\text{I}_3]/d\theta = 2[\text{OH}'][\text{I}_3]^2/[\text{I}]^3$  (reaction equation *B*), whilst when it is small the velocity equation is:  $-d[\text{I}_3]/d\theta = 1.5 \times 10^{-11}[\text{OH}]^4[\text{I}_3]^3/[\text{I}]^6$  (reaction equation *C*); at intermediate velocities the course of reaction is given by a combination of *B* and *C*.

The reaction *B* was determined by the method of Harcourt and Esson, using a solution containing sodium carbonate and sodium hydrogen carbonate to furnish the necessary concentration of hydroxyl ions. The temperature quotient is 6. The reaction *C*, which was also carried out in a solution of sodium carbonate and hydrogen carbonate, is of the 13th order, and has a temperature quotient of 23.

Consideration of the above results, together with those obtained by Dushman (Abstr., 1904, ii, 718), make the following reaction schemes probable: (1)  $\text{IOH} + \text{I}' \rightleftharpoons \text{I}_3\text{OH} + \text{OH}'$ ;  $\text{I}_3\text{OH} \rightarrow \text{IO}_3$ .

(2)  $2\text{I}'_3 + \text{OH}' \rightleftharpoons \text{I}_3\text{OH} + 3\text{I}'$ ;  $\text{I}_3\text{OH} \rightarrow \text{IO}'_3$ . (3)  $3\text{I}'_3 + 4\text{OH}' \rightleftharpoons \text{I}_3\text{O}'_2 + 6\text{I}' + 2\text{H}_2\text{O}$ ;  $\text{I}_3\text{O}'_2 \rightarrow \text{IO}'_3$ . (4)  $\text{IO}'_3 + 2\text{I}' + \text{H}_2\text{O} \rightleftharpoons \text{I}_3\text{O}'_2 + 2\text{OH}'$ ;  $\text{I}_3\text{O}'_2 \rightarrow \text{I}'_3$ . (5)  $\text{IO}'_3 + \text{I}' + \text{I}'_3 + \text{H}_2\text{O} \rightleftharpoons \text{I}_5\text{O}'_2 + 2\text{OH}'$ ;  $\text{I}_5\text{O}'_2 \rightarrow \text{I}'_3$ . The substances  $\text{I}_3\text{OH}$ ,  $\text{I}_3\text{O}'_2$ , and  $\text{I}_5\text{O}'_2$  are to be considered as loose compounds of iodine with hypoiodous acid, and with  $\text{IO}'_2$ , the anion of iodic acid, respectively. They result by the very rapid establishment of an equilibrium, and it is their further decomposition into  $\text{IO}'_3$  or  $\text{I}'_3$  which determines the velocity of reaction.

The author further develops a theory by means of which he is able to calculate the constants of the iodine-iodate and iodine-hypoiodite equilibria from the velocities of reaction, and the heats of reaction of the following reactions from the temperature quotients:  $\text{IO}'_3 + 8\text{I}' + 3\text{H}_2\text{O} = 3\text{I}'_3 + 6\text{OH}'$ ;  $\text{I}_2 + \text{OH}' = \text{I}' + \text{IOH}$ . The calculated and experimental numbers are in good agreement.

The paper concludes with a theoretical discussion of the relations between equations *B* and *C*. T. S. P.

**Re-investigation of the Velocity of Sugar Hydrolysis.** I. MARTIN A. ROSANOFF, R. H. CLARK, and R. L. SIBLEY (*J. Amer. Chem. Soc.*, 1911, 33, 1911—1924).—Armstrong and Caldwell (Abstr., 1904, i, 1070) made measurements of the velocity of hydrolysis of sucrose by very dilute acids which indicated that the reaction was not strictly unimolecular throughout, but that in the earlier stages the velocity coefficient showed a regular increase. Meyer (Abstr., 1908, ii, 265) made similar determinations in which the velocity coefficient showed a gradual decrease. The solutions used in such measurements are usually prepared by adding equal amounts of acid to equal volumes of a standard sucrose solution, and diluting with water to a multiple of the original volume. The solutions thus obtained are equally concentrated with respect to acid, but contain unequal quantities of water per unit volume. As the effect of unequal quantities of water on the catalytic power of an acid is not known, measurements have been made with three pairs of solutions, the concentrations of formic acid and water being the same in each pair, but the sugar in one solution of each pair being partly replaced by a sufficient quantity of an inert substance, such as dextrose, mannitol, or acetone to equalise the volumes. The two velocity coefficients of each pair were practically identical in each of the three cases. The results show that the constancy of the velocity of sucrose hydrolysis is not due to any specific effect of the invert sugar which gradually replaces the sucrose in an ordinary single experiment, and that the velocity coefficient is independent of the initial concentration of the sucrose.

It is shown that the variations in both Armstrong and Caldwell's and Meyer's results were due, not to side-reactions or deviations from the mass law, but to slight errors in the assumed values of the initial rotation. On re-calculating these authors' results with a correct value for the initial rotation, the velocity coefficient is constant, and proves that the hydrolysis proceeds in accordance with the mass law as a strictly unimolecular reaction.

Other experiments were carried out which show that in a sucrose

solution in course of hydrolysis, the specific rotation of lævulose is constant. In this case the water concentration remains practically constant, but in aqueous solutions of lævulose used in studying its rotatory power, the water concentrations are varied together with those of the lævulose itself. This suggested that the cause of the variation of the specific rotatory power of lævulose may lie in the varying water-content of the solutions employed. It is shown that such is the case, and that when the concentration of the water is kept constant, the specific rotation of lævulose is independent of its concentration.

E. G.

**The Limit of Diastatic Hydrolysis of Starch.** HENRI VAN LAER (*Bull. Soc. chim. Belg.*, 1911, 25, 393—401. Compare Abstr., 1910, ii, 839; 1911, ii, 28, 478).—A further critical consideration of the difference between the results of Brown and Glendinning (*Trans.*, 1902, 81, 388) and V. Henri (*Lois générales de l'action des diastases*, Paris) as to the law governing the hydrolysis of starch by diastase. The conclusions arrived at, after further experiments, using a solution of starch filtered through collodion, are the same as expressed in a previous paper (Abstr., 1911, ii, 28).

W. G.

**The Development of the Atomic Theory. VII. The Rival Claims of William Higgins and John Dalton.** ANDREW N. MELDRUM (*Mem. Manchester Phil. Soc.*, 1911, 55, No. 22, 1—11. Compare Abstr., 1911, ii, 708).—Historical.

**A Structural Theory of the Chemical Elements.** J. W. NICHOLSON (*Phil. Mag.*, 1911, [vi], 22, 864—889).—The theory put forward assumes that the elements are derived from certain primary substances or "protyles," the groupings of which in the different elements give rise to systems which appear to throw considerable light on the mutual relations of the elements. The primary elements, from the constituents of which all the others are supposed to be constructed, consist of single rings of electrons rotating round small nuclei of positive electricity. These nuclei are small compared with the electron, and represent almost the entire mass of the atom. Four such primary elements are supposed to exist, but only three are actually made use of in the synthesis of the other elements. The atoms of the four "protyles" contain respectively two, three, four, and five electrons which rotate round a positive nucleus.

If in a neutral atom of one of the primary elements there are  $n$  electrons with a charge,  $e$ , rotating round a positive nucleus of radius  $a$ , the inertia will be proportional to  $n^2e^2/a$ . If the positive electrical nucleus is of uniform density, its volume will be proportional to  $ne$ , and from this it follows that the inertia must be proportional to  $n^{\frac{5}{2}}$ . On the further assumption that the hydrogen atom contains three electrons, then by taking its atomic weight as 1.008, the atomic weights of the other three primary forms are respectively: coronium (Cn), 0.5131; nebulium (Nu), 1.6277; and protofluorine (Pf), 2.3604. The three primaries actually used in the structural synthesis are hydrogen, nebulium, and protofluorine, and it is shown

that the atomic weight values calculated for the various elements are in remarkably good agreement with the accepted experimental values. This result is particularly interesting in the case of the elements of low atomic weight, and the structure of these may be indicated. Helium (atomic weight = 3.99),  $\text{Nu} + \text{Pf} = 3.99$ ; glucinum (9.10),  $3\text{Pf} + 2\text{H} = 9.097$ ; boron (11.00),  $2(\text{Nu} + \text{Pf}) + 3\text{H} = 11.00$ ; carbon (12.00),  $2(\text{Nu} + \text{Pf}) + 4\text{H} = 12.008$ ; nitrogen (14.01),  $2(\text{Nu} + \text{Pf}) + 6\text{H} = 14.02$ ; oxygen (16.00),  $3(\text{Nu} + \text{Pf}) + 4\text{H} = 15.996$ ; fluorine (19.0),  $3(\text{Nu} + \text{Pf}) + 7\text{H} = 19.02$ ; neon (20.21),  $6(\text{Pf} + \text{H}) = 20.21$ ; sodium (23.005),  $4(\text{Nu} + \text{Pf}) + 7\text{H} = 23.008$ ; magnesium (24.32),  $2\text{H} + 5(\text{Nu} + \text{Pf}) + \text{Pf} = 24.32$ ; argon (39.88),  $10(\text{Nu} + \text{Pf}) = 39.88$ . The atomic weight of lithium appears to be somewhat uncertain, but the value accepted for the time being = 6.94 is very approximately represented by  $3\text{Nu} + 2\text{H} = 6.90$ .

In the case of the elements of higher atomic weight, the same method of representation can be carried out quite readily, but these cases obviously do not furnish such a satisfactory test of the author's hypothesis as do the elements of low atomic weight.

Special consideration is devoted to the inert gases, including the radioactive emanations, and it is shown that the structural hypothesis affords a plausible explanation of some of the radioactive processes and is consistent with certain spectroscopic observations. H. M. D.

**Chemical Compounds in Space.** PIETRO PALLADINO (*Riv. Fis. Mat. Sci. Nat. Pavia*, 1911, 12, No. 141, Reprint 44 pp.).—The ideas concerning the structure of substances mentioned previously (Abstr., 1909, ii, 562), which are based on the theory that matter is uniform, have been developed and rendered more precise in a paper already published (*Mon. Sci.*, 1910, 489), in which it was shown that the forms and relative dimensions of the combining quantities of elements can be calculated. In the present paper the physical and chemical properties of a number of elements and their compounds are discussed and explained by means of their space structure deduced in this way. The paper is illustrated by a large number of diagrams showing the structure of the elements and compounds considered. As a simple instance it may be mentioned that the unit combining quantity of oxygen is regarded as composed of five tetrahedra, which may be arranged in the "open" form (two solid edges of each tetrahedron in contact) or in the "closed" form (two faces of each tetrahedron in contact). Ordinary gaseous oxygen,  $\text{O}_2$ , is regarded as composed of a combination of a "closed" with an "open" form, and liquid oxygen,  $\text{O}_4$ , as consisting of a combination of two "open" with two "closed" forms. The elements discussed are sulphur, nitrogen, phosphorus, iron, manganese, and their compounds, and an explanation of optical activity in certain carbon compounds is also given. T. A. H.

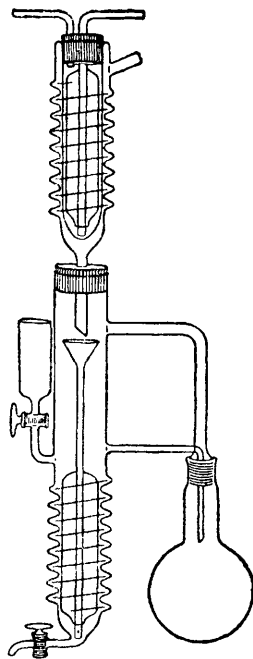
**The Periodic System.** K. SCHERINGA (*Chem. Weekblad*, 1911, 8, 868—869).—A graphic representation of the periodic system, considered by the author to combine the advantages of the usual arrangement and those of the atomic volume curve having as ordinates the logarithms of the atomic volumes, as suggested by Baur (Abstr., 1911, ii, 480). A. J. W.

**Manometer.** DAN RADULESCU (*Chem. Zentr.*, 1911, 82, ii, 1505; from *Bul. Soc. Sti. Bucuresti*, 20, 288—289).—The barometer tube is widened above into a bell-shaped chamber, and is closed by a thin glass slide. The apparatus is filled by dismantling the tube, removing the stopper, pouring in warm dry mercury, closing one end of the T-piece attached to the barometer tube, and blowing at the other end of the T-piece with a rubber bellows until the mercury sinks to the required level. The stopper is then placed in position, and is kept tight by the mercury remaining in the bell chamber. T. A. H.

**Simplified Arrangement for the Admittance of Air into Automatic Delivery Apparatus.** AUGUST SCHMIDT (*Chem. Zeit.*, 1911, 35, 1300).—An improved stopcock is described and figured for the use of automatic pipettes, burettes, and similar instruments. L. DE K.

**Automatic Filling Apparatus for a Constant Level of Liquid.** ERIK SCHIRM (*Chem. Zeit.*, 1911, 35, 1333).—The apparatus consists of a large bulb having a long stem; at the top of the bulb is a tap, the bore of which may be placed in communication with a side-tube on the neck of the bulb, and with a central tube reaching nearly to the lower end of the stem. When the bulb has been filled with liquid, the tap is turned so as to place the central tube in connexion with the side-tube (and thus with the open air), whilst the stem of the bulb is placed in the flask, basin, or filter into which the liquid is to be delivered gradually. W. P. S.

**A New Extraction Apparatus.** FRITZ FRIEDRICHS (*Zeitsch. anal. Chem.*, 1911, 50, 756).—The apparatus will be readily understood from the annexed figure. Ether is boiled in the flask, and the vapour escaping through the wide vapour tube is fully condensed in the screw-condenser, from whence it is carried through the funnel tube to the bottom of the screw-cylinder. From there it ascends in minute drops through the liquid to be extracted. When the ether layer reaches the lower tube the excess runs back into the flask, and so the process goes on. By means of the stopcock funnel and the lower stopcock, liquid may be introduced or drawn off without interrupting the extraction process. L. DE K.



**Improved Extractor.** C. A. JACOBSON (*J. Amer. Chem. Soc.*, 1911, 33, 2051—2052).—Extraction apparatus is described which acts on the well known continuous percolation principle. It consists of a

tube,  $3\frac{1}{2}$  feet long and 2 inches wide, the lower end of which is ground to fit into an adapter containing a perforated porcelain plate to support the material to be extracted. After the tube and the adapter have been filled with the substance, they are placed in an outer tube,  $2\frac{1}{2}$  inches wide, up which the vapours of the solvent ascend to the condenser. The condensed liquid falls into the inner tube, and thus renders the extraction continuous. Three glass beads are fused on to the exterior of the adapter in order to enable it to rest in the outside tube, and afford a space for the passage of the vapour from the receiving flask. The advantages of this apparatus are its simplicity, its large capacity, and the facility with which it can be emptied and refilled.

E. G.

**A Filtering Apparatus for Low Temperatures.** H. J. PRINS (*Chem. Weekblad*, 1911, 8, 874—875).—A description, with figures, of two forms of a readily constructed apparatus for the separation of solid and liquid phases at low temperatures.

A. J. W.

**Apparatus for Carrying Out Reactions under Exclusion of Air.** J. A. SIEMSEN (*Chem. Zeit.*, 1911, 35, 1317).—Fused into opposite sides of the neck of a conical flask are (1) a right-angled tube, which is further fused on to a separating funnel; (2) a right-angled tube with the open limb pointing vertically upwards. Fused into the hollow ground glass stopper of the flask, and opening into the flask, are two tubes, which, by appropriate turning of the stopper, can be connected at the same time with the funnel and right-angled tube.

The apparatus can be used by treating substances with various gases or liquids under exclusion of air, for bromination, acetylation, benzylation, etc.

T. S. P.

**Lecture Experiment on Nascent Hydrogen.** GEORGE S. FORBES (*J. Amer. Chem. Soc.*, 1911, 33, 1965—1966).—A few grams of magnesium ribbon are introduced into a flask containing sulphuric acid (15 c.c. of the concentrated acid per litre). Dilute solutions of ferric chloride and potassium ferricyanide are added in sufficient quantity to give the liquid a decided colour. On shaking the flask for a short time, a dark blue precipitate appears. To show that this effect is not produced, except in the presence of the nascent hydrogen, (a) magnesium is added to a dilute neutral solution of ferric chloride and potassium ferricyanide; (b) dilute sulphuric acid and magnesium sulphate are added to a second portion, and (c) hydrogen is bubbled through a third portion.

E. G.

## Inorganic Chemistry.

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**The Hydrogen Ion Concentration of Sea-water.** SVEN PALITZSCH (*Biochem. Zeitsch.*, 1911, 37, 116—130).—By means of Sørensen's indicator method, with the use of phenolphthalein and  $\alpha$ -naphtholphthalein, the concentration of the hydrogen ions was determined in sea-water taken in different parts of the North Sea, Mediterranean, and Black Sea during a voyage of investigation. The variations (with the exception of certain measurements made with water from the Black Sea) lay between  $p_H = 7.95$  and  $p_H = 8.35$ . S. B. S.

**The Iodine Oxides  $I_6O_{13}$  and  $I_{10}O_{19}$ , and Iodine Nitrate.** HANS KAPPELER (*Ber.*, 1911, 44, 3496—3501).—The author has prepared the compounds usually denoted as  $I_{10}O_{19}$  and  $I_6O_{13}$ , according to the details given by their discoverers (Millon, *J. pr. Chem.*, 1845, 34, 321; Kämmerer, *ibid.*, 1861, 83, 65, 72), and finds that they are identical with basic iodine iodate,  $I_2O_4$ . The analysis was carried out by decomposing them with water into iodine and iodic acid, and determining the ratio of the iodine to the iodic acid.

By the action of concentrated nitric acid ( $D = 1.52$ ) on finely powdered iodine at the ordinary temperature, a voluminous, yellow powder is produced, which can be collected and dried on a porous plate. It rapidly decomposes on exposure to light or moisture. Analysis by decomposition with water and estimation of the free iodine and iodic acid showed it to be an iodine nitrate, either  $I(NO_3)_3$ , or  $IO(NO_3)$ ; the decision between these two formulæ could not be made.

If in the oxidation of iodine or in the reduction of iodic acid, water is excluded as much as possible, the reaction ceases as soon as the stage  $I_2O_3$  is reached, and salts of tervalent iodine are produced; thus oxidation of iodine (1) with ozone gives  $I(IO_3)_3$  (Fichter and Rohner, *Abstr.*, 1909, ii, 991), (2) with nitric acid gives iodine nitrate; reduction of iodic acid by heating with concentrated sulphuric acid gives an iodine sulphate  $(IO)_2SO_4 \cdot \frac{1}{2}H_2O$ , whilst reduction with sulphur dioxide gives a similar sulphate or else a sulphite. Exposure of the iodine salts of volatile or deliquescent acids to moist air brings about slow decomposition. Hydrolysis takes place, and the residual oxide,  $I_2O_3$ , or the hydroxide,  $I(OH)_3$ , decomposes into hydriodic acid and iodic acid, or into iodine and iodic acid:  $15I(OH)_3 = 5HI + 10HIO_3 + 15H_2O = 3I_2 + 9HIO_3 + 18H_2O$ . This decomposition takes place so slowly with the sulphate, nitrate, and sulphite that the resulting iodic acid can react, to some extent, with part of the undecomposed salt, forming insoluble basic iodine iodate,  $I_2O_4$ , for example, according to the equation:  $(IO)_2SO_4 + 2HIO_3 = 2(IO)IO_3 + H_2SO_4$ ; the free iodine volatilises. With iodine acetate (Schützenberger, *Compt. rend.*, 1861, 52, 135; 1862, 54, 1026) and the iodine iodate,  $I_4O_9$ , the decomposition with water is too rapid for the formation of the basic iodine iodate to take place.

T. S. P.

**Action of Hydrogen Peroxide on Iodine Compounds Containing Oxygen.** VICTOR AUGER (*Compt. rend.*, 1911, 153, 1005—1007. Compare Abstr., 1911, ii, 386; Tanatar, Abstr., 1899, ii, 414; Péchard, *ibid.*, ii, 477).—The salt  $\text{Na}_2\text{H}_3\text{IO}_6$  is very slowly decomposed by hydrogen peroxide with formation of sodium iodate and liberation of a larger amount of oxygen than corresponds with the equation, this being due to catalytic decomposition of the peroxide. With periodic acid, the results vary considerably according to conditions. In dilute solutions the acid is rapidly and completely reduced to iodic acid, only a trace of iodine being liberated, whilst in concentrated solutions the reaction is incomplete and much iodine is formed. Cold solutions of hydrogen peroxide slowly decompose iodic acid in solutions containing less than 0.6%, iodine being set free. If the concentration of acid exceeds 0.8%, however, the solution remains colourless, owing to the fact that the reaction  $\text{I}_2 + 5\text{H}_2\text{O}_2 = 2\text{HIO}_3 + 4\text{H}_2\text{O}$  proceeds more rapidly than the reaction  $2\text{HIO}_3 + 5\text{H}_2\text{O}_2 = \text{I}_2 + 6\text{H}_2\text{O} + 5\text{O}_2$ . W. O. W.

**Production of Solid Oxygen by the Evaporation of the Liquid.** SIR JAMES DEWAR (*Proc. Roy. Soc.*, 1911, 85, A, 589—597).—By the use of charcoal as a gaseous condensing agent at low temperatures, combined with the employment of suitable vacuum vessels, the change from liquid oxygen into the solid can be easily effected. Pure liquid oxygen, contained in a properly isolated vessel, is subjected to the exhaust produced by a quantity of charcoal kept at about the temperature of boiling oxygen; the pressure is thereby lowered sufficiently to produce solidification to a transparent jelly.

The pressure at which solidification took place was determined by connecting a McLeod gauge to the vessel containing the solid oxygen, and from the results obtained and the application of the Rankine or Willard Gibbs vapour-tension equation, the melting point is calculated to be 53—55° abs. at a vapour pressure of 1.12 mm. Actual measurement with a hydrogen gas thermometer gave the value 54° abs. (compare Onnes and Crommelin, Abstr., 1911, ii, 854). T. S. P.

**The Formation of Ozone.** ANTON KAILAN (*Zeitsch. Elektrochem.*, 1911, 17, 966—967).—In the residues obtained in the fractionation of a gas containing a very high percentage of ozone, Harries found that there was a discrepancy between the iodometric and gravimetric estimations of the ozone, and came to the conclusion that this was caused by the presence of a constituent  $\text{O}_4$  (compare *ibid.*, 17, 629). The author points that if the molecule  $\text{O}_4$  contains two available oxygen atoms ( $\text{O}_4 = \text{O}_2 + \text{O} + \text{O}$ ), as assumed by Harries, both the iodometric and gravimetric estimations will give the same result for a mixture of  $\text{O}_3$  and  $\text{O}_4$ , so that the observations of Harries cannot be used in support of the existence of the molecule  $\text{O}_4$ ; they must be due to some, as yet, unknown cause. T. S. P.

**The System Sulphur.** ANDREAS SMITS and H. L. DE LEEUW (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 461—468. Compare Abstr., 1910, ii, 400).—An account is given of experiments to deter-

mine the influence of the percentage of  $S_{\mu}$  present on : (a) the transition point of monoclinic to rhombic sulphur ; (b) the freezing point of sulphur, with the formation of the monoclinic modification. The transition point may be lowered as much as  $10^{\circ}$ , and in some cases freezing-point temperatures as low as  $108^{\circ}$  were obtained, care being taken to avoid supercooling.

The apparent separation of liquid sulphur into two phases is brought about by the differences in temperature which arise in a column of the liquid, owing to the bad conduction of heat. In reality there is no formation of two phases, the differences in colour being accounted for by the differences in temperature.

T. S. P.

**The Electrolytic Preparation of Persulphates.** A. BLUMER (*Zeitsch. Elektrochem.*, 1911, 17, 965—966).—A platinum wire anode is described, which is held together by a glass frame of such shape that it forms a cage round the porous cell containing the catholyte ; the frame fits into a glass cylinder containing the anolyte. The whole apparatus is cooled by surrounding it with a jacket through which water flows continuously. The anode had a total length of 96 cm., the wire being 0.15 mm. in diameter, and current densities of 2.5—4.9 amperes per sq. cm. could be used, without the temperature of the anolyte rising above  $28$ — $29^{\circ}$  (compare Levi, Abstr., 1903, ii, 474). Lead cathodes did not give satisfactory results, but with nickel cathodes, keeping the electrolyte strongly acid by addition of sulphuric acid from time to time, yields of persulphate varying from 51—81% were obtained without a diaphragm, and 95—97½% yields with a diaphragm. (The particular persulphate obtained is not stated ; presumably it was ammonium persulphate.)

The claims of the Ger. Pat. 205067—8 (Abstr., 1909, ii, 312) with respect to the effect of the addition of ferrocyanides on the yield of ammonium persulphate were verified, yields as high as 93.5% being obtained. The addition of aluminium sulphate did not give such good results (50—62% yield) ; with cobalt sulphate a 60% yield was obtained.

T. S. P.

**The Oxidation of Nitrogen by the Electric Discharge in the Presence of Ozone.** VIKTOR EHRLICH and FRANZ RUSS (*Monatsh.*, 1911, 32, 917—996).—By the action of the silent electric discharge on still mixtures of nitrogen and oxygen, the authors have been able to obtain high percentage oxidation of the nitrogen, in accordance with the following table :

Original % (vol.) of oxygen in the mixture.....	5	20.8	50	75	91.5%
Maximum % (vol.) of nitric oxide, in terms of the final volume of gas .....	0.2	4.1	13.2	18.0	21%

The high percentage of nitric oxide thus obtained is not due to an equilibrium attained under the influence of the electrical discharge, but to a coupling of electrical and chemical processes. Ozone in excess oxidises the nitric oxide formed to nitrogen pentoxide, thus causing the further formation of nitric oxide. The formation of nitric oxide is one

of zero order, and takes place so long as ozone is in excess ; when all the ozone has been used up, further discharge decomposes the nitrogen pentoxide with the formation of nitrogen tetroxide. This then further decomposes almost completely, giving a new equilibrium which is conditioned by the nitric oxide equilibrium under the conditions of experiment, and by the velocity of formation of ozone.

The available ozone increases with increasing concentrations of oxygen in the initial mixture, and consequently also the maximum amount of nitric oxide formed, until all the nitrogen has been oxidised. Above this limiting concentration a stationary condition is attained, which is dependent on the ozone and nitrogen pentoxide.

Under given electrical conditions the velocity of formation of nitric oxide is independent, within wide limits, of the composition of the initial mixture, whereas the velocity of ozone formation increases with the oxygen content of the original mixture. However, when the gaseous mixtures are poor in nitrogen, there is some retardation in the velocity, probably because of diminished conductivity.

Variation in the electrical conditions for a given mixture has no effect on the course of reaction, since the velocities of formation of nitric oxide and ozone are affected in the same direction ; there are, however, effects on the relative velocities of these reactions, so that the maximum amount of nitric oxide formed is altered. For example, increase in the electrical energy, or diminished gas pressure, gives lower values for the maximum amount of nitric oxide produced.

The increased velocity of decomposition of ozone, caused by the presence of nitrogen pentoxide, is independent of the concentration of the ozone within certain limits.

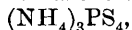
T. S. P.

**Thiophosphates and Thiophosphites.** FRITZ EPHRAIM and REBECCA STEIN (*Ber.*, 1911, 44, 3405—3413. Compare Glatzel, *Abstr.*, 1905, ii, 318).—In aqueous solution the tetrathiophosphates are subject to a kind of hydrolysis whereby the sulphur is either completely or partly replaced by oxygen. It is probable that sodium tetrathiophosphate, for example, gives rise to the equilibrium:  $2\text{Na}_3\text{PS}_4 \rightleftharpoons 3\text{Na}_2\text{S} + \text{P}_2\text{S}_5$ , and that the phosphorus pentasulphide then undergoes decomposition with evolution of hydrogen sulphide, whereby the equilibrium is disturbed. A consideration of this equilibrium equation shows that the tetrathiophosphates would probably exist in the presence of excess of the alkali sulphide, and the authors have succeeded in preparing a number of such salts by the interaction of phosphorus pentasulphide and excess of alkali sulphide. When tetraphosphorus trisulphide or heptasulphide is used in place of the pentasulphide, the thiophosphites are formed.

*Potassium tetrathiophosphate*,  $\text{K}_3\text{PS}_4 \cdot \text{H}_2\text{O}$ , is prepared by heating an intimate mixture of 100 grams of crystallised potassium sulphide and 7.5 grams of phosphorus pentasulphide until the former compound melts in its water of crystallisation. Before fusion is complete, 30 c.c. of water are added, and after the whole mass has become liquid it is filtered through a hot water funnel. On cooling, the filtrate deposits microscopic crystals of the required salt, in the form of quadratic rods. The yield is only 0.4 gram, the main quantity of the salt remaining

in solution, from which it is impossible to obtain it free from potassium sulphide. The crystals are fairly stable in the air, and can be preserved unchanged for weeks over concentrated sulphuric acid, except for gradual loss of water of crystallisation; they undergo dehydration at  $90^{\circ}$ .

The preparation of other thiophosphates is similar in principle to that of the potassium salt. *Ammonium tetrathiophosphate*,



forms thin, rhombic leaflets, or else thick prisms, which can be dried in the air without loss of ammonia. The yield is better than that obtained with the potassium salt. *Barium tetrathiophosphate*,  $\text{Ba}_3(\text{PS}_4)_2$ , aq., forms microscopic needles, as also does *strontium trithiophosphate*,  $\text{Sr}_3\text{H}_6(\text{PS}_3\text{O})_4$ , aq.; the sulphur content of the latter compound varies with small changes in the conditions, in one case a compound of the composition  $\text{Sr}_2\text{H}_6(\text{PS}_{3.5}\text{O}_{0.5})_4$  being obtained. Calcium and aluminium thiophosphates could not be prepared.

The thiophosphites are prepared similarly to the thiophosphates, as indicated above; phosphorus hydrides are, however, evolved to some extent, showing that the reaction is not purely one of addition of the components. *Sodium trithiophosphite*,  $\text{Na}_3\text{PS}_3$ , aq., forms rectangular plates, which are very soluble in water; the crystals are stable in dry air and do not lose their glance. *Barium trithiophosphite*,  $\text{Ba}_3(\text{PS}_3)_2$ , aq., forms white, microscopic, rhombic prisms, whilst *barium oxythiophosphite*,  $\text{Ba}_3(\text{PS}_{5/6}\text{O}_{1/6})_2 \cdot 8\text{H}_2\text{O}$ , forms microscopic, flat crystals.

T. S. P.

**Arsenic Tri-iodide.** ERW. RICHTER (*Chem. Zentr.*, 1911, 82, ii, 935; from *Apoth. Zeit.*, 26, 728—730, 742—743).—The product obtained by keeping a mixture of arsenious acid (10 grams) with iodine (5 grams) is extracted with carbon disulphide and the solvent allowed to evaporate, when garnet- to scarlet-red, hexagonal crystals of arsenic tri-iodide separate, and may be dried at  $50$ — $70^{\circ}$ . This leaves 8—9% of residue when treated with water, and rather more when water containing alcohol is used. A 1% solution in water, or in water containing 5—10% of alcohol, is stable. The product may be assayed by titration first with  $N/10$ -potassium hydroxide and then with  $N/10$ -iodine. Commercial preparations should contain 97% of real iodide.

T. A. H.

**Properties and Preparation of Boron.** EZECHIEL WEINTRAUB (*J. Ind. Eng. Chem.*, 1911, 3, 299—301).—A description of the properties of boron when isolated in the pure fused condition, an account of the methods used in its preparation, with a discussion on the agreement of these properties with its position in the periodic classification and the possibilities of its future industrial employment.

Boron has a curved conchoidal fracture, is very hard, scratching all known substances except diamond; the surface is very shiny, black, and takes a beautiful polish, but as at present prepared it lacks toughness. The m. p. lies between 2000 and  $2500^{\circ}$ , and it is somewhat volatile, exhibiting an appreciable vapour-tension at  $1200^{\circ}$ .

The electrical properties are entirely unexpected, when cold boron is a very poor conductor its specific resistance being about  $10^{12}$  times

that of copper; this resistance drops as the temperature rises, and between room temperature and about  $400^{\circ}$  this drop is in the approximate ratio of  $2 \times 10^6$  to 1. Its behaviour is more like that of a spark gap or arc than that of a solid conductor, there existing a "break down" voltage in the case of boron as in that of an air gap; this relationship between temperature and resistance has been studied up to red heat.

Two methods of preparation are employed: in the first boric anhydride is reduced by means of magnesium, and the impure boron so obtained then heated to almost its melting point, when magnesium and nitrogen volatilise in the elemental form, and oxygen is eliminated as boric anhydride.

The second method is based on the decomposition of boron chloride by hydrogen at a red heat, and is carried out in two ways: (a) in an arc discharge taking place between two boron or (water-cooled) copper electrodes in an atmosphere of boron chloride and hydrogen; (b) by deposition on a hot graphite tube heated by a current passing through it, when, if the conditions are properly adjusted, there is practically no combination between the graphite and boron.

Boron chloride is best obtained by passing chlorine over boron carbide, which may be prepared in the electric furnace from boric anhydride and carbon.

F. M. G. M.

**Silicon Hydride at Low Temperatures.** KAROL ADWENTOWSKI and EDWARD DROZDOWSKI (*Bull. Acad. Sci. Cracow*, 1911, 4, 330—344).—Pure silicon hydride can only be obtained after repeated fractionation of the gas prepared either by the method of Friedel and Ladenburg (*Annalen*, 1867, 143, 123) or that of Moissan and Smiles (*Abstr.*, 1902, ii, 318). By the latter method (the action of concentrated hydrochloric acid on magnesium silicide), liquid as well as gaseous fractions were obtained; the liquid was not a pure substance, but probably a mixture of several silicon hydrides.

The pure gas is spontaneously inflammable in open vessels where the surface in contact with the air is large; the inflammability is not due to the presence of impurity. One litre at  $0^{\circ}$  and 760 mm. weighs 1.4538 grams. The critical temperature is  $-3.5^{\circ}$ , the critical pressure 47.8 atmospheres, and the boiling point  $-116^{\circ}/740$  mm. E. F. A.

**The Melting of Carbon by means of the Joule Effect.** M. LA ROSA (*Ann. Physik*, 1911, [iv], 36, 841—847.\* Compare *Abstr.*, 1909, ii, 399, and *Ann. Physik*, 1911, [iv], 34, 95).—The changes observed by Watts and Mendenhall (*Abstr.*, 1911, ii, 881) in carbon rods subjected to a strong current are considered to be mainly due to impurities in the carbon. When rods, purified by heating for some hours in a current of chlorine, are employed, deformation is not observed until much higher temperatures are reached. In opposition to Watts and Mendenhall, the author maintains that the structural changes found in carbon after the passage of a strong current can only be accounted for satisfactorily on the assumption that a partial liquefaction takes place.

H. M. D.

\* and *Nuovo Cim.*, 1911, [vi], 2, ii, 418—424.

**The Deposition of Carbon in the Form of Diamond.** WERNER VON BOLTON (*Zeitsch. Elektrochem.*, 1911, 17, 971—972).—In 1910 the author found that hydrocarbons are decomposed by amalgams, for example, by sodium amalgam, with deposition of carbon, which is amorphous for the most part, but contains some crystalline particles which are probably diamonds. The amount of these crystals obtained hitherto has been too small for analysis, and the author has endeavoured to increase the quantity as follows: a 14% sodium amalgam was put in a test-tube and covered with a dilute solution of sodium silicate containing very fine diamond dust in suspension. The test-tube was heated at 100° for four weeks, moist coal gas being passed continually over the surface of the amalgam by means of a tube passing through the sodium silicate solution. The diamond dust used showed a few crystalline particles under a magnification of 68, but after the end of the experiment the number of such particles had greatly increased. These particles had the properties of diamonds, disappearing completely on heating in a current of oxygen and dissolving in fused sodium carbonate; their amount (less than 1 mg.) was, however, too small for analysis. The results show that the crystalline particles in the diamond dust act as nuclei for the deposition of carbon in the form of diamond from the hydrocarbons in the coal gas.

T. S. P.

**The Formation of Carbamide by Heating Ammonium Carbamate.** FRITZ FICHTER and BERNHARD BECKER (*Ber.*, 1911, 44, 3473—3480).—A systematic investigation of the dehydration of ammonium carbamate to carbamide (compare Basaroff, this Journ., 1868, 21, 194, and Bourgeois, *Abstr.*, 1898, i, 564).

Ammonium carbamate was prepared by the interaction of gaseous ammonia and carbon dioxide in a wide glass tube enclosing a water-cooled narrower tube; the salt deposited on the latter in hard crusts. The results of earlier workers appear to have been vitiated by the presence of traces of alcohol introduced by the method of preparation involving the use of this liquid.

For the experiments, the substance was enclosed in a small steel bomb lined with tin; after heating, the bomb was re-opened and the yield of carbamide estimated. The results of a series of tests show that under otherwise similar conditions the yield of carbamide rises rapidly from 115° to 135°, and then slowly falls again. Experiments performed at 135° indicate that the yield is improved considerably by a closer packing of the substance; under these optimum conditions 40% of the carbamate is converted into carbamide in the course of four days, whilst the final yield is approached even at the end of twenty-four hours.

The investigation indicates that it is the unvaporised ammonium carbamate which undergoes dehydration to carbamide, the diminution in the yield above 135° being due to the larger proportion vaporised. A calculation elicits the fact that at 135°, whatever the amount of carbamate taken, an approximately constant percentage (42%) of the unvaporised portion is converted into carbamide. The change is an equilibrium one, and a final mixture of the same composition

is reached whether, for example, one starts with ammonium carbamate or with a corresponding amount of an equimolecular mixture of carbamide and water.

Ammonium carbonate and hydrogen carbonate likewise give an incomplete change into carbamide, the results indicating that, of the compounds of ammonia and carbon dioxide, only ammonium carbamate is stable under pressure at 135°.

D. F. T.

**The Gaseous Condensable Compound, Explosive at Low Temperatures, Produced from Carbon Disulphide Vapour by the Action of the Silent Electric Discharge.** II. SIR JAMES DEWAR and HUMPHREY O. JONES (*Proc. Roy. Soc.*, 1911, 85, A, 574—588).—The explosive properties of the product previously described (now called the "ozoniser product") (*Abstr.*, 1910, ii, 408) are not due to the presence of impurities in the carbon disulphide used. The ozoniser product is formed whether the ozoniser is cooled to  $-80^{\circ}$  or heated to  $220^{\circ}$ , but the quantity obtained is less than under the ordinary conditions of temperature. No difference in its behaviour has been traced to variations in the amount of carbon disulphide condensed with it.

The interposition of a cotton-wool filter between the ozoniser and the condenser for collecting the ozonised product diminishes the intensity of the phenomena observed in the condenser to a very considerable extent, and at the same time increases the rate at which brown solid is deposited in the ozoniser and leading tubes. At  $-210^{\circ}$  the ozoniser product collected is perfectly white at first, but even at this temperature it becomes brown after about fifteen minutes. Examination of the gas after it left the ozoniser by means of a beam of light did not reveal the presence of solid particles, indicating that the transformation into the brown solid takes place only in contact with solid surfaces. The spectrum of the flash produced during the transformation showed the presence of sulphur bands (wave-lengths 384—392), hydrocarbon bands, especially that of wave-length 436—443, the cyanogen line (3885), and various other bands. There is practically no electric effect, even with the brightest flashes, during the transformation.

By the passage of the ozoniser product through a U-tube at  $-120^{\circ}$  and then into one at  $-185^{\circ}$ , it was found possible to separate it into two parts. A white, crystalline deposit collects at  $-120^{\circ}$ , which does not melt until the temperature has risen almost to  $0^{\circ}$ ; the substance which gives rise to the brown solid is not condensed at  $-120^{\circ}$ , but is collected at  $-185^{\circ}$ .

The ozoniser product is absorbed, destroyed, or caused to polymerise by coconut charcoal, either at  $-78^{\circ}$ , or at  $250^{\circ}$ , or at the ordinary temperature. When passed over finely shredded rubber some of the carbon disulphide is removed from the gas.

The brown solid product, and also the material deposited in the ozoniser, after removal of free sulphur had a composition agreeing approximately with the formula CS.

The ozoniser product is destroyed by finely-divided platinum, nickel, or silver; ferric oxide (not ignited), yellow mercuric oxide,

silver oxide, and barium peroxide react with it, giving sulphides. Solid potassium hydroxide, silver nitrate, lead acetate, and sodium peroxide have little or no action. Nitric acid and concentrated sulphuric acid bring about decomposition.

Mixture of carbon disulphide vapour with hydrogen, nitrogen, ether, methyl iodide, or chloroform has no effect on the phenomena observed. The vapours of thiocarbonyl chloride, ethyl thiocarbonate, ethyl dithiocarbonate, ethyl trithiocarbonate, and thiophen do not give rise to carbon monosulphide.

Comparison of the properties of the brown substance produced as above and the polymeric form of carbon monosulphide obtained from thiocarbonyl chloride (Abstr., 1910, ii, 408) shows that they possibly differ in degree of polymerisation. The product obtained by Sidot (this Journ., 1875, 28, 1236) is also a polymeric form of carbon monosulphide.

The specific heat between  $15^{\circ}$  and  $-185^{\circ}$  of the polymeric form of carbon monosulphide obtained from thiocarbonyl chloride is 0.127, the molecular heat being 5.59, as compared with the calculated value 5.556. The heat of combustion is 178,050 cals., and the heat of formation  $-10,000$  cals.

T. S. P.

**Ratios of the Rare Gases to One Another and to Nitrogen in Mine Gases.** CHARLES MOUREU and ADOLPHE LEPAPE (*Compt. rend.*, 1911, 153, 1043—1045. Compare Abstr., 1911, ii, 808, 1087, 1134).—The results of new analyses are given. The ratios of the rare gases to one another confirm the conclusions set forth in previous communications. There is evidence that coal exerts a selective action towards the heavier rare gases, thus tending to reduce slightly below normal the ratio between argon and the other gases in mixtures occurring in coal mines.

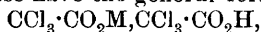
W. O. W.

**The Thermal Analysis of Binary Mixtures of Chlorides of Elements of the Same Valency.** CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 503—510).—The binary mixtures of chlorides which have been studied by means of thermal analysis are examined in the light of the rules given by Tamman for metallic alloys (Abstr., 1906, ii, 346; 1907, ii, 857) and by Herrmann for salts (Abstr., 1911, ii, 801), and the results confirm the latter's conclusions. Of the univalent metals, a close similarity occurs between potassium, rubidium, and thallous chlorides, whilst lithium, sodium, cuprous, and silver chlorides also form a group. The bivalent metals are also compared, the three sub-groups being calcium, strontium, and barium chlorides; cadmium and mercuric chlorides; and stannous, lead, and manganous chlorides.

C. H. D.

**A Remarkable Case of Isopolymorphism with Salts of the Alkali Metals.** FRANS M. JAEGER (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 356—369).—The author points out that the conclusions drawn by Tutton from his researches on the sulphates, selenates, double sulphates, and double selenates of the alkali metals are too general, since they are not supported by the results obtained

with other salts of these metals. As a further contribution to the subject, the full crystallographic data for various acid trichloroacetates are given; these have the general formula



where M represents a univalent metal, and a comparison of them is given in the following table:

Salt.	Habit.	D <sup>18</sup> -20.	Molec. vol.	Axial ratio.
Potassium	Tetragonal-trapezohedric	2.005	182.04	$a:c=1:0.7808$
Ammonium	"	1.775	193.80	$a:c=1:0.7678$
Rubidium	Monoclinic-prismatic ...	2.150	191.21	$a:b:c=1.4649:1:3.1596$
Cæsium	{ Monoclinic-prismatic (pseudo-tetragonal) }	2.143	214.18	{ $a:b:c=1.0434:1:0.9706$ $a:b:c=0.9968:1:0.2538$ }
Thallium	Tetragonal-trapezohedric	2.822	187.74	$a:c=1:0.7672$
Thallium*	Monoclinic-prismatic ...	3.923	203.16	$a:b:c=1.5515:1:3.3007$

\* *Acid thallium tribromoacetate*,  $\text{CBr}_3 \cdot \text{CO}_2\text{Tl}$ ,  $\text{CBr}_3 \cdot \text{CO}_2\text{H}$ .

The acid trichloroacetates of the alkali metals thus give an isopolymorphous series; in all probability it is an isotetramorphous series with three monoclinic and one tetragonal-trapezohedric modification.

The thallium and ammonium salts probably give a continuous series of mixed crystals; they are undoubtedly isomorphous. From mixtures of potassium and rubidium salts the first fractions are crystals analogous to those of the rubidium salt, whilst the last fractions contain both monoclinic and tetragonal double pyramids. Mixed crystals of the potassium and cæsium salts exhibit the form of the rubidium salt. The potassium and ammonium salts give mixed crystals possessing solely the tetragonal-bipyramidal form. From solutions containing the rubidium and thallium salts, mixed crystals of the form of the rubidium salt alone are obtained. Mixtures of cæsium and thallium salt of low thallium content give mixed crystals having the form of the rubidium salt; when the concentration of the cæsium salt is very great there are also found mixed crystals exhibiting the form of the first cæsium salt. Mixed crystals of the rubidium type appear first from mixtures of the cæsium and rubidium salts; with very high concentration of the cæsium salt, mixed crystals of the cæsium type are also deposited.

T. S. P.

**The Capacity of Potassium Halides for Forming Solid Solutions in Relation to Temperature.** MARIO AMADORI and G. PAMPANINI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 473—480).—In the present paper, the miscibility of pairs of the solid potassium halides at 25° is studied, as the first part of an investigation of the change of miscibility with temperature. The solubility in water is determined at 25°, fifteen to twenty days being allowed for the attainment of equilibrium, and curves are drawn showing the ratio between the two salts in the crystals and in the solution.

Potassium chloride and potassium bromide are completely miscible in the solid state at 25°. The curve for potassium bromide and iodide is discontinuous, indicating a gap in the miscibility from 25 to 94 mol. % KBr, and the curve for potassium chloride and iodide shows a similar gap, extending from 7 to 99 mol. % of chloride. C. H. D.

**Occurrence of Potassium Nitrate in Western America.** ROBERT STEWART (*J. Amer. Chem. Soc.*, 1911, 33, 1952—1954).—Crude potassium nitrate containing some calcium sulphate has been found in sandstone in the State of Utah. It is suggested that the existence of such deposits may have some bearing on the occurrence of excessive quantities of nitrates in some of the agricultural soils of the Western States. E. G.

**Experiments with Sodium Silicate.** W. J. CLUNIES ROSS (*J. Proc. Roy. Soc. New South Wales*, 1910, 44, 583—592).—Crystals of various salts are dropped into a solution of sodium silicate, D 1.08, contained in test-tubes or cylinders. Growths, resembling plant shoots, are obtained from salts of silver, mercury, lead, copper, iron, aluminium, cobalt, nickel, manganese, zinc, cadmium, calcium, zirconium, yttrium, and cerium. Antimony, uranium, tin, and bismuth do not yield shoots. The growths are coloured when coloured salts are used, but the silicate solution surrounding them does not become coloured, except in the case of manganese. The form of the growths is generally characteristic of the metal, cadmium giving hair-like filaments, and nickel, thick, fungoid forms. The growths are probably tubular, and act as semi-permeable membranes. C. H. D.

**Dimorphism of Rubidium Dichromate.** JOSEPH A. LEBEL (*Compt. rend.*, 1911, 153, 1081).—From acid solutions of rubidium dichromate the red variety alone crystallises, whilst in presence of a little alkali, only the yellow modification separates. It has usually been supposed that the dimorphism is conditioned by temperature alone, and that the solubility of the two forms is the same. This is negatived by the observation that a red crystal placed in a solution from which yellow ones are separating goes completely into solution. W. O. W.

**Solubility of Silver Chloride in Chloride Solutions and the Existence of Complex Argentichloride Ions.** GEORGE S. FORBES (*J. Amer. Chem. Soc.*, 1911, 33, 1937—1946).—Determinations have been made of the solubility at 25° of silver chloride in concentrated solutions of the chlorides of sodium, calcium, ammonium, strontium, potassium, and barium, and also of hydrochloric acid. The temperature-coefficient of the solubility was determined in 3*N*-potassium and calcium chlorides at 1°, 25°, and 35°. The solubility is nearly doubled by an increase of the temperature from 0° to 25°, the rate of increase above and below 25° being nearly logarithmic. The solubility is closely proportional to integral powers of the chloride concentration throughout considerable ranges, which is explained by assuming the existence of the complex anions,  $\text{AgCl}_3''$ ,  $\text{AgCl}_4'''$ , and possibly  $\text{AgCl}_5''''$ . No evidence was obtained of the existence of the ion  $\text{AgCl}_2'$ . It is shown that the extent of complex formation by mercurous and silver chlorides is not proportional to the activity of the chloride ion in concentrated solutions. The data obtained in this investigation lead to the conclusion that silver chloride should be least soluble in *N*/100-chloride solutions, a fact which is of importance in analytical work. E. G.

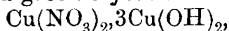
**Thermal Analysis of Binary Mixtures of Calcium Chloride with Chlorides of Other Bivalent Elements.** CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 496—503).—Calcium chloride forms a continuous series of solid solutions with strontium, cadmium, and manganous chlorides, the freezing-point curve in each case having a minimum, which occurs at 646°, 545°, and 583° respectively. In the case of mixtures of calcium chloride with strontium and manganous chlorides, a development of heat at lower temperatures is also observed over a certain range of composition, indicating a decomposition of the solid solutions.

Mixtures of calcium chloride with barium chloride and with lead chloride form simple eutectiferous series, the eutectic points being at 600° and 35 mol. %  $\text{BaCl}_2$ , and at 468° and 83 mol. %  $\text{PbCl}_2$  respectively.  
C. H. D.

**The Plasticity of Barium Sulphate.** ALBERT ATTERBERG (*Zeitsch. angew. Chem.*, 1911, 24, 2355).—Polemical. A reply to Ehrenberg's criticism (*Abstr.*, 1911, ii, 972) of the author's paper (*ibid.*, 605).  
C. H. D.

**The Replacement of Metals from Aqueous Solutions of their Salts by Hydrogen at High Temperatures and Pressures.** WLADIMIR IPATIEFF (*Ber.*, 1911, 44, 3452—3459. Compare *Abstr.*, 1911, ii, 716).—In the presence of copper, *N*-nitric acid is reduced completely to ammonia by hydrogen under 100 atmos. pressure at 150—160°; in the absence of copper no reduction takes place.

In solutions of 2*N*-copper nitrate at temperatures of 100—180° and initial pressures of 100 atmos., hydrogen gives rise, at first, to the production of emerald-green crystals of the compound



which is identical with the mineral gerhardtite; nitrous acid is produced at the same time, in quantities varying with the experimental conditions. Prolonged reaction produces black, hard crystals of cupric oxide, and finally a mixture of cupric oxide and copper forms the only product. With *N*-copper nitrate the above-mentioned complex compound is produced only in traces, even at 140—160°; at 100—120° crystallised cuprous oxide is formed, together with traces of metallic copper. Above 120°, cupric oxide and copper are deposited, the quantity of copper increasing with the time of reaction. At 155°, after forty-eight hours, pure copper is the final product, a result which could not be obtained with 2*N*-copper nitrate.

At 155° and an initial hydrogen pressure of 100 atmos., a 2*N*-solution of cupric chloride gives crystals of cuprous chloride; under the same conditions, and even at 180°, a *N*/5-solution gives rise to a mixture of cuprous chloride and copper.

In a quartz tube at 186—240° and initial pressures of 100 atmospheres, hydrogen causes precipitation of nickel from a *N*/5-solution of nickel sulphate, but the precipitation is not complete, even after thirty hours; when a glass tube is used, complete precipitation of the nickel takes place. From a 2*N*-solution of nickel sulphate in quartz tubes, the compound  $\text{NiSO}_4 \cdot \text{H}_2\text{O}$  is produced, whether the tube contains

hydrogen, nitrogen, or air, under pressure. This compound is green and crystalline, insoluble in water, and does not lose water at  $270^{\circ}$ ; when hydrogen is used, it is always mixed with traces of nickel.

In the presence of reduced nickel, *N*- and *N*/10-solutions of nitric acid are reduced completely to ammonia by hydrogen under pressure. In a glass tube at  $200^{\circ}$ , and initial pressure of 100 atmospheres, hydrogen causes the precipitation of a green hydrated nickelous oxide (61.04—61.95% Ni) from a *N*/5-solution of nickel nitrate. In a quartz tube, metallic nickel is also deposited (at  $210^{\circ}$ ), and at  $230$ — $250^{\circ}$  a blackish-grey precipitate of a mixture of nickel and nickelous oxide is formed.

A *N*/5-solution of nickel acetate at  $120^{\circ}$  gives a precipitate of hydrated nickelous oxide; nickel is deposited at  $168^{\circ}$ . From a *N*/5-solution of nickel chloride at  $230$ — $240^{\circ}$ , small quantities of nickel are deposited, but the reaction is far from complete. T. S. P.

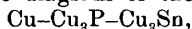
**Preparation of Colloidal Copper.** J. GAUBE DU GERS and W. KOPACZEWSKI (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 239—240).—Twenty grams of powdered egg-albumin are treated with 20 c.c. of 15% sodium hydroxide and diluted to a litre. The liquid is then heated to its boiling point, filtered from the coagulated albumin, again heated to boiling, after which a 1% solution of copper sulphate is added drop by drop. The liquid assumes a red colour, but this changes to violet and finally to reddish-brown. On dialysing the reddish-brown solution, a colloidal solution of copper albuminate is obtained. This solution does not give the reactions for copper unless the complex albuminate is decomposed. It is almost neutral towards litmus, can be concentrated on a water-bath, and its refractive index at  $20^{\circ}$  is 1.319.

The albuminate is reduced by hydrazine hydrate only after prolonged boiling of the solution. H. M. D.

**Constitution of Phosphor Bronzes.** MARIO LEVI-MALVANO and F. S. OROFINO (*Gazzetta*, 1911, 41, ii, 297—314).—The study of the system Cu—P has shown the existence of a compound  $\text{Cu}_3\text{P}$  (Heyn and Bauer, Abstr., 1906, ii, 855), whilst in the examination of the system Cu—Sn a compound  $\text{Cu}_3\text{Sn}$  was encountered (Giolitti and Tavanti, Abstr., 1908, ii, 946). The authors have, therefore, investigated the binary system  $\text{Cu}_3\text{P}$ — $\text{Cu}_3\text{Sn}$ , and the ternary system Cu— $\text{Cu}_3\text{P}$ — $\text{Cu}_3\text{Sn}$ .

The compound  $\text{Cu}_3\text{Sn}$  has m. p.  $710^{\circ}$  (Giolitti and Tavanti found  $725^{\circ}$ ); its transformation point lies at  $630^{\circ}$  (Giolitti and Tavanti gave  $659^{\circ}$ ). The diagram of the binary system  $\text{Cu}_3\text{P}$ — $\text{Cu}_3\text{Sn}$  is characterised by the presence of an eutectic corresponding with  $650^{\circ}$  and (probably) 22% of  $\text{Cu}_3\text{P}$ .

The authors discuss the diagram of the ternary system



as constructed with the aid of those of its three constituent binary systems. The results of the thermal investigation of a number of alloys belonging to this ternary system are also given and interpreted. The paper is illustrated with a number of photomicrographs.

R. V. S.

**Constitution of Aluminium Brasses.** MARIO LEVI-MALVANO and M. MARANTONIO (*Gazzetta*, 1911, 41, ii, 282—297).—Aluminium brasses contain 58—70% of copper, 1—4% of aluminium, and zinc. The ternary system Cu—Zn—Al may be divided into two other systems, namely, Cu—Cu<sub>3</sub>Al—Zn and Cu<sub>3</sub>Al—Al—Zn (compare Gwyer, *Abstr.*, 1908, ii, 284). The authors have investigated the binary system Cu<sub>3</sub>Al—Zn and those portions of the ternary system Cu—Zn—Cu<sub>3</sub>Al, which include the aluminium brasses. The fusion and solidification of the alloys was effected in an atmosphere of carbon dioxide.

The diagram of the binary system Cu<sub>3</sub>Al—Zn shows that the temperature falls from the melting point of Cu<sub>3</sub>Al to that of zinc. It exhibits two transformation points, and a third lies at 570°. Evidence was obtained of the existence of various solid solutions, and corresponding with the first two transformation points there are two gaps of miscibility in the solid state, which were also demonstrated microscopically.

In view of the character of its constituent binary systems, the ternary system Cu—Cu<sub>3</sub>Al—Zn yields various mixed crystals and gaps of miscibility. The ternary alloys in the region examined develop heat at the beginning and at the end of crystallisation, but no heat changes mark the passage over gaps of miscibility. These have, therefore, been partially explored by microscopic methods.

The paper is accompanied by a number of photomicrographs.

R. V. S.

**The Solubility of Iron Carbide in  $\gamma$ -Iron.** N. J. WARK (*Metallurgie*, 1911, 8, 704—713).—The determination of the form of the curve of solubility of iron carbide in  $\gamma$ -iron by thermal methods is uncertain. Better results are obtained by heating steels containing varying quantities of carbon in a salt-bath to 1100°, cooling to a definite temperature, maintaining that temperature constant for some time, quenching rapidly, and examining microscopically. Barium chloride is used for baths above 1000°, and a mixture of sodium and potassium chlorides for lower temperatures. The maximum solubility of carbon in solid  $\gamma$ -iron is found to be 1.70%. Equilibrium between the solid solution and the separated carbide (cementite) is rapidly attained, being complete after ten minutes at constant temperature. The highest temperature at which the separation of cementite occurs, and the lowest temperature at which pure martensite is observed, are both determined, the mean of the two being taken as the temperature of crystallisation of cementite for that alloy. Equilibrium is also reached from the other side by heating quenched specimens in a salt-bath and again quenching. The two series of observations coincide. The solubility curve thus obtained lies somewhat above that determined by the thermal method.

C. H. D.

**The Removal of Rust from Iron in Reinforced Concrete.** EDUARD DONATH (*Zeitsch. angew. Chem.*, 1911, 24, 2355—2356. Compare *Abstr.*, 1911, ii, 897).—Rohland's view, that the active agent in the removal of rust is calcium hydrogen carbonate, is not confirmed by experiment. Only that part of the ferric iron which is in combination with ferrous oxide is converted into calcium ferrite. C. H. D.

**The Removal of Rust from Iron in Reinforced Concrete.** PAUL ROHLAND (*Zeitsch. angew. Chem.*, 1911, 24, 2356).—Polemical against Donath (preceding abstract). C. H. D.

**Coagulation of Ferric Hydroxide.** NICOLA PAPPADÀ (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 233—239).—The coagulation of ferric hydroxides by different electrolytes has been examined. The hydroxide was prepared according to Graham's dialytic method, and the concentration of the added electrolytes was varied. The observations show that the coagulation is brought about by the anions, and that the chlorine, bromine, iodine, and nitrate ions are about equally effective, whereas the coagulating power of the hydroxyl ion is much greater. For anions of different valency, the efficiency increases with the magnitude of the electrical charge. Non-electrolytes, even in concentrated solution, have no action on colloidal solutions of ferric hydroxide. H. M. D.

**Cobalt-Zinc Alloys.** F. DUCELLIEZ (*Bull. Soc. chim.*, 1911, [iv], 9, 1017—1023).—A study of these alloys has been made on the lines adopted by Vigoroux and Bourbon for nickel-zinc alloys (Abstr., 1911, ii, 1095), and a definite compound,  $\text{CoZn}_4$ , has been isolated and characterised (compare Lewkonja, Abstr., 1908, ii, 853). Alloys of these two metals, containing more than 81.6% of zinc, are non-magnetic, and become more brittle as the quantity of zinc diminishes. When powdered and treated with cold 1% hydrochloric acid, the acid being frequently renewed, they leave a residue having the composition expressed by the formula  $\text{CoZn}_4$ ; this compound may also be isolated by treating the alloys with dilute nitric acid. It has  $D^{20}_4$  7.43 (calc. 7.11), is non-magnetic, oxidises in the air, is attacked slightly by boiling water, feebly by 1% hydrochloric acid, and more strongly by 1% sulphuric acid. In these acids, the residue slowly becomes magnetic, due to deposition of cobalt from the solution. The compound also becomes magnetic when placed in aqueous solution of cobalt sulphate or chloride, due to solution of the zinc, but not in a solution of cobalt nitrate. When heated to a red heat, it burns in oxygen, air, or chlorine. Alloys containing less than 81.6% of zinc are all magnetic, and are attacked by acids without leaving any characteristic residue. The results of determinations of the *E.M.F.* developed by a series of the alloys opposed to a pole of zinc in a solution of zinc sulphate are plotted in the original, and the curve shows a break when the amount of zinc in the alloy reaches 81% and corresponds with the formation of  $\text{CoZn}_4$ .

The analyses were made by dissolving the alloy in nitric acid, adding excess of hydrochloric acid, evaporating to dryness, re-dissolving in water containing a few drops of hydrochloric acid, and precipitating the zinc as sulphide. A little sulphuric acid was added to the filtrate, which was then evaporated to dryness and the cobalt weighed as sulphate. T. A. H.

**Preparation of Stannic Iodide and its Solubility in Certain Organic Solvents.** F. ALEX. McDERMOTT (*J. Amer. Chem. Soc.*, 1911, 33, 1963—1965).—A method is described for the preparation of

stannic iodide by heating tin and iodine with carbon tetrachloride. The salt is much more soluble in the solvent at the b. p. than at the ordinary temperature, and therefore separates on cooling. Stannic bromide can be prepared by adding bromine, dissolved in carbon tetrachloride, in small quantities at a time through the open end of the condenser to which the flask containing the tin and carbon tetrachloride is attached. Sufficient heat is generated spontaneously to effect the reaction.

The following solubilities of stannic iodide are recorded. In carbon tetrachloride at 22.4°, 8.35 grams per 100 c.c. of solution or 5.25 grams per 100 grams of solution; at 50.0°, 20.47 grams per 100 c.c. or 12.50 grams per 100 grams. In chloroform at 28.0°, 12.32 grams per 100 c.c. or 8.21 grams per 100 grams. In benzene at 20.2°, 12.02 grams per 100 c.c. or 12.65 grams per 100 grams. E. G.

**Bismuthides and Inter-metallic Compounds.** ALEXANDER C. VOURNASOS (*Ber.*, 1911, 44, 3266—3271).—To prepare, for example, sodium bismuthide, the author proceeds as follows. One hundred grams of sodium, free from crust, are added to an excess of pure anhydrous paraffin (b. p. 375—400°), the mixture carefully heated on the sand-bath until the sodium melts, and then the temperature raised to 300—310°. Sticks of pure bismuth (30 grams) are then gradually immersed in the paraffin; as the bismuth melts, the drops fall on to the sodium and combine with it, crystals of the bismuthide immediately separating. The heat of reaction is so great that the paraffin is heated to the boiling point. The crystals are taken out with a perforated spoon, washed with benzene or light petroleum, and, if necessary, treated with amyl alcohol or liquid ammonia to remove any free alkali metal; this latter process is seldom necessary. Other compounds are prepared similarly.

*Sodium bismuthide*,  $\text{Na}_3\text{Bi}$ , forms small, dark grey, crystalline laminæ, m. p. approx. 776°. *Potassium bismuthide*,  $\text{K}_3\text{Bi}$ , forms small, shining crystals. These bismuthides are readily oxidised on exposure to the air, and are decomposed by moisture. The compounds  $\text{Na}_2\text{Pb}$  (m. p. 405°) and  $\text{Na}_2\text{Sn}$  (m. p. 477°) were also obtained.

When potassium bismuthide is heated at 380—400° in a current of dry hydrogen, gas is absorbed, producing a pyrophoric substance. On further heating to 700°, potassium vaporises away, and a grey, amorphous powder is left containing hydrogen and bismuth, approximately in the proportions corresponding with the compound  $\text{BiH}_3$ . This substance is being further investigated. T. S. P.

**A New Element, Probably of the Platinum Group.** ANDREW GORDON FRENCH (*Chem. News*, 1911, 104, 283).—The new element, to which the name *canadium* is given, was discovered by the author in the dyke rocks in the Nelson district of British Columbia, running in quantities from a few penny-weights up to three ounces to the ton. It occurs pure in semi-crystalline grains, and in short rods about half a millimetre in length by one-tenth of a millimetre in thickness. It is also found in metallic particles in the form of scales in platinum-bearing ores. These particles, which have a bluish-white colour, con-

tain the metal alloyed with a volatile substance which may be osmium, as it is dispelled by the blowpipe flame, leaving a brilliant bead of canadium, which is white.

It is not platinum, ruthenium, palladium, or osmium. It is much softer than these, and is quite easily melted by the blowpipe.

The new metal does not become tarnished by lengthened exposure to moisture, and it is not oxidised by continued heating in the blowpipe oxidising flame. It is soluble in nitric and hydrochloric acids, and in aqua regia without residue, and its solution in nitric acid yields no precipitate with sodium chloride solution. It is not blackened by lengthened exposure to moist hydrogen sulphide or to alkali sulphides, nor is it blackened by iodine; its nitrate solution is not precipitated by potassium iodide. Its melting point is somewhat lower than that of fine gold and silver, and very much lower than that of palladium. It is electro-negative to silver in dilute acid solution.

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T. S. P.

## Mineralogical Chemistry.

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**Determination of the Density of Minerals by means of Rohrbach's Solution of Standard Refractive Index.** H. E. MERWIN (*Amer. J. Sci.*, 1911, [iv], 32, 425—428).—The density of mineral grains may be determined by measuring the refractive index of a heavy liquid in which they remain suspended. The liquid, with the suspended grains, is contained in the small glass cell of a refractometer. A table is given showing the variation of the refractive index with the density for Rohrbach's solution (barium-mercuric iodide) at 20°, ranging from  $D_{20} 3.449$  and  $n 1.7686$  to  $D_{20} 2.067$  and  $n 1.5148$ .

L. J. S.

**Quartz and Fluorite as Standards of Density and Refractive Index.** H. E. MERWIN (*Amer. J. Sci.*, 1911, [iv], 32, 429—432).—The use of these minerals as standards for checking the accuracy and adjustment of instruments is recommended, since for material from different localities the constants named vary but slightly. Clear, colourless quartz, in twelve specimens from various localities, was found to have  $D_4^{20} 2.6495 \pm 0.0010$  and (in five specimens)  $\omega_D 1.54425 \pm 0.00005$ . Clear, pale-coloured fluorite from different localities has  $D_4^{20} 3.180 \pm 0.001$  and  $n_D 1.4338 \pm <0.0001$ .

L. J. S.

**Lignite. II. Volatile Constituents.** GEORGE B. FRANKFORTER and ANDREW P. PETERSON (*J. Amer. Chem. Soc.*, 1911, 33, 1954—1963).—Analyses have been made of samples of lignite from North Dakota, Canada, and Alaska. It has been shown by Frankforter (*J. Amer. Chem. Soc.*, 1907, 29, 1488) that the lignites vary widely in the amount of moisture they contain, samples from the South

containing more than those from more northern districts. It has been found that the total amount of volatile constituents is greater in the latter. The composition of the volatile constituents varies to some extent, but not in any regular order. The amount of carbon monoxide is nearly constant, and that of methane shows but little variation. The quantity of hydrogen, however, is greater the further north the locality from which the lignite is obtained.

E. G.

**Some Minerals from Beaver County, Utah.** B. S. BUTLER and WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1911, [iv], 32, 418—424).—In the Horn Silver mine, near Frisco, the sulphide ores of lead, zinc, copper, silver, and iron give place in the upper levels to a large variety of secondary minerals consisting of oxides, sulphates, carbonates, chlorides, and silicates of the same metals. *Beaverite*, described as a new species, is one of these secondary minerals, being a hydrous sulphate of copper, lead, and ferric iron. It occurs in some quantity as canary-yellow, earthy and friable masses, intermixed with other secondary lead and copper minerals. Under the microscope, it is seen to be minutely crystallised in hexagonal plates. Anal. I agrees with the formula  $\text{CuO}, \text{PbO}, (\text{Fe}, \text{Al})_2\text{O}_3, 2\text{SO}_3, 4\text{H}_2\text{O}$ . None of the water is expelled below  $250^\circ$ :

	$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{PbO}$	$\text{CuO}$	$\text{ZnO}$	$(\text{K}, \text{Na})_2\text{O}$	$\text{SO}_3$	$\text{H}_2\text{O}$	Insol.	Total.
I.	17.28	3.64	29.44	9.70	—	—	21.32	9.02	10.05	100.45
II.	42.11	—	18.32	—	0.30	0.13	27.59	9.16	2.64	100.25

*Plumbojarosite* (Abstr., 1910, ii, 966) occurs abundantly, together with jarosite and alunite, in the same mine, and it has also been observed in several other mines in Beaver Co. It forms dark brown, micaceous masses, and under the microscope shows golden-yellow, hexagonal plates, which are optically uniaxial and negative;  $D\ 3.60$ . Anal. II agrees with the usual formula  $\text{PbO}, 3\text{Fe}_2\text{O}_3, 4\text{SO}_3, 6\text{H}_2\text{O}$ . The associated jarosite and plumbojarosite can only be distinguished by chemical tests.

The rare mineral corkite, a hydrous phosphate and sulphate of lead and ferric iron [differing from beudantite in containing phosphate in place of arsenate], was found in two mines as a light yellowish-green, earthy and friable material, which under the microscope shows minute crystals. It is readily soluble in hot hydrochloric acid, and contains a trace of copper, but no arsenic.

Wurtzite (hexagonal zinc sulphide) occurs in considerable abundance in the Horn Silver mine, and when struck with a pick it phosphoresces; crystals are described.

L. J. S.

**Thortveitite, a New Mineral.** J. SCHETELIG (*Centr. Min.*, 1911, 721—726).—This new mineral, remarkable in containing scandium as an essential constituent, occurs together with euxenite, monazite, beryl, etc., in pegmatite, near Iveland, in Setersdalen, Norway. It forms radiating groups of large, prismatic crystals (up to 25 cm. in length and 4 cm. in thickness) somewhat resembling epidote in appearance. The crystals are orthorhombic with  $a : b : c =$

0.7456 : 1 : 1.4912, and are always twinned on the prism (110), this being also a direction of good cleavage. The mineral is transparent to translucent, with a greyish-green colour and bright vitreous to adamantine lustre. It is extremely brittle, and the crystals are much fissured;  $H = 6\frac{1}{2}$ ;  $D = 3.57$ . It is fusible only with difficulty, and is partly decomposed by hot concentrated sulphuric acid. Partial and preliminary analyses gave:  $\text{SiO}_2$ , 42.86;  $\text{R}_2\text{O}_3$ , 57.67 (including about 3%  $\text{Fe}_2\text{O}_3$ );  $\text{CaO}, \text{MgO}$ , traces; loss on ignition, 0.44 = 100.97. The oxides  $\text{R}_2\text{O}_3$  have mol. wt. 157.1, and consist mainly of scandia (about 37%  $\text{Sc}_2\text{O}_3$ ), with yttria, dysprosia, and erbia (about 17%), but no cerium earths. The mineral is essentially a scandium silicate,  $(\text{Sc}, \text{Y})_2\text{O}_3, 2\text{SiO}_2$ .  
L. J. S.

**Minerals from the Deposits of Tiriolo (Catanzaro).** U. PANICHI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 518—523).—A pink, fibrous zeolite has the composition of mesolite (I). Brandisite (II) is found as white, lamellar masses, almost without action on polarised light. Crystals of fassaite are found, and have been characterised by crystallographic measurements. These minerals are associated with calcite, spinel, idiochase, and garnet:

	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{Na}_2\text{O}$ .	$\text{H}_2\text{O}$ .	Loss.	Total.
I.	45.08	24.86	—	8.76	—	6.02	14.25	—	98.97
II.	22.83	43.20	5.38	2.53	21.78	—	—	3.29	99.01

C. H. D.

## Physiological Chemistry.

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**The Influence of Moderate Changes of Temperature of the Surrounding Atmosphere on the Respiratory Exchanges of Infants.** ARTHUR SCHLOSSMANN and HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1911, 37, 1—22).—The methods of investigation employed were the same as those used in the earlier experiments of the authors. It was found that moderate changes of temperature exert practically no influence on the respiratory exchanges. Even in earliest years, man is capable of regulating the temperature of the body, so as to be more or less independent of the changes in the surrounding atmosphere. S. B. S.

**The Influence of Crying on the Respiratory Exchanges of Infants.** ARTHUR SCHLOSSMANN and HANS MURSCHHAUSER (*Biochem. Zeitsch.*, 1911, 37, 23—29).—The respiratory exchanges of infants in a calorimeter during periods of rest and crying were investigated. It was found that the consumption of oxygen increased 44%, and the production of carbon dioxide increased 59·4%, during a period of crying as compared with the period of rest, in the case of the infant which was used as the subject of investigation. S. B. S.

**The Temperature-coefficient of the Rate of Reproduction of *Paramoecium Aurelia*.** LORANDE LOSS WOODRUFF and GEORGE ALFRED BAITSELL (*Amer. J. Physiol.*, 1911, 29, 147—155).—The optimum temperature for the culture of *Paramoecium aurelia* is between 24° and 28·5°. Continued subjection to temperatures below 21·5° and over 31·5° is sooner or later fatal. The temperature-coefficient of the average rate of reproduction is approximately 2·7, and therefore the rate of cell-division is influenced by temperature at a velocity similar to that for a chemical reaction. W. D. H.

**The Effect of Organ Extracts on Blood-pressure.** JOSEPH L. MILLER and E. M. MILLER (*J. Physiol.*, 1911, 43, 242—246).—Intravenous injection in dogs of saline extracts of parathyroid, thymus, cerebrum, cerebellum, spinal cord, liver, kidney, pancreas, prostate, ovary, and testis always lowers arterial blood-pressure without affecting the heart. Saline extracts of spleen always produced a rise, usually followed by a fall in pressure. Aqueous extracts of spleen always produced a fall of pressure. Alcoholic extracts redissolved in normal saline solution were without effect in the case of the liver, kidney, pancreas, spleen, parathyroid, thyroid, thymus, prostate, ovary, testis, and anterior lobe of the pituitary body. Alcoholic extracts of nervous tissue contained a depressor substance. Prolonged heating destroyed the depressor substance in brain and anterior lobe of the pituitary, but did not materially affect that in the posterior lobe. W. D. H.

**Inter-relation of the Ammonia and Carbon Dioxide of the Blood.** RALPH HOPKINS and W. DENIS (*J. Biol. Chem.*, 1911, 10, 407—415).—Asphyxiation of unfed animals by increasing the carbon dioxide of the blood causes a decrease in the ammonia present in that fluid. Artificial respiration of unfed dogs causing a decrease of the carbon dioxide leads to an increase of ammonia; inhalation of oxygen has the same effect. Curare slightly increases the ammonia in unfed dogs; low blood-pressure decreases oxidation, and so decreases the ammonia of the blood in unfed dogs. Asphyxiation of dogs in full digestion increases the ammonia in the blood. W. D. H.

**The Distribution of Reducing Substances in Mammalian Blood.** LEONOR MICHAELIS and PETER RONA (*Biochem. Zeitsch.*, 1911, 37, 47—49).—The authors reply to the criticisms of Lyttkens and Sandgren (*Abstr.*, 1911, ii, 994), maintaining their previous results as to the distribution of sugar between the serum and corpuscles, and quote similar results by other authors in support. S. B. S.

**Viscometric and Cryoscopic Changes in the Blood Produced by Antipyrin, Phenacetin, and Antifebrin.** GUIDO M. PICCININI (*Chem. Zentr.*, 1911, ii, 1468; from *Arch. farm. speriment.*, 12, 193—209).—All three drugs given in doses of 2—5 grams in dogs increase the viscosity, and the lowering of the freezing point of the serum. This is attributed to changes in the serum proteins. The cryoscopic change may be related to an increase of alkalinity

which occurs. Antifebrin and phenacetin act in the same way on the defibrinated blood, probably because they are hæmolytic. Antipyrin, on the other hand, diminishes the viscosity of defibrinated blood; this is attributed to changes in the corpuscles which leads to increase of oxygen and alkali.

W. D. H.

**The Removal of the Blood-pigment from Corpuscles Under the Influence of Carbon Monoxide.** F. BUBANOVIĆ (*Biochem. Zeitsch.*, 1911, 37, 139—141).—Blood treated with coal-gas lost pigment when treated with 0.60% sodium chloride, whereas the control normal blood lost pigment in 0.65% saline. In the latter case the degree of hæmolysis was greater. A weaker saline solution than required by the normal was also necessary to cause the exit of the pigment when the blood had been treated only with air. In both cases the result is ascribed to the expulsion of carbon dioxide from hæmoglobin, which is then more readily able to take up water.

S. B. S.

**The Changes in the Blood-clotting Produced by Loss of Blood in an Animal.** HEINRICH STROMBERG (*Biochem. Zeitsch.*, 1911, 37, 218—237).—Numerous experiments were carried out on the time required for the blood to clot, which had been withdrawn from animals (rabbits) after successive losses of definite quantities of blood. Although the blood was found, as a rule, to clot more rapidly after loss of blood by the animal, no definite relationships between the clotting time and the loss of blood could be discovered. The results obtained were, generally, irregular.

S. B. S.

**The Methods of Investigation and Characters of the Blood-clotting Process.** HEINRICH STROMBERG (*Biochem. Zeitsch.*, 1911, 37, 177—217).—Wohlgemuth's method of estimating the fibrin ferment, which consists in determining the maximum amount of dilution in which it is just possible to coagulate a definite fibrinogen solution within twenty-four hours at 0°, was subjected to a critical examination, and the results were compared with those obtained in a parallel investigation, in which the time durations were determined in which varying dilutions of the ferment solution produced clotting. The conclusion was drawn that Wohlgemuth's method does not give a real quantitative estimation of the amount of fibrin ferment in blood. It was found that, as a rule, those sera which in undiluted form produced a clot in the shortest interval gave the largest values for the quantities of fibrin ferment by Wohlgemuth's method. This was, however, by no means always the case, and considerable caution must be used in drawing conclusions as to the amount of thrombin present when both the Wohlgemuth and the time methods are employed in investigations. It would seem advisable to generally employ both methods, but in the present state of knowledge no very definite conclusions can be drawn from either. Numerous experiments were also carried out on the quantitative relationship between the fibrinogen and the thrombin, and the relative quantities necessary to produce a complete clot. It was found that, for this purpose, there is a definite

quantitative relationship between the interacting substances, a fact which is not in accord with the conception of the ferment-like character of the thrombin. In this respect the author's conclusions are in accord with those of Arthus. S. B. S.

**Intravenous Injection of Thrombin.** DANIEL DAVIS (*Amer. J. Physiol.*, 1911, 29, 160—164).—In four experiments on two dogs, one rabbit, and one cat, the injection of thrombin into the circulation within the limits of 20 to 36 mg. per kilo. of animal did not cause intravascular coagulation; in fact, the coagulation time of the shed blood was slightly lengthened; the effect soon passed off. The injection of thrombin no doubt excites the rapid formation of antithrombin, the agent which normally prevents intravascular clotting.

W. D. H.

**Preparation of Thromboplastic Extracts (Thromboplastin) from Tissues.** H. L. CECIL (*Amer. J. Physiol.*, 1911, 29, 156—159).—Aqueous or saline extracts of many tissues accelerate blood coagulation; such extracts (thromboplastic) are best tested with "peptone" plasma. Witte's peptone was often found to be ineffective for the purpose of obtaining peptone plasma. This is intelligible if Pick and Spiro's view is accepted, that the agent in Witte's peptone is not peptone or proteose, but the unknown substance peptozym. Instead of Witte's peptone, a crude preparation of peptozym which worked excellently was prepared by digesting fibrin with 0.4% hydrochloric acid at 38° for several days. The solution was boiled, filtered, and evaporated to dryness; the residue was powdered, dissolved in boiling water, neutralised with sodium carbonate, filtered, and again evaporated to dryness on a water-bath. The residue thus obtained was used for injection; it was dissolved by boiling in physiological saline solution; the solution was filtered before injection, and used in the proportion 0.3 gram per kilo. The plasma obtained was clotted by extracts of muscle, liver, lung, spleen, thymus, lymph gland, and salivary glands. Extracts from pancreas and intestine were inactive. Glycerol was found to be an excellent vehicle for dissolving out the thromboplastic substance; such extracts keep well. W. D. H.

**The Rôle of Antithrombin and Thromboplastin in the Coagulation of Blood.** WILLIAM H. HOWELL (*Amer. J. Physiol.*, 1911, 29, 187—209).—By the use of solutions of pure fibrinogen and thrombin it is shown that an antithrombin is present in normal mammalian plasma, in birds' plasma, and in "peptone" plasma. This is neutralised by thromboplastin. Circulating blood contains all the necessary fibrin factors, fibrinogen, prothrombin, and calcium. These substances are prevented from reacting, and the blood remains fluid because antithrombin is also present, which prevents the calcium from activating prothrombin to thrombin. In shed blood, the restraining effect of antithrombin by thromboplastin is furnished by the tissue elements. In mammalian blood this is derived in the first place from the elements of the blood itself (blood-platelets). In the lower vertebrates the supply of thromboplastin comes from the external tissues.

W. D. H.

**Reaction of the Blood-serum of Some Mammals Studied by the Electrometric Method.** G. QUAGLIARIELLO (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 418—420. Compare *Abstr.*, 1911, ii, 1114; Michaelis and Rona, *Abstr.*, 1909, ii, 680).—The values obtained for the concentrations of hydrogen and hydroxyl ions in the blood-serum of the dog and rabbit are in agreement with those of previous investigators. The blood-serum of the fowl has  $C_{H^+}$   $0.214 \times 10^{-7}$ ,  $C_{OH^-}$   $2.98 \times 10^{-7}$ . In the case of human blood-serum,  $C_{H^+}$  varied from  $0.096$ — $0.171 \times 10^{-7}$ ,  $C_{OH^-}$  from  $3.41$ — $6.72 \times 10^{-7}$ . This degree of alkalinity is somewhat higher than that found by most other authors.

R. V. S.

**A New Viscometer and Its Application to Viscosity Measurement of Blood and Serum.** GEORGE F. WHITE (*Biochem. Zeitsch.*, 1911, 37, 482—489).—The apparatus, which is figured, is a modification of the viscometer of Thorpe and Rodger, and is provided with a valve, by means of which the volume of the liquid which is to pass through the capillary tube is kept constant. Dog-fish blood at  $0^\circ$  was found to be 3.896 times as viscous as water at the same temperature. Between  $30^\circ$  and  $52^\circ$  the time of passage of the blood through the capillary was found to be a linear function of the temperature. Above this point, there is a fall in the curve, owing to separation of the fibrinogen, which had been kept in solution by the blood salts. The rate of coagulation can be measured by viscosity determinations at different temperatures.

S. B. S.

**Relation of the Pancreas to the Serum and Lymph Diastases.** L. K. GOULD and ANTON J. CARLSON (*Amer. J. Physiol.*, 1911, 29, 165—181).—Ligature of both pancreatic ducts and of all the pancreatic tissue along the duodenum in dogs causes a great rise of diastatic power in the blood-serum within twenty-four hours. This is probably due to absorption of amylase from the gland; the condition returns to normal, and then occurs a second rise; later, there may be a third rise. A considerable atrophy of the pancreas is not followed by a corresponding decrease in the diastatic power of the serum, but a marked decrease follows removal of the atrophied pancreas. Almost complete removal of the pancreas in pigs does not cause a decline in the diastatic power of the serum until a considerable time after the operation; in dogs the decline is usually rapid, but it may be delayed for eight days. In pigs, the depression when it does appear is slight. Serous exudations rich in leucocytes, obtained by the injection of aleuronat into the pleural cavity, have much less diastatic power than the serum. The pancreas or leucocytes are, therefore, not the main seat of the production of the blood diastases. The pancreas probably acts indirectly by its internal secretion; the decrease in diastatic power that follows extirpation of that organ is regarded as due to a depression of all the tissue cells, particularly the liver cells, which results in the decreased output of diastase into the body fluids.

W. D. H.

**The Rôle of the Kidneys in the Regulation of the Concentration of the Serum Diastases.** J. VAN DE ERVE (*Amer. J. Physiol.*, 1911, 29, 182—186).—In dogs ligature of the renal arteries

produces no change in the serum diastase. Diuresis caused by cutting the renal nerves has also no effect; but if the diuresis is due to ingestion of excess of salt solution, the dilution of the blood so produced is accompanied by a diminution of the diastatic power of the serum. The polyuria which follows complete extirpation of the pancreas is therefore not an important factor in the great diminution of this power which is observed after the operation. W. D. H.

**Physiology of Lymph. XVIII. The Relation of the Pancreas to the Lipase of the Blood and the Lymphs.** C. L. VON HESS (*J. Biol. Chem.*, 1911, 10, 381—398).—Extirpation of the pancreas in dogs does not alter the concentration of lipase in the serum; in rabbits there may be a temporary fall. The same negative results in dogs follow ligation of the pancreatic ducts. Partial atrophy of the pancreas in dogs, and almost complete atrophy in rabbits, produces no change in sero-lipase. Ligation of the renal arteries in dogs may sometimes cause a fall in the amount of sero-lipase; this result is independent of pancreatic lesions. Bile salts do not activate sero-lipase. Ether anaesthesia has no effect.

Aleuronin injected into the pleural cavity gives a serous exudation teeming with leucocytes, with a smaller lipolytic power than the serum. Hyper and hypo-thyroidism has no effect. The pancreas and thyroid are thus not the main sources of the lipase of the serum.

W. D. H.

**Comparative Proteolysis Experiments with Trypsin.** GEORGE F. WHITE and WILLIAM CROZIER (*J. Amer. Chem. Soc.*, 1911, 33, 2042—2048).—The work hitherto done on the artificial digestion of proteins with reference to their relative food value is of limited importance, as the extent to which the soluble products had been hydrolysed was not ascertained.

van Slyke (Abstr., 1911, ii, 779) has devised a method for estimating the amino-nitrogen in proteins and their hydrolytic products, and this has now been applied to a study of the comparative digestibility by trypsin of boiled beef, cod, and dog-fish.

The time of digestion, the soluble and insoluble nitrogen, and the amino-nitrogen before and after complete hydrolysis with hydrochloric acid are stated in tabular form. Cod is the most readily converted into the soluble form, and its soluble proteins are shown to be more easily hydrolysed than those of beef or dog-fish, as they yield more amino-nitrogen. Beef is the least easily soluble, but the hydrolysis of its soluble proteins lies between that of the cod and the dog-fish. The results agree with those of the metabolism experiments of van Slyke and White (Abstr., 1911, ii, 623), in which dogs were fed with beef and cod, and indicate that dog-fish would be digested slowly in the organism and would be more capable of maintaining nitrogenous equilibrium than either beef or cod. The flesh of the dog-fish contains 0.84% of carbamide (compare van Slyke and White, Abstr., 1911, ii, 624). Dog-fish is recommended as a valuable food. E. G.

**The Nature of the Repair Processes in Protein Metabolism.** E. V. MCCOLLUM (*Amer. J. Physiol.*, 1911, 29, 215—237).—Michaud states that when a starving dog is fed on dog's flesh in amount equivalent to its daily loss of nitrogen, the whole of the protein so given is used for repair purposes. In the present experiments pigs were used. They were fed on different vegetable proteins in quantity equivalent to the lowest possible level of protein metabolism; the results do not indicate as wide differences in the nutritive values of the proteins of wheat, oat, and maize as would be expected from the known chemical differences between these proteins. Zein and gelatin are, for instance, "incomplete proteins." But the pig can utilise the nitrogen of zein very efficiently for the repair of losses due to endogenous metabolism; about 80% was so used. The figure for gelatin was 50—60%; but there was no evidence of the formation of additional body tissue. On the other hand, feeding with casein as the only protein given, resulted in increases of the body protein of 20—25%. Repair processes are of a different character from those of growth; probably in cell katabolism and repair, the processes do not involve the destruction and re-synthesis of an entire protein molecule.

W. D. H.

**Studies in Nutrition. III. The Utilisation of the Proteins of Corn.** LAFAYETTE B. MENDEL and MORRIS S. FINE (*J. Biol. Chem.*, 1911, 10, 345—352. Compare Abstr., 1911, ii, 1109).—The proteins of maize (usually called corn in America) partly purified were somewhat less thoroughly utilised than meat. The small difference may in great part be attributed to cell residues remaining in the preparation employed.

W. D. H.

**Biological Importance of Caseinogen Phosphorus for the Growing Organism.** ALEXANDER LIPSCHÜTZ (*Pflüger's Archiv*, 1911, 143, 99—108).—According to Bayliss and Plimmer, the phosphorus of caseinogen is converted into inorganic phosphate before absorption. This opens up the question whether feeding on the milk proteins has from the phosphorus point of view any special advantage in growth. The experiments recorded are not regarded as absolutely conclusive, but so far as they go they show that in phosphorus metabolism the inorganic phosphates are equally beneficial; and if organic phosphorised materials are given, the phosphorus enters the blood-stream as inorganic phosphate.

W. D. H.

**Physiology of Phosphorus Hunger in Growth.** ALEXANDER LIPSCHÜTZ (*Pflüger's Archiv*, 1911, 143, 91—98).—Liebig's law of minimums does not hold in animal life for iron or calcium; on diets poor in these substances growth continues. It is now shown that this is true also for phosphorus; bony growths show certain changes, but the total increase in the weight of growing animals is equally great on diets poor in phosphorus as on those rich in that element. The meaning and possible explanations of the observed data are discussed.

W. D. H.

**The Physiological Utilisation of the Phosphorus Compounds in Fodders by Ruminants.** GUSTAV FINGERLING (*Biochem. Zeitsch.*, 1911, 37, 266—271).—When various phosphorus compounds (phytin,

lecithin, nuclein, sodium nucleate, and inorganic phosphorus compounds) were added to certain phosphorus poor diets and fed to lambs and goats in milk, the phosphorus was not utilised to much more than the extent of 50%, whereas in other diets, including oats, sesame oil, and linseed oil cakes, the phosphorus was utilised to the extent of 90%. Furthermore, in a certain grass, the phosphorus compounds were utilised to the extent of 91%, whereas in the hay made from the same grass, they were only utilised to the extent of 53.4%. The author draws the conclusion that the differences are due to the differences in the physical characters of the fodders, the cell-walls of the food material being in certain cases relatively indiffusible to the phosphorus compounds, which are therefore prevented from being resorbed.

S. B. S.

**The Protective Action of the Bran of Padi in a Diet of White Rice.** L. BRÉAUDAT (*J. Pharm. Chim.*, 1911, [vii], 4, 447—451).—Polyneuritis of fowls, which is produced by an exclusive diet of white rice, is prevented if the diet contains 25—30% of rice bran. This protective action is not due to the glutinous matter, fatty matter, carbohydrates, or inorganic salts of the bran, since these substances extracted from bran had no protective action either singly or together.

The protective constituent may be extracted from the bran by water. This aqueous extract contains only a very small proportion of the nitrogen of the bran, so its protective action is not to be attributed merely to a supplementing of the nitrogen of the rice. W. J. Y.

**Water Drinking. VIII. Utilisation of Ingested Fat under the Influence of Copious and Moderate Water Drinking with Meals.** H. A. MATTILL and PHILIP B. HAWK (*J. Amer. Chem. Soc.*, 1911, 33, 1978—1998).—Experiments are described in which men, living on a uniform diet, ingested small quantities of water with their meals for a preliminary period, then large quantities for a period, and finally returned to small quantities. When an additional litre of water was taken with each meal, the amount of fat excreted was considerably reduced, and this diminution was usually evident for several days after the return to a normal quantity of water. A slight gain in weight accompanied the water drinking, and was not subsequently lost. After several months of drinking moderate quantities with meals, a marked improvement in the digestion of fat was observed, the utilisation having increased from 94.3 to 96.5%. The factors to which the better absorption and more complete utilisation of the fats are probably due are discussed. E. G.

**Water Drinking. IX. Distribution of Bacterial and Other Forms of Faecal Nitrogen and the Utilisation of Ingested Protein under the Influence of Copious and Moderate Water Drinking with Meals.** H. A. MATTILL and PHILIP B. HAWK (*J. Amer. Chem. Soc.*, 1911, 33, 1999—2019).—Experiments were carried out on the same lines as those described in the previous paper (preceding abstract). The ingestion of a litre of water with meals resulted

in a more complete utilisation of the proteins of the food, as was indicated by a decrease in all forms of nitrogen in the fæces, but when only 500 c.c. were taken, no significant changes could be observed. The beneficial results were more or less permanent, and no indication was obtained of any detrimental effect, even when more than four litres of water were drunk daily.

E. G.

**Water Drinking. X. Fæcal Output and its Carbohydrate Content under the Influence of Copious and Moderate Water Drinking with Meals.** H. A. MATTILL and PHILIP B. HAWK (*J. Amer. Chem. Soc.*, 1911, 33, 2019—2032).—The experiments were conducted on the same lines as those already described (preceding abstracts). The ingestion of a litre of water with meals caused a decrease in the amount of fæcal matter excreted as well as of the carbohydrates. The improved utilisation of the food lasted for some time after the water drinking had been discontinued. The ingestion of 500 c.c. of water with meals caused a similar, but smaller, reduction in the amount of carbohydrate excreted. The average daily amount of dry bacterial substance in the fæces was 8.27 grams. The causes of the beneficial effect of water drinking on the utilisation of carbohydrates are discussed. Many desirable, and no undesirable, effects were obtained by the use of water with meals, and, in general, the greater the amount of water taken, the greater were the benefits.

E. G.

**Fasting Studies. V. Studies on Water Drinking. XI. The Influence of Excessive Water Ingestion on a Dog after a Prolonged Fast.** PAUL E. HOWE, H. A. MATTILL, and PHILIP B. HAWK (*J. Biol. Chem.*, 1911, 10, 417—432).—The details given of the various nitrogenous substances in the urine are believed to substantiate the hypothesis that the increased nitrogen output associated with increased water ingestion is due to a true stimulation of protein katabolism rather than to a flushing of the tissues.

W. D. H.

**The Effect of Substances which Dissolve in Fat on the Mobility of Phagocytes and Other Cells.** HARTOG J. HAMBURGER and J. DE HAAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 314—324).—The acceleration of phagocytosis by substances dissolving fats is attributed to a weakening of the fatty surface layer, and this facilitates amœboid movement. Alcohol, butyric acid, propionic acid, and Peruvian balsam act in this way; this explains why Peruvian balsam has a good effect on infected wounds. The acceleration of phagocytosis is parallel to the solubility of the substances used in fat. Among animals cells which show increased mobility must be reckoned, not only phagocytes, but nerve-cells, eggs of lower marine animals, and ciliated epithelium. The germination of wheat grains is accelerated by chloroform 1 in 100,000, but delayed by 1 in 1000, as the latter strength paralyses the protoplasm of the cells.

W. D. H.

**The Influence of Bases on the Development and Oxidative Processes in the Eggs of the Sea-urchin (*Arbacia*).** JACQUES LOEB and HARDOLPH WASTENEYS (*Biochem. Zeitsch.*, 1911, 37, 410—423).—The bifurcation and oxygen consumption of recently fertilised eggs of *Arbacia* in solutions of sodium, potassium and calcium chlorides, in which the hydroxyl ion concentration was varied by means of sodium hydroxide and hydrogen chloride, were investigated. It was found that change of  $C_{OH}$  from  $10^{-10}$  to  $10^{-4}$  corresponded with an increased oxygen consumption of only 20%. After this the oxygen consumption rapidly increased, a change of  $C_{OH}$  from  $10^{-4}$  to  $8 \cdot 10^{-4}$  increasing the amount of oxygen utilised two-fold. The inhibition of bifurcation by sodium hydroxide in higher concentrations, previously noted by Loeb and Warburg, does not depend only on the increase in oxidative processes, for if this increase is produced by rise of temperature only, there is a quicker bifurcation rather than inhibition. The differences in the previously observed toxicity effects produced by the addition of sodium hydroxide to sodium and potassium chloride solution, on the one hand, and sodium and calcium chloride solution, on the other, cannot, it was found, be ascribed to differences in the oxidation rates in the two solutions. In view of the fact that ammonium hydroxide produces about the same effect as sodium hydroxide in the same relative concentration, the conclusion is drawn that the action of the latter cannot be ascribed merely to the concentration of the hydroxyl ions. S. B. S.

**The Organic Bases in the Flesh of Wild Rabbits.** KIYOHISA YOSHIMURA (*Biochem. Zeitsch.*, 1911, 37, 477—481).—The only bases which the author has succeeded in isolating from the flesh of wild rabbits were creatine, hypoxanthine, xanthine, and carnosine. The usual methods were employed. S. B. S.

**The Imbibition and the Loss of Water by Resting and Stimulated Frogs' Muscles when Immersed in Isotonic Saline Solution.** CARL SCHWARZ (*Biochem. Zeitsch.*, 1911, 37, 34—46).—von Fürth and Lenk (*Abstr.*, 1911, ii, 750) have shown that the muscles in isotonic saline solution first of all take up water until a maximum is reached, and then lose water. The first stage is an imbibition process, which is accelerated by the presence of lactic acid. The loss of water is due to a gradual coagulation of the muscle proteins. The action of isotonic saline on resting and stimulated muscles is similar, but the stage of maximum imbibition and subsequent loss of water is reached sooner in the case of the stimulated than in that of the resting muscles. This result can be readily explained by the presence of larger quantities of lactic acid in the stimulated muscles. In the case of the resting muscles, the lactic acid is only formed slowly post-mortem. The results confirm generally, therefore, the theories of von Fürth and Lenk. The rate of imbibition and loss of water in slightly hyper- and hypo-tonic solutions was also investigated, and the results obtained were those which would, from the theory of osmosis, be expected. S. B. S.

**The Potassium, Sodium, and Chlorine Content of Plain and Striated Muscles from Various Animals.** A. COSTANTINO (*Biochem. Zeitsch.*, 1911, 37, 52—77).—A large number of analyses made by a wet-ashing method of different kinds of muscular tissue from various mammals, fowls, and turkeys were made, and are tabulated by the author. No very definite generalisations as to the distribution of potassium, sodium, or chlorine in the various materials examined can be drawn from the results. S. B. S.

**The Alleged Formation of Lactic Acid in Muscle during Autolysis and in Post-survival Periods.** W. M. FLETCHER (*J. Physiol.*, 1911, 43, 286—312).—The production of lactic acid in excised mammalian and amphibian muscle is accelerated by mechanical injury. The rate of production varies with the temperature, and at body temperature reaches its maximum within an hour. If the muscle is destroyed by heating, production of lactic acid ceases. After the maximum is once reached, no further production of lactic acid occurs during autolysis. No glycolytic enzyme leading to the production of lactic acid from added dextrose is present. If bacterial infection occurs, the result depends on the specific action of the bacteria; the *d*-lactic acid is commonly diminished. W. D. H.

**The Innervation of the Coronary Vessels.** THOMAS GREGOR BRODIE and WINIFRED C. CULLIS (*J. Physiol.*, 1911, 43, 313—324).—Adrenaline in great dilution causes a temporary contraction of the vessels which supply the heart. This is followed by dilatation. This is considered to prove the existence of both vaso-constrictor and vaso-dilator nerves in the coronary vessels, but a secondary cause of the dilatation is the action of metabolites, particularly carbon dioxide. Earlier observers have failed to detect the primary constriction, because the solutions of adrenaline used have been too strong, so that the first effect is masked by the second. W. D. H.

**The Action of Homologous Alcohols and Aldehydes on the Tortoise Heart.** HORACE M. VERNON (*J. Physiol.*, 1911, 43, 325—342).—When the tortoise heart is perfused with oxygenated Ringer's solution containing alcohol, the beats are depressed to a definite level. On washing out with fresh Ringer's solution, the heart completely and rapidly recovers. The toxicity of the alcohols increases with their molecular weights, the order being the same as that found by Overton for the narcotisation of tadpoles. It also corresponds with their capacity for laking red corpuscles. Aldehydes also depress cardiac action to a constant level, but recovery with fresh Ringer's solution is not so complete as with the alcohols. These relative toxicities are: propaldehyde 1.0, acetaldehyde 1.2, formaldehyde 40: that is, there is no relationship to molecular weights.

W. D. H.

**Comparative Histological and Chemical Investigations of the Fat Contents of Organs.** NAGAMICHI SHIBATA and SHIGEKIYO ENDO (*Biochem. Zeitsch.*, 1911, 37, 399—409).—The organs (liver and

kidneys) from individuals who had died from various diseases were examined histologically with the use of the ordinary fat-staining reagents, and chemically by the Kumagawa-Suto method. It was found that, with few exceptions, those organs which appeared to be histologically rich in fats did actually contain relative large amounts, as determined by the chemical process. S. B. S.

**Fatty Infiltration [into the Liver] after Phosphorus Poisoning and the Origin of Fat in the Animal Body.** NAGAMICHI SHIBATA (*Biochem. Zeitsch.*, 1911, 37, 345—398).—The experiments were carried out on mice and frogs, and the fat and nitrogen distribution between the liver and the remainder of the body in normal and poisoned animals was determined and compared, the Kumagawa-Suto method being employed for the estimation of the fat. The main conclusion drawn is that there is no evidence of the synthesis of fat from proteins. Phosphorus poisoning causes a marked diminution in the amount of total body fat, but an increase in the fat of the liver. The fat diminution is, however, less after phosphorus poisoning in starving animals than it is in normal starving mice. Whereas in the normal starving animals the diminution of fat amounted to 50% in phosphorus-poisoned starving animals it was from 50 to 65% of the normal value, when the poisoned and control animals had been deprived of food for the same period. The results were somewhat similar, but not so definite in the case of frogs. In the case of both mice and frogs there was loss of nitrogen, which was not, however, as great as that which occurs during fasting. The fat in the livers of the animals poisoned by phosphorus is derived from the subcutaneous fat depôts. This fact was determined by injection of foreign fats, and the estimation of the iodine-numbers of the liver fat. Very marked was the fat diminution after phosphorus poisoning when the mice were fed with a bread diet. Whereas after simple fasting, phosphorus poisoning caused a fat diminution of 50%, after feeding with bread, under otherwise similar conditions, the fat sank to 84% of the normal. The fat content of the liver had sunk from 15 to 30%. The energy consumed both by the normal and phosphorus-poisoned animals on a bread diet was the same (about 33 cal. per kilo. body-weight per hour). It appears according to the author, that the administration of glycogen-forming substances causes an oxidation of the infiltrated fat in the liver of phosphorus-poisoned animals, and that, therefore, on a carbohydrate-rich diet there is no fatty liver, but even the fat is less than normal. The results leave, according to the author, no doubt as to the fact that the fat in the livers of phosphorus-poisoned animals is due to infiltration, and is not derived from proteins.

Kumagawa's theory as to the action of phosphorus on the liver cells and the metabolism of fat and carbohydrates in the liver is given in brief outline. S. B. S.

**Inhibition of Post-mortem Production of Sugar in the Liver and of Certain Forms of Glycosuria by the Intravenous Injection of Dilute Solutions of Sodium Carbonate.** FREDERICK W. PAVY and WILLIAM GODDEN (*Proc. Physiol. Soc.*, 1911, vii—x; *J. Physiol.*, 43).—Pavy and Bywaters (*Abstr.*, 1910, ii, 1098) have

previously shown that acids activate inverting and diastatic enzymes. In the case of liver-diastrase, the post-mortem production of sugar can be inhibited by previous injection of a 2% solution of sodium carbonate. Some forms of glycosuria are dependent on sugar being thrown into the circulation by the liver; this occurs, for instance, in the glycosuria produced by chloroform inhalation; this in the cat can be reduced, and even completely inhibited, by injection of sodium carbonate; the injection of normal saline or Ringer's solution has no such effect.

W. D. H.

**The Influence of Iodine on Autolysis,** LEON KEPINOW (*Biochem. Zeitsch.*, 1911, 37, 238—248).—The addition of iodine accelerates the autolysis of the liver, whereas that of potassium iodide does not. The injection of Lugol's solution also increases the liver autolysis when the organ is removed from the animal within six to twenty-four hours after the injection. The injection of potassium iodide produces a similar effect. Long-continued injections of the iodide produce a still more marked effect. The serum of animals which had been subjected to a long-continued treatment also produced an accelerating effect. Iodine did not accelerate the action of pancreatin on heated liver tissue. The injection of both iodine and potassium iodide increased the anti-tryptic index.

S. B. S.

**Ingestion of Acids by a Dog after Partial Extirpation of the Pancreas.** HENRI LABBÉ and L. VIOLE (*Compt. rend.*, 1911, 153, 1085—1087).—A dog from which six-sevenths of the pancreas had been removed was given a considerable amount of hydrochloric acid with its food. Contrary to expectation, the operation did not diminish the capacity of the organism to prevent intoxication by an increased output of nitrogenous bases. Nevertheless, the effort necessary to resist the action of the acid was apparent from the animal's loss in weight and by a fall in the coefficient of nitrogenous equilibrium. No such changes were produced by the acid in healthy animals, neither was the proportion of amino-nitrogen in the urine altered. Removal of the pancreas appears to lead to an increased destruction of amino-acids.

W. O. W.

**The Enzymes of the Spleen.** TAMIO TANAKA (*Biochem. Zeitsch.*, 1911, 37, 249—261).—The dried powder of pig's spleen contains the following enzymes: catalase, oxydase, starch, and glycogen-splitting diastase, inulase, invertase, lipase, urease, and enzymes of the type of pepsin, trypsin, and erepsin. The following enzymes were absent: lactase, deamidase, and glycolytic enzymes.

S. B. S.

**The Vesicular Fluid of the Hedgehog.** F. GOWLAND HOPKINS (*J. Physiol.*, 1911, 43, 259—260).—The secretion of the vesiculæ seminales is a glairy, milky, slightly alkaline fluid, which contains a crystalloid substance in suspension, that can be removed by the centrifuge. The crystals look like ill-formed crystals of edestin; it gives the protein colour tests, and contains phosphorus. Prolonged boiling with water and prolonged action of alcohol do not affect the

form or transparency of the crystals. It differs also from other phospho-proteins in its comparative resistance to the solvent action of alkalis. Its solution in sodium hydroxide gives an amorphous precipitate on acidifying, and evolution of hydrogen sulphide. The crystals are soluble in dilute hydrochloric acid, and this solution reduces Fehling's solution. In the clear residual fluid obtained by removing the crystals, small quantities of albumin and globulin are present.

W. D. H.

**The Enzymes of Bull's Testes.** SHINJI MIHARA (*Zeitsch. physiol. Chem.*, 1911, 75, 443—455).—An enzyme was found which is capable of splitting arginine into ornithine and urea. The intensity of action of the deamidase contained in the extract of the testes varies largely according to the amino-compounds employed. Asparagine is readily decomposed into ammonia, whilst glycine is only slightly attacked, and urea remains unchanged. It is not clear from the present stage of the investigations whether or not specific enzymes are required for the decomposition of various amino-compounds. Nuclease is present and also an enzyme acting on salicin but not on amygdalin. H. B. H.

**The Relation between the Corpus Luteum and the Growth of the Mammary Gland.** CHARLES H. O'DONOGHUE (*Proc. physiol. Soc.*, 1911, xvi—xvii; *J. Physiol.*, 43).—Experiments and observations are adduced which show that in the marsupial, *Dasyurus*, the corpus luteum of the ovary is a ductless gland, which produces an internal secretion which is the inciting cause of the growth of the mammary glands.

W. D. H.

**Formation of Glycine in the Body. I.** ALBERT A. EPSTEIN and SAMUEL BOOKMAN (*J. Biol. Chem.*, 1911, 10, 353—371).—The production of glycine in the body is progressive, depending to a certain extent on the amount of benzoic acid present in the circulation; no reserve store of glycine exists. Benzoic acid does not cause a massive decomposition of protein, but its action is selective; it combines with glycine or with other groups which can be changed into glycine. This occurs independently of the rest of protein metabolism.

W. D. H.

**Cooking and Composition of Some English Fish.** KATHERINE I. WILLIAMS (*Chem. News*, 1911, 104, 271—274. Compare *Trans.*, 1897, 71, 649).—Results of analyses are given showing the quantities of water, ash, protein, fat, reducing substances (as dextrose), etc., yielded by some twenty-five different kinds of fish after these had been cooked by boiling. The loss in weight of the fish during the cooking is recorded, and attention is drawn to the phosphorus-content of fish; the quantities of phosphoric anhydride found on the analysis of the mineral constituents of the different kinds of fish show that, as a rule, fish does not contain a larger quantity of phosphorus compounds than is present in the flesh of animals.

W. P. S.

**The Effects of Asphyxia, Hyperpnœa, and Sensory Stimulation on Adrenal Secretion.** WALTER B. CANNON and R. G. HOSKINS (*Amer. J. Physiol.*, 1911, 29, 274—279).—The method used for testing

for adrenaline in blood was Hoskins', namely, a strip of intestine is placed in oxygenated Ringer's solution, and then transferred to the blood; the amount of inhibition of the contractions indicates the amount of adrenaline in the blood. Cats were used. Asphyxia was found to result in increased secretion from the adrenal bodies. Hyperpnœa does not lead to this result. Stimulation of large sensory nerves (and probably, therefore, surgical shock) causes increased adrenal secretion; adrenal fatigue may therefore be a factor in shock.

W. D. H.

**Isolation of Choleic Acid, Stearic Acid, and Cholesterol from Ox Gall-stones.** HANS FISCHER and P. MEYER (*Zeitsch. physiol. Chem.*, 1911, 76, 95—98).—Powdered ox gall-stones when extracted with ether yield to the extract choleic and stearic acids and cholesterol. The choleic acid obtained, m. p. 185—188°,  $[\alpha]_D + 48.2^\circ$ , was tasteless.

E. F. A.

**The Influence of Colloids on Diuresis.** FRANK P. KNOWLTON (*J. Physiol.*, 1911, 43, 219—231).—Colloids which possess an osmotic pressure, such as gelatin and gum acacia, inhibit in rabbits the diuresis produced by normal saline solution, or by hypertonic solutions of sodium chloride, but are largely ineffective on the diuresis caused by sodium sulphate. The diuresis produced by the latter salt is accompanied by an increased oxygen-consumption by the kidney; that produced by sodium chloride is apparently mechanical, or, at least, is not accompanied by detectable increase of metabolic activity. The colloids given cause no alteration in the blood-flow through the kidney, and do not affect its gaseous metabolism. Change in the concentration and, therefore, in the osmotic pressure of the blood colloids is thus a factor in the production of urine in the glomeruli. Colloids possessing no osmotic pressure have no such action.

W. D. H.

**The Influence of Hydrocyanic Acid on the Excretion of Sulphur in the Urine.** R. MAGNANIMI (*Chem. Zentr.*, 1911, ii, 1467—1468; from *Arch. farm. speriment.*, 12, 210—216).—Sub-lethal doses depress oxidative changes in the body, and, as would be expected, therefore cause an increase in the "neutral sulphur" of the urine. In rabbits, the effect is a lessened secretion of urine, and a percentage increase of sulphur. The total sulphur is slightly raised, but the increase is not in the neutral sulphur. This shows that other factors than mere oxidation have to be reckoned with.

W. D. H.

**Influence of Phloridzin on the Distribution of Nitrogen in the Urine of Starved Rabbits.** JUNZI YOSHIKAWA (*Zeitsch. physiol. Chem.*, 1911, 75, 475—487).—Following the injection of phloridzin into starved rabbits, there is an immediate marked increase in the output of amino-acids capable of being titrated by the formaldehyde method, which more than keeps pace proportionally with the total output of nitrogen. The absolute amount of carbamide excreted is parallel to the total nitrogen. A remarkable absolute and relative increase in the excretion of ammonia takes place shortly before death.

The increased protein decomposition under the influence of the poison is confirmed.

In parallel cases of exposure to extreme hunger, without the administration of phloridzin, the separation of total nitrogen, carbamide, and ammonia slowly increased, their relative proportions being the same as in the phloridzin experiments. An increased excretion of amino-acids was only observed just before death. Phloridzin accordingly exerts a specific action in causing the excretion of amino-acids.

E. F. A.

**The Occurrence of Lysine in the Urine in Cystinuria.** DANKWART ACKERMANN and FRIEDRICH KUTSCHER (*Zeitsch. Biol.*, 1911, 57, 355—359).—In cystinuria there is a metabolic condition in which the breakdown of amino-acids is inhibited. In numerous cases, leucine, tyrosine, as well as cadaverine and putrescine have been found in the urine. To this list it is now necessary to add lysine.

W. D. H.

**The Action of Alanine on the Excretion of Acetone.** GUNNAR FORSSNER (*Chem. Zentr.*, 1911, ii, 1049—1050; from *Skand. Arch. Physiol.*, 1911, 25, 338—342).—On a customary diet and muscular work, a slight acetonuria occurs, lasting about twelve hours (0.06 gram per hour). The addition of alanine diminishes this considerably. The “anti-ketogenic” action of alanine is thus considered to be proved.

W. D. H.

**Creatinine Excretion of the Pig.** E. V. MCCOLLUM (*Amer. J. Physiol.*, 1911, 29, 210—214).—Most pigs will take a sufficient amount of starch solution containing the necessary salts to meet all the energy requirements day after day with no evidence of anorexia, and no appreciable loss of weight. Under such conditions, exogenous protein metabolism would vanish, and the ratio of creatinine-nitrogen to total nitrogen should be constant. In six animals it averaged 18.5. About 60% of the total nitrogen was in the form of urea. No creatine was present. To determine endogenous protein metabolism in the pig it is necessary to determine the creatinine-nitrogen in the urine when the diet is free from nitrogen, and multiply by 5.5.

W. D. H.

**Action of Certain Lipoids in Producing Caseation.** H. GAEHLINGER and A. TILMANT (*Compt. rend.*, 1911, 153, 982—983).—Animals treated with subcutaneous injections of hepatic lipoids develop tumours consisting of a fibrous envelope enclosing a casein-like magma. Similar results have been obtained by Lefebvre (*Thèse*, Lille, 1911), using a meconium culture, and by Auclair, who employed a toxin from tubercle bacilli. These three materials all contain a considerable amount of cholesterol with fatty acids, and these are supposed to be the active agents in producing the substance resembling casein.

W. O. W.

**Emotional Glycosuria.** WALTER B. CANNON, A. T. SHOHL, and W. G. WRIGHT (*Amer. J. Physiol.*, 1911, 29, 280—287).—Fright or rage in a cat leads to glycosuria. This does not occur after removal of

the adrenals. Emotional glycosuria is possibly useful; fear and anger in wild life are likely to be followed by muscular struggles, and a mobilisation of sugar in the blood may be of service to the labouring muscles.

W. D. H.

**The Action of Phosphoryl Chloride on the Body of Man and of Animals.** ROBERT MÜLLER (*Chem. Zentr.*, 1911, ii, 41—42; from *Zeitsch. exp. Path. Ther.*, 1911, 9, 103—125).—Clinical experiences obtained on the human subject in cases of phosphorus poisoning, and poisoning after chloroform narcosis are discussed and amplified by direct experiments on rats. Inhalation experiments on the latter in a Dreser inhalation apparatus with solutions of phosphoryl chloride in benzene were carried out. The effects of the benzene could be readily distinguished from those of the phosphoryl chloride. The effects of the latter were found to depend far more on the concentration in the inhaled air and the time of action than on the absolute quantities in the animal organism. In an atmosphere of phosphoryl chloride containing 0.05—0.2 vol. % of the gas, the animals die within a few hours with serious lesions, whereas they can withstand several inhalations and live for a long time when it is only 0.0123 vol. %. The histopathological effects were also investigated. By oral ingestion of the aqueous solution, intense local irritant action was observed.

The coefficient of division of phosphoryl chloride between water and benzene was found to be 0.764 : 0.736.

S. B. S.

[Physiological Action of] Electrically Prepared Colloidal Rhodium. ANDRÉ LANCIEU (*Compt. rend.*, 1911, 153, 1088—1090. Compare Gutbier, Abstr., 1905, ii, 396, 533).—Colloidal rhodium has been obtained by Bredig's method, in the form of an unstable solution containing 0.002 gram per litre. This solution is toxic towards pathogenic organisms, but is without poisonous action on fish, frogs, and dogs, unless employed in very large doses. When rendered isotonic to blood by means of sodium chloride, and stable by the addition of a trace of sodium glycocholate, it was found to have a very beneficial effect in cases of pneumonia, typhoid, peritonitis, enteritis, post-operative septicæmia, and in tuberculosis during febrile periods. The injections were painless, and in fever reduced the temperature to normal. The patient's urine showed an increase in chlorine and uric acid, but a marked diminution in urobilin and in scatole and indole derivatives. Leucocytosis was increased.

W. O. W.

**The Influence of Guaiacol Derivatives on the Excretion of Glycuronic Acid.** TH. KNAPP (*Chem. Zentr.*, 1911, ii, 41; from *Schweiz. Woch. Chem. Pharm.*, 1911, 49, 229—231).—The amounts of guaiacol derivatives excreted after ingestion, in combination with glycuronic and sulphuric acids were estimated. The glycuronic acid was estimated by Tollens' method. After ingestion of potassium guaiacolsulphonate, the glycuronic acid increased above the normal only after large doses (3 grams). The increase of conjugated acids after administration of guaiacol glycerol ether is due, not only to the presence of paired acids with guaiacol, but also to conjugated acids of a non-volatile derivative.

S. B. S.

**The Action of Choline and Neurine.** J. PAL (*Chem. Zentr.*, 1911, ii, 1253—1254; from *Zeitsch. exp. Path. Ther.*, 1911, 9, 191—206).—Synthetically prepared choline when intravenously injected acts either as a depressor or pressor substance, and the effect is largely determined by the state of narcosis. After protracted ether narcosis or the use of some kinds of curare, the pressor effect comes out. Subcutaneously injected, it has but little toxic action. The effect of neurine hydrochloride is much more powerful, and very minute doses raise the blood pressure; it produces the same effect when given hypodermically. The effect of choline on the heart is inconstant, but there is usually a primary weakening of its action, followed by an increase. W. D. H.

**The Behaviour of Betaine, Trigonelline, and 1-Methylpyridinium Hydroxide in the Animal Organism.** ARNT KOHLRAUSCH (*Zeitsch. Biol.*, 1911, 57, 273—308).—If betaine is given to an animal, much of it passes unchanged into the urine; the amount so unaffected in its passage through the body is greater in herbivora than in carnivora. This occurs whether it is given by the mouth or injected hypodermically. Some is broken down to trimethylamine. Trigonelline and methylpyridinium hydroxide are excreted completely as such. In man, during abstinence from nicotine and caffeine, no pyridine derivatives occur in the urine. Betaine chloride acts on the isolated heart and on blood pressure, as Waller, Plimmer, and Miss Sowton stated. Trigonelline acts in a similar way. Methylpyridinium hydroxide, however, increases the arterial pressure and diminishes pulmonary ventilation. W. D. H.

**Strychnine Reversal.** A. G. W. OWEN and CHARLES S. SHERRINGTON (*J. Physiol.*, 1911, 43, 232—241).—Under the influence of strychnine, certain inhibitory reflex phenomena in skeletal muscles are converted into excitatory reflex effects. The possible explanations are discussed, but no definite decision arrived at. W. D. H.

**Some Iodine Compounds and Preparations in Common Therapeutic Use.** EDUARDO FILIPPI (*Arch. Farm. sper. Sci.*, 1911, 12. Reprint 22 pp.).—The catalases of the blood and of the liver readily absorb iodine, for instance, from an alcoholic iodine solution. The product obtained may contain 10—20% of adsorbed iodine, and when the iodocatalase is administered to an animal, the elimination of the iodine is very slow. The iodocatalases do not affect the progress of peptic digestion, and their own catalytic activity is not sensibly less than that of the non-iodised catalases.

The author discusses the probable mode of attachment of the iodine in several preparations intended for use as drugs. Some are adsorption products, others true iodine compounds in which the iodine is linked either to carbon or oxygen; many so-called organic iodine compounds are really derivatives of hydriodic acid. R. V. S.

**The Physiological Action of Extracts of the Pineal Body.** H. E. JORDAN and J. A. E. EYSTER (*Amer. J. Physiol.*, 1911, 29, 115—123).—The effect of injecting extracts of the pineal body

intravascularly in cats is small and unimportant, as stated by Dixon and Halliburton; in dogs the fall of blood-pressure is more marked, and is associated with vaso-dilatation in the intestinal area. The beat of the isolated cat's heart is slightly improved by the addition of the extract; transitory diuresis associated with glycosuria occurred in about 80% of the cases.

W. D. H.

**Physiological Action of Atoxyl (*p*-Aminophenylarsinic Acid).** MAXIMILIAN NIERENSTEIN (*Ber.*, 1911, 44, 3563).—A claim for priority. Bertheim (*Abstr.*, 1911, i, 1055) has attributed to Ehrlich the suggestion that the amino-group in atoxyl plays the same rôle as the chromogenic group in a dye. It was made previously by Breinl and Nierenstein (*Abstr.*, 1909, ii, 509).

E. F. A.

**Bio-chemical Investigations of Aromatic Mercury Compounds.** WALTHER SCHRAUTH and WALTER SCHOELLER (*Biochem. Zeitsch.*, 1911, 37, 510—511).—Further reply to Blumenthal (*Abstr.*, 1911, ii, 1017).

S. B. S.

**Narcosis and Want of Oxygen.** IV. ELISABETH HAMBURGER (*Pflüger's Archiv*, 1911, 143, 186—188).—Various narcotics of the fatty series dissolved in olive oil diminish its capacity to absorb oxygen. Sulphonal and trional act most, and tetronal, among the narcotics tested, least, strongly.

W. D. H.

**Action of an Oxazine (3:5:9-Triaminophencxazonium Chloride) and of Acridine on Trypanosomes.** A. LAVERAN and D. ROUDSKY (*Compt. rend.*, 1911, 153, 916—919. Compare *Abstr.*, 1911, ii, 911).—When the centrosomes of trypanosomes (*Tr. evansi*) from the blood of mice have been caused to disappear by administration of an oxazine, as described in an earlier communication, it is possible to produce a similar condition in untreated mice by inoculating them with such modified trypanosomes. Acridine has a similar action on the centrosomes. The action is attributed to autoxidation, since substances, such as alkaloids or potassium cyanide, which diminish oxidation also prevent absorption of the dyes by the centrosomes.

W. O. W.

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## Chemistry of Vegetable Physiology and Agriculture.

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Formation of Calcium Carbonate in the Soil by Bacteria.  
CONRAD T. GIMMINGHAM (*J. Agric. Sci.*, 1911, 4, 145—149. Compare Munro, *Trans.*, 1886, 49, 648 ; Hall and Miller, *Abstr.*, 1906, ii, 119). —Six organisms were obtained, from two soils, which have the power of producing calcium carbonate from calcium oxalate. The time required, as measured by the number of days which elapsed before crystals of calcium carbonate could be detected, varied from fourteen to sixty-five

days. An impure, mixed culture was found to be more active. No production of carbonate took place under anaerobic conditions.

It is probable that soils contain a number of organisms which oxidise calcium oxalate; the organisms seem to be more active in this respect when the soil is deficient in organic matter. N. H. J. M.

**Toxic Effects of "Alkali Salts" in Soils on Soil Bacteria. I. Ammonification.** CHARLES B. LIPMAN (*Centr. Bakt. Par.*, 1911, ii, 32, 58—64).—Chlorides of sodium, potassium, calcium, and magnesium have been shown to exert a marked toxic effect on *Bacillus subtilis*, and it appeared of interest to ascertain the effect of alkali salts on the ammonia producing flora of normal soils.

To 100 grams of air-dried soil were added 2 grams of dried blood and 18 c.c. of water, or of a solution of sodium chloride, sulphate, or carbonate, so that the amount of salt added varied from 0.2 to 2.0% of the soil. After incubation at 26—28° for four days, the ammonia formed was distilled over with magnesium oxide. It was found that even such quantities as 0.2% of sodium chloride exerted a marked toxic effect on the soil bacteria, and the amount of ammonia was only about one-third of that formed by the untreated soil. Sodium sulphate acts more gradually, but leads to a similar diminution of bacterial activity. Sodium carbonate stimulates ammonification in doses up to 1%, and only begins to be toxic when present in quantities above 1.4%. This may serve to explain the presence of large amounts of plant food associated with "black alkali" (sodium carbonate) soils. Increased or decreased bacterial activity cannot be correlated with plant growth on such soils, as the behaviour of bacteria towards these salts is the reverse of that of higher plants. H. B. H.

**The Bio-chemical Conversion of Pyrrolidine-2-carboxylic Acid into *n*-Valeric and  $\delta$ -Aminovaleric Acids.** CARL NEUBERG (*Biochem. Zeitsch.*, 1911, 37, 490—500).—By treatment of proline with the putrefactive bacteria derived from putrid meat in a suitable medium, the two above-mentioned acids were obtained, the valeric acid being separated by distillation with steam, and the amino-acid left in the residue along with unchanged proline, which latter substance was separated by means of its copper salt. A recapitulation of the putrefactive changes of the amino-acids already investigated by the author is also given. S. B. S.

**The Origin of Optically Active Valeric Acid in the Putrefaction of Proteins.** CARL NEUBERG (*Biochem. Zeitsch.*, 1911, 37, 501—506).—*d*-isoLeucine yields on treatment with putrefactive bacteria, as chief product, *d*-valeric acid ( $\alpha$ -methylbutyric acid), and also *d*-hexoic (*d*- $\beta$ -methylvaleric) acid. The isoleucine employed was prepared synthetically. S. B. S.

**Does *d*-Ornithine Undergo Racemisation on Treatment with Putrefactive Bacteria?** CARL NEUBERG (*Biochem. Zeitsch.*, 1911, 37, 507—509).—The author could detect no racemisation of the *d*-base during putrefaction, and in this respect obtained a result not in accordance with that obtained by Ackermann. S. B. S.

**Nitrogen Nutrition of *Aspergillus niger*.** WIDAR BRENNER (*Ber. Deut. botan. Ges.*, 1911, 29, 479—483).—Experiments with *Aspergillus niger* on the assimilation of various forms of nitrogen showed that the most suitable of the compounds employed were ammonium lactate, tartrate, succinate and oxalate, and asparagine. Carbamide and the mineral salts of ammonium come next in the following order: sulphate, chloride, nitrate, and phosphate; then ammonium acetate and formate, formamide, nitrosodimethylamine hydrochloride, and pyridine nitrate. In the case of pyridine nitrate only the nitric nitrogen seems to be assimilated.

Normal butylamine hydrochloride follows immediately after nitrates. Guanidine nitrate and hydrochloride come next, then isobutylamine hydrochloride, and, lastly, isoamylamine hydrochloride, hydroxylamine sulphate, benzylamine sulphate, dicyanodiamide, and acetonitrile.

Free ammonia, sodium nitrite, ammonium valerate, and potassium cyanide are toxic, whilst tetramethylammonium chloride, nitroguanidine, nitromethane, isoamylamine acetate, and pyridine and piperidine chlorides were not utilised as sources of nitrogen.

N. H. J. M.

**Cellobiose as a Source of Energy for Nitrogen Fixation by *Azotobacter*.** ALFRED KOCH and SIEGFRIED SEYDEL (*Centr. Bakt. Par.*, 1911, ii, 31, 567—570).—Cellulose cannot be utilised directly by *Azotobacter*, and must undergo a preliminary decomposition by certain soil organisms before any nitrogen is assimilated. An attempt was made to cultivate *Azotobacter* on agar with 2% cellobiose, but only one culture showed any gain (10.7 mg. N per gram of cellobiose supplied). This was due, no doubt, to the presence of soil bacteria capable of attacking the compound tested with the formation of sugar. Other cultures gave slight gains (2.55 mg.) when *Aspergillus* was grown on the medium previous to inoculation with *Azotobacter*.

The conclusion is drawn that this organism is unable to utilise cellobiose in pure culture, but does so in the presence of certain soil bacteria or of *Aspergillus niger*.

H. B. H.

**The Process of Nitrogen Assimilation by *Azotobacter*.** ALFRED KOCH and SIEGFRIED SEYDEL (*Centr. Bakt. Par.*, 1911, ii, 31, 570—577).—The usual method of estimating the nitrogen-fixing power of *Azotobacter*, whereby the amount of nitrogen gained is calculated on the amount of carbohydrate supplied, does not accurately represent the intensity of the process.

By means of a series of sugar and nitrogen estimations, it is shown that nitrogen fixation only occurs during active growth, and comes to an end after five to eight days. The rest of the carbohydrate is used for respiration and other purposes.

In one series of estimations, the amounts of nitrogen fixed per gram of dextrose used were 53, 70—80, 20—30, 5—8 mg. on the second, third, seventh, and eighth days respectively.

H. B. H.

**The Permeability of the Yeast Cell.** SYDNEY G. PAINE (*Proc. Roy. Soc.*, 1911, B, 84, 289—307).—Pressed brewers' yeast was

immersed for varying times in solutions of various substances, and the distribution of the substance between the cells and the surrounding liquid ascertained.

With dilute alcohol in concentrations varying from 5 to 20%, the ratio of the concentration within the cells to that without rapidly becomes constant, and is independent of the absolute concentration. Alcohol is believed to diffuse readily into the cell, and as this ratio is not unity, but approximately 0.85, it is probable that all the water within the yeast cell is not available for diffusion of the alcohol.

All salts which have been tried are taken up by yeast from moderately concentrated solutions, but differ from alcohol in that equilibrium is reached very much more slowly, and the absorption is not nearly so complete. Thus in the case of alcohol, equilibrium was reached within three hours, whereas with 0.1 molar sodium chloride, none had entered in the same time, and only a small quantity after twenty hours. With 0.1 molar disodium hydrogen phosphate no salt had entered the cells even after twenty hours' immersion, but from 0.3 molar solutions a marked entrance was observed in the same time. Sodium hexose-phosphate behaved in a similar manner to sodium phosphate. As there is no evidence that the latter is fermented by living yeast, whilst it is readily fermented by yeast-juice, it seems probable that this salt does not penetrate into the seat of fermentative activity of the yeast-cell.

W. J. Y.

**Fermentations with Yeast in Absence of Sugar.** VI. CARL NEUBERG and L. KARCZAG (*Biochem. Zeitsch.*, 1911, 37, 170—176. Compare Abstr., 1911, ii, 320, 520, 1019, 1020).—The action of the yeast "carboxylase," under the influence of which aldehyde and carbon dioxide are formed from oxalylacetic and pyruvic acids, was investigated in the presence of the following substances: Acetonedicarboxylic acid, chelidonic acid, dihydroxytartaric acid, benzoylacetic acid, phenylpyruvic acid, *p*-hydroxyphenylpyruvic acid, phenylglyoxylic acid, and acetylenedicarboxylic acid. A negative result was obtained with benzoylacetic acid, and a doubtful one with acetylenedicarboxylic acid. All other acids showed evolution of carbon dioxide when treated with the enzyme.

S. B. S.

**Behaviour of Pentoses in Fermenting Mixtures.** W. E. CROSS and BERNHARD TOLLENS (*J. Landw.*, 1911, 59, 419—428. Compare Schöne and Tollens, *ibid.*, 1901, 21; Cross, Bevan, and Smith, *Trans.*, 1898, 73, 462).—The results of experiments with arabinose, xylose, and rhamnose show that solutions free from sugars of the hexose series do not ferment, and that the pentoses remain unchanged for a long time. Similar results were obtained in presence of dextrose when yeast-water was employed. In artificial nutritive solutions, however, containing only small amounts of organic matter, the pentoses are utilised for the growth of the yeast.

N. H. J. M.

**Chemical Composition of Some Higher Fungi.** A. GORIS and M. MASCRÉ (*Compt. rend.*, 1911, 153, 1082—1084. Compare Abstr., 1909, ii, 175).—Two cholesterols, probably identical with Tanret's ergosterol and fongosterol, have been isolated from fungi of various species, such as *Lactarius piperatus*, *Psalliota campestris*, *Tricholoma album*, etc. A new compound, apparently not a cholesterol, has been obtained from certain fungi, notably from *Collybia maculata*. This substance is extracted from the dried material by means of acetone, and occurs as large, colourless crystals, m. p. 201—202°. It is neutral, does not contain nitrogen, and is insoluble in water and ether.

Carbamide is not invariably present in the higher fungi. The extent to which it occurs depends on the season and the mode of cultivation. W. O. W.

**Narcosis and Want of Oxygen.** III. The Action of Narcotics and Oxygen-withdrawal on Germinating Seeds. G. MANSFIELD [with, in part, B. FARKAS] (*Pflüger's Archiv*, 1911, 143, 175—185. Compare Abstr., 1910, ii, 222).—The experiments recorded support Meyer's views on the action of narcotics. They delay germination in exactly the same way as does the withdrawal of oxygen. W. D. H.

**Probable Function of the Essential Oils and Other Volatile Products of Plants as the Cause of the Movement of Sap in Living Tissues.** ITALO GIGLIOLI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 349—361).—The vapours of carbon dioxide, ether, chloroform, and formaldehyde, and of many essential oils decrease the surface tension of aqueous solutions, as may be shown by the rapid disintegration of soap-films exposed to them. Porous rock or sand which contains just as much water as it can hold by capillarity gives out water in an atmosphere containing these substances. A similar behaviour is observed in the case of many plants. When the dried, compressed yeast of commerce is exposed to air containing the vapour of chloroform, oil of eucalyptus or camphor, or of camphor, it becomes soft and juicy in a few hours; in a few days the mass is wet enough to filter, and the filtrate is not water, but a juice containing zymase. *Boletus* behaves in the same way, exuding a liquid containing much organic matter. The organs of the higher plants are similarly affected by these vapours, and by those of a large number of essential oils; the tissues become more succulent and sap is exuded. The action may be revealed in the earlier stages by the activity of the enzymes which the moving saps contain; thus the seeds of the apricot and the leaves of the cherry-laurel are caused to produce hydrogen cyanide by the vapours of a large number of essential oils and other substances. The evolution of hydrogen cyanide is explained by the author as being due to the action of enzymes brought into contact with their substrates by the movement of the sap which the vapour initiates. Since the activity of plant enzymes often leads to the formation of essential oils, the author regards the effect as cumulative, and finds in it an explanation of the movement of sap in plants. R. V. S.

**Plants Containing Essential Oils.** ANNE W. K. DE JONG (*Rec. trav. chim.*, 1911, 30, 211—219. Compare Abstr., 1905, i, 802).—The quantity of essential oil in the plant is measured by distilling a definite weight of leaves with about five times the weight of water, the water distilling over being returned from time to time until the quantity of essence in the distillate no longer increases.

In the case of Singapore Patchouli (*Pogostemon tomentosus*) it is found that the essence is formed in the three top leaves, and that the quantity only diminishes slightly with age. The branches also contain the essence, and the roots contain an essence heavier than water. With Java Patchouli, the quantity of essence also diminishes after the third leaf.

Contrary to the idea in text-books on the subject, the author finds that the quantity of essence in fermented leaves is not greater than in dried leaves. The first leaves, however, show, by distillation, a much smaller amount of essence than the other two. W. G.

**Formation of Anthocyanin.** (Miss) MURIEL WHELDALÉ (*J. Genetics*, 1911, 1, 133—158. Compare Nierenstein and Wheldale, this vol., i, 42).—From the consideration of analogous reactions and the results of observations on the distribution of anthocyanin, and from experimental evidence on the concentration of sugars and glucosides in various tissues, on the existence of enzymes, and on sugar feeding, the following conclusions are drawn.

The soluble pigments in flowering plants, collectively termed anthocyanin, are oxidation products of colourless chromogens, existing in the tissues as glucosides. The production of the glucoside from the chromogen and sugar is of the nature of a reversible enzyme reaction:  $\text{chromogen} + \text{sugar} \rightleftharpoons \text{glucoside} + \text{water}$ , and the oxidation of the chromogen, which is effected by one or more enzymes, can only take place after its liberation from the glucoside. The amount of free chromogen (and hence of pigment) formed at any time is thus inversely proportional to the concentration of sugar and directly proportional to the concentration of glucoside in the same tissue.

The local production of anthocyanin is due to local variation in concentration, either of the free sugars or the glucosides. Abnormal production of pigment results from similar differences in concentration caused by changes in metabolism due to altered conditions.

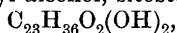
The above hypothesis brings the formation of anthocyanin into line with that of other pigments produced after the death of the plant (indigotin, etc.). N. H. J. M.

**Myristone Obtained from Alfalfa.** C. A. JACOBSON (*J. Amer. Chem. Soc.*, 1911, 33, 2048—2051).—Experiments are described which indicate that alfalfa contains myristone in combination with one or more other substances. The compound, or compounds, can be extracted with hot 95% alcohol, and the myristone can be isolated by means of dilute nitric acid. E. G.

**Amount of Hydrogen Cyanide during the Ripening of Bitter and Sweet Almonds.** G. DE PLATO (*Chem. Centr.*, 1911, ii, 882; from *Staz. sper. agrar. ital.*, 1911, 44, 449—458).—In bitter

almonds the amount of free hydrogen cyanide diminishes, whilst the glucoside hydrogen cyanide increases, with the growth of the cotyledons. The hydrogen cyanide in sweet almonds disappears as ripening proceeds. N. H. J. M.

**Chemical Examination of the Leaves of *Anona muricata*.** THOMAS CALLAN and FRANK TUTIN (*Pharm. J.*, 1911, [iv], 33, 743—745).—The alcoholic extract of the leaves, on distillation in steam, yielded a small amount of a green, volatile oil having a strong, rather agreeable odour. The water-soluble portion of the extract contained potassium chloride, tannin, dextrose, uncrystallisable alkaloid, and amorphous products, the latter being extracted in turn by ether, chloroform, and amyl alcohol. The portion of the extract insoluble in water consisted of a soft, oily green resin, which was extracted successively with (a) light petroleum, (b) ether, (c) chloroform, (d) ethyl acetate, and (e) alcohol, of which the first two alone gave extracts which yielded definite products. (a) This was a dark green, oily mass, which when hydrolysed by potassium hydroxide in alcohol furnished myricyl alcohol and sitosterol with linoleic, oleic, and stearic acids and a fourth acid, which may be lignoceric acid,  $C_{24}H_{48}O_2$ ; (b) this formed a dark green, soft mass, which after the removal of a dark green solid, sparingly soluble in ether, was hydrolysed by potassium hydroxide in alcohol, and yielded a mixture of acids giving non-volatile methyl esters, together with myricyl alcohol, sitosterol, and *anonol*,



m. p. 294—298° (decomp.), crystallising in colourless leaflets and giving colour reactions similar to those of ipurganol; the *diacetyl* derivative, m. p. 166°, forms colourless, flattened needles, and the *dibenzoyl* derivative, m. p. 197—198°, small, colourless needles. No glucoside was present. T. A. H.

**Crystalline Protein from the Latex of *Antiaris toxicaria*.** YASHIRO KOTAKE and FRANZ KNOOP (*Zeitsch. physiol. Chem.*, 1911, 75, 488—498).—The residues of *Antiaris toxicaria* latex, after extraction with 85% alcohol (compare Kiliani, Abstr., 1911, i, 138), when extracted with 0·8% acetic acid yield a substance crystallising in needles or short, characteristic prisms. When purified by crystallisation from normal hydrochloric acid, it forms polyhedra, and is free from ash. It is precipitated from solution in acetic acid by half-saturation with ammonium sulphate, and shows the protein colour reactions, excepting that of Molisch. It has the composition C 48·02, H 5·7, N 15·6, S 7·2,  $[\alpha]_D -19·25^\circ$ , and contains 15·7% of water of crystallisation. On hydrolysis the formation of cystine, tyrosine, lysine, glycine, alanine, proline, and valine was detected. E. F. A.

**The Enzymes in Young Bamboo Shoots.** KAN KATO (*Zeitsch. physiol. Chem.*, 1911, 75, 456—474).—The sap of bamboo shoots contains nuclease and a “deamidase,” which decomposes urea strongly and asparagine slightly, but does not attack glycine.

A proteolytic enzyme acting on fibrin was detected, and is being investigated, and one or more diastases. Amygdalin and salicin are also decomposed. H. B. H.

**The Influence of Chemicals on the Germinating Capacity of *Cuscuta arvensis* and *Cuscuta trifolia*.** G. D'IPPOLITO (*Chem. Zentr.*, 1911, ii, 370; from *Staz. sperim. agrar. ital.*, 44, 301—308).—The action of chemicals in sterilised and ordinary soils on the germinating capacity of the seeds was investigated. Ammonium nitrate, sodium carbonate, calcium cyanamide, and formalin kill the seeds, potassium nitrate and carbonate almost entirely inhibit the germinating capacity, sodium and calcium nitrates act less powerfully, and magnesium sulphate has hardly any action. For killing *Cuscuta*, the author recommends the treatment of the soil with either 2% ammonium nitrate or 1% formaldehyde solution. S. B. S.

**The Presence of Sucrose in Gentian Root Dried in the Air without Fermentation.** MARC BRIDEL (*J. Pharm. Chim.*, 1911, [vii], 4, 455—458).—Gentian root which has been dried without undergoing fermentation contains large quantities of carbohydrates hydrolysable by invertase. On the other hand, commercial preparations which are fermented in the process employed in their production contain very much less of these carbohydrates.

The principal carbohydrate is sucrose, which was isolated from the root by extraction with alcohol.

No gentianose could be obtained.

W. J. Y.

**A Proteolytic Enzyme in the Must of Over-ripe Grapes.** ENRICO PANTANELLI (*Centr. Bakt. Par.*, 1911, ii, 31, 545—559).—The must from over-ripe white and black grapes contains an enzyme which breaks down the proteins with the formation of soluble products not precipitated by copper hydroxide. This change is probably due to the action of several enzymes, since it occurs also when the reaction is neutral or slightly alkaline. The presence of tannin does not inhibit the change.

The decomposition products primarily formed become condensed by the action of a substance to which the name *synprotease* has been given, and a state of equilibrium is established.

Among the antiseptics employed, thymol and potassium meta-hydrogen sulphite allow of a greater enzyme action than formaldehyde, but the sulphite probably acts chemically, as the amount of change increases with the sulphur dioxide content of the solution.

H. B. H.

**Action of Certain Diureides and of Hippuric Acid on the Development and Tuberisation of Radishes.** MARIN MOLLIARD (*Compt. rend.*, 1911, 153, 958—960).—Radishes were grown in nutrient solutions to which 0.1% of different nitrogen compounds were added. Glycine, carbamide, xanthine, sodium urate, and allantoin increased the yield of dry material in the plants, whilst sarcosine, theobromine, caffeine, and sodium hippurate exerted a toxic action, diminishing the yield. Caffeine was the only compound which completely stopped development. Xanthine was less toxic than sarcosine; sodium urate and allantoin exerted the most favourable effect on development. The proportion of water in the plants showed an

increase with all the compounds examined except caffeine. Sodium urate increases the number of tubers formed, and raises their total content of dry material. W. O. W.

**Presence of Glycogen in Phanerogams and its Relation to Calcium Oxalate.** IOANNES POLITIS (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 431—439).—Glycogen, which has hitherto been found among plants only in the cryptogams, occurs also in certain phanerogams, but always in cells in which deposits of calcium oxalate afterwards appear. The mucilage of the tubers of *Orchis Morio*, which has been considered to be cellulose, is shown by its microchemical behaviour to be glycogen, which has been similarly demonstrated in *Bletia hyacinthina*, *Pitcairnia xanthocalyx*, and *Billbergia nutans*.

R. V. S.

**The Action of the Respiratory Enzymes of *Sauromatum Venosum*.** TH. WEEVERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 370—377).—If the juice expressed from the spadices of *Sauromatum venosum* is precipitated with alcohol, a crude preparation of an enzyme is obtained, which decomposes dextrose with the formation of carbonic and organic acids, but without the production of alcohol either in air or an atmosphere of hydrogen. Destruction of the cellular structure and treatment with alcohol or acetone do not inactivate this respiratory enzyme. A crude enzyme is similarly obtained from the leaves of the plant, but its action is weaker. In the ethereal extract of the acid liquid, citric acid was demonstrated; this is probably formed by the respiratory enzyme at the expense of the dextrose. W. D. H.

**Formation of the Alkaloids in Tobacco.** CIRO RAVENNA and V. BABINI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 393—398. Compare Ciamician and Ravenna, *Abstr.*, 1911, ii, 761).—The authors have estimated the amount of nicotine produced in tobacco plants in culture solutions, with a view to determining the effect of nitrates, dextrose, and light. No final conclusions are drawn from the experiments, but the amount of nicotine produced was greater in all cases than the amount found in plants grown in soil, and the increase was greatest where both dextrose and nitrates were supplied to plants growing in the light. R. V. S.

**The Ammonia Content of Tobacco Smoke.** WILHELM VAUBEL (*Chem. Zeit.*, 1911, 35, 1331—1332).—The change in colour of the leaves of certain flowers when these are exposed to tobacco smoke is due to the presence of ammonia in the smoke; when the smoke from a cigar is drawn into the mouth, the ammonia is absorbed, and the smoke expelled from the mouth is without effect on the flowers. The author also discusses the physiological action of tobacco smoke. W. P. S.

**Manuring of Sugar Beets with Sodium Chloride.** FRIEDRICH STROHMER and OTTOKAR FALLADA (*Chem. Zentr.*, 1911, ii, 386; from *Österr.-ung. Zeitsch. Zucker-Ind. Landw.*, 1911, 40, 425—441).—Experiments were carried out on the replacement of sodium nitrate

with ammonium sulphate containing the same amount of nitrogen, together with sodium chloride. With the exception that the beets contained more chlorine and sodium, the results were nearly the same.  
S. B. S.

**The Treatment of Soil with a Strong, Continuous Electric Current.** JOSEF KÖNIG, JULIUS HASENBÄUMER, and C. HASSLER (*Zeitsch. angew. Chem.*, 1911, 24, 2341—2348. Compare Abstr., 1910, ii, 1104).—The soil is mixed with water and introduced into a dialysing vessel, in which a platinum cathode is placed. The platinum anode is placed in the outer vessel, below the parchment diaphragm. A current of 3 amperes is then passed, and the inner and outer solutions are renewed whenever the temperature reaches 50°.

The collected anodic and cathodic solutions are filtered and analysed. With sandy soils, the organic content of the acid liquid, as shown by titration with permanganate, is greater than that of the alkaline solution, whilst with marly and clayey soils the proportions are reversed. This is due to the larger proportion of humic acids, which do not coagulate but pass through the diaphragm, in sandy soils. Other experiments, with soils previously treated with potassium phosphate, show that only readily soluble salts and those retained by colloids are dissolved by the current. A comparison of three processes: heating the soil with water under five atmospheres pressure, oxidation with hydrogen peroxide, and electrolysis, shows that the two former methods dissolve about equal quantities of potash, whilst oxidation dissolves rather more phosphoric acid. Electrolysis dissolves much greater quantities, even a single passage of the current dissolving more potash and phosphates.  
C. H. D.

**Hygroscopic Moisture of Soils.** CHARLES B. LIPMAN and LESLIE T. SHARP (*J. Physical Chem.*, 1911, 15, 709—722).—In the estimation of the amount of moisture absorbed from a saturated atmosphere by dried soils, the soil must be exposed in a thin layer. If the soil is much more than one millimetre deep, a very long time is necessary for the attainment of equilibrium. A rise in temperature with corresponding rise in the pressure of the aqueous vapour leads to a greater absorption of water by the various soils studied, but no definite law of absorption could be found.

The absorptions appeared to be lower at a steady temperature in the incubator than with fluctuating room temperatures of about the same degree. It is suggested that plants in the arid regions are protected by the great amounts of hygroscopic moisture absorbed by the soil with rising temperatures.  
R. J. C.

**Loew's Lime-Magnesium Ratio.** ROBERT STEWART (*J. Ind. Eng. Chem.*, 1911, 3, 376—378).—The beneficial action of lime on agricultural soils is a well-known and undisputed fact, but that of magnesium is not understood, and according to some authorities it has beneficial results only when present in a certain ratio to the calcium, whilst others state that it has a detrimental or even toxic effect on plant life.

After discussing previous work on this subject, the author describes the conditions prevailing on a farm belonging to the Utah experiment station, where analysis of the soil at a depth of 1—8 feet shows the presence of 30—41% of calcium carbonate and 11—20% of magnesium carbonate, and although the land has been continuously cropped for forty years without the addition of manure, its average yield in bushels per acre is oats 82·0, wheat 50·4, and potatoes 262. The author suggests that possibly magnesium when present as the double salt,  $\text{MgCa}(\text{CO}_3)_2$ , reacts differently to the simple salt,  $\text{MgCO}_3$ . F. M. G. M.

**Effect of Ignition on the Solubility of Soil Phosphates.** GEORGE S. FRAPS (*J. Ind. Eng. Chem.*, 1911, 3, 335).—An account of experiments which demonstrate that the ignition of soil during ten minutes at a dull red heat greatly increases the solubility of some of its inorganic constituents in hydrochloric acid, and therefore the experimenters who consider the increased amount of soluble phosphoric acid found in soils after ignition to be due to liberated organic phosphorus are in error.

The author finds that ignition (1) increases the solubility ten times of the phosphoric acid in wavellite, dufrenite, and variscite in *N/5*-nitric acid; (2) it renders these minerals almost completely soluble in 12% hydrochloric acid, and (3) it converts considerable quantities of iron and aluminium oxides into a soluble condition.

F. M. G. M.

**After-effect of Palmaer Phosphate, Basic Slag, and Superphosphate on Peat Soil.** HJALMAR VON FEILITZEN (*J. Landw.*, 1911, 59, 371—374).—Potatoes and blue lupins were grown in large boxes containing peaty soil previously manured with the three phosphates ( $\text{P}_2\text{O}_5 = 50$  and 100 kilos. per ha.). The after-effect with potatoes was greatest with basic slag, next with Palmaer phosphate, whilst with superphosphate somewhat lower results were obtained. The percentage of starch was highest in the soil containing the residue of Palmaer phosphate, and where the larger amount had been applied ( $\text{P}_2\text{O}_5 = 100$  kilos.) the greatest yield of starch was also with Palmaer phosphate.

In the case of lupins the highest yield, after an application of 50 kilos. of phosphoric acid, was with superphosphate, whilst with the higher amount of phosphates the best result was obtained from the residue of Palmaer phosphate.

As regards after-effects, Palmaer phosphate seems therefore to be at least equal to superphosphate on peat soil containing plenty of lime and nitrogen. The after-effect of basic slag is somewhat greater.

N. H. J. M.

**Volatilisation of Ammonia and Changes of Ammonia in Soils.** JOHANN VON WLODECK (*Bied. Zentr.*, 1911, 40, 729—734; from *Inaug. Diss.*).—The loss of ammonia from soils containing considerable amounts of calcium carbonate is much reduced when ammonia-superphosphate is employed instead of ammonium sulphate.

A light soil manured with ammonium sulphate showed a loss of

nitrogen, whilst the same soil manured with ammonia-superphosphate showed a gain. This is attributed to increased fixation of nitrogen by soil organisms due to the application of phosphate. A loam soil, containing over 10% of phosphoric acid soluble in hydrochloric acid, gave the same results with ammonium sulphate as with ammonia superphosphate.

As regards the fixation of the ammonia applied to soils, manuring with ammonia-superphosphate, as compared with ammonium sulphate, seems to have a retarding effect.

N. H. J. M.

**Origin of Creatinine in Soils.** MICHAEL X. SULLIVAN (*J. Amer. Chem. Soc.*, 1911, 33, 2035—2042).—The occurrence of creatinine in soils has been demonstrated by Shorey (*Science*, 1910, 33, 340). A study has now been made to determine its mode of origin.

It has been found that creatinine occurs more abundantly in soils which have recently borne a crop than in those which have not been planted for some time. It has also been detected in water in which wheat-seedlings had been grown, and also in wheat, wheat-bran, rye, clover, alfalfa, cowpeas, and potatoes. Although creatinine and creatine are only present in small amounts in vegetable matter, they are of importance, since by the decay of plant tissues and by green manuring they collect in the soil and exercise a beneficial influence on the growth of the crops.

E. G.

**Estimation of Solubility in Agricultural Chemistry.** ARTHUR RINDELL (*Akad. Einladungsschr. Helsingfors.*, 1910, 67 pp.).—The difficulties in estimating the solubilities of different manures (especially phosphates) due to varying conditions are discussed.

Since the mineral constituents of plants can only be assimilated when in solution, and it is probably correct to assume that the production of dry matter in crops has a constant relation to the amount of water used, it is possible to calculate the concentration of the nutritive solutions taken up at different periods. The following figures are given for a normal crop of barley (2500 kilos. of grain and 3000 kilos. of straw and chaff per hectare).

Period .....	I.	II.	III.	IV.	I.—IV.
Days .....	19	28	20	24	91
N, mg. per litre .....	76.6	21.9	2.4	22.4	31.1
K <sub>2</sub> O „ „ .....	108.6	35.9	(1.4)	—	37.9
P <sub>2</sub> O <sub>5</sub> „ „ .....	37.7	15.9	10.0	13.1	17.3

N. H. J. M.

### **Analytical Chemistry.**

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**A Modified Explosion Eudiometer.** F. H. CAMPBELL (*Chem. News*, 1911, 104, 235—236).—A three-way capillary tap is fitted at the top of the eudiometer; this arrangement is convenient when it is desired to demonstrate the proportions in which various gases combine,

as the latter may be introduced separately through the tap into the apparatus.

W. P. S.

**Simplification of Gravimetric Analysis.** ERNST MURMANN (*Zeitsch. anal. Chem.*, 1911, 50, 742—747).—Instead of an ordinary filter, a small disk of wet filter paper is placed over a perforated porcelain disk, and when filtering, suction is applied. A special apparatus is recommended, which is figured in the original.

Introduction of a minute quantity of filter-paper pulp is recommended. In cases where the precipitate has to be ignited, the precipitation as sulphide is much assisted by the addition of mercuric chloride, or, in the case of stannic oxide, some mercuric sulphide may be added in order to get a clear filtrate. The weight of the filter disk being seldom more than 0.02 gram, the process is very suitable for the direct weighing of dried precipitates, as it is not necessary to employ a weighing tube. Of course, no pulp is then added.

L. DE K.

**Standardising of Acids Without the Aid of Alkali Solutions.** FRIEDRICH KLINKERFUES (*Chem. Zeit.*, 1911, 35, 1274).—A definite volume of the acid intended for titrations is placed in a suitable receiver, in which is then collected the ammonia evolved from an accurately known weight of ammonium sulphate. Care should be taken that there shall be a slight excess of ammonia at the end of the distillation.

After adding a suitable indicator, the free ammonia present is titrated with the same acid, and the strength of the latter is then found by an easy calculation.

L. DE K.

**The Application of Methyl-red to the Colorimetric Measurement of Hydrogen Ion Concentrations.** SVEN PALITZSCH (*Biochem. Zeitsch.*, 1911, 37, 131—138).—The substance *p*-dimethyl-aminoazobenzene-*o*-carboxylic acid is specially adapted to the measurement of the hydrogen ion concentrations between the zones  $p_H = 4.2$  and  $p_H = 6.3$ , in which the colours vary from violet-red to yellow. The author gives a table of corrections to be applied in the presence of salts and proteins, in which cases the  $[H]^+$ -concentrations were determined by him electrometrically. The corrections to be applied are only small.

S. B. S.

**The Analysis of Chlorates.** VON BUTTLAR (*Chem. Zeit.*, 1911, 35, 1374).—Calcium carbonate is generally used in the neutralisation of reduced chlorate solutions before reduction. Time is saved by using magnesium hydroxide, made into a cream with water. Neutralisation is complete when a permanent turbidity appears, and filtration is unnecessary.

C. H. D.

**Estimation of Perchloric Acid in Certain Perchlorates.** HENRYK GOLBLUM (*Zeitsch. anal. Chem.*, 1911, 50, 741—742).—The author estimates perchloric acid in the nickel or cobalt compounds as follows: About 0.2 gram of the salt is dissolved in 300 c.c. of water, and electrolysed at the ordinary temperature for some seventy hours,

using as cathode a platinum gauze and a very weak current up to 0.1 ampere. The potential is rather high on account of the strong resistance, and varies between 10 and 12 volts.

The liquid containing the liberated perchloric acid is then titrated with *N*/10-alkali with phenolphthalein as indicator. L. DE K.

**Detection of Fluorine.** ERWIN RUPP (*Zeitsch. Nahr. Genussm.*, 1911, 22, 496—497).—The ash of the material to be tested for the presence of fluorine (fluorides) is placed in a platinum or lead crucible and moistened with 3 drops of water and 1 c.c. of sulphuric acid. The crucible is then closed with a rubber stopper, through which passes a glass rod, the end of the rod below the stopper being moistened with a drop of water. The crucible and its contents are now heated on a water-bath for about twenty minutes; during this time the water on the glass rod evaporates, and, should fluorides be present, the rod becomes coated with a film consisting of silica, sodium silicofluoride, and calcium silicofluoride. When only traces of fluoride are present, the portion of the glass rod below the stopper may be covered with a piece of rubber tubing, leaving only the end of the rod exposed; the action of the hydrofluoric acid is thus concentrated on a small surface of the glass. W. P. S.

**Estimation of Fluorides.** G. B. VAN KAMPEN (*Chem. Weekblad*, 1911, 8, 856—860).—For estimating calcium fluoride in the basic slag of the Talbot process, the author recommends Penfield's method (Abstr., 1879, 829), the conversion into silicon tetrafluoride, the decomposition of the fluoride with water in accordance with the equation:  $3\text{SiF}_4 + 4\text{H}_2\text{O} + 4\text{KCl} = \text{H}_4\text{SiO}_4 + 2\text{K}_2\text{SiF}_6 + 4\text{HCl}$ , and the titration of the hydrochloric acid formed, using lacmoid as indicator.

A. J. W.

**The Estimation of Oxygen in Iron and Steel.** ALLERTON S. CUSHMAN (*J. Ind. Eng. Chem.*, 1911, 3, 372—374).—The three important methods for estimating oxygen in steel are: (1) heating the sample in a stream of dry chlorine; (2) dissolving in special solvents, such as copper sulphate or bromine; (3) combustion in a stream of hydrogen, and the paper contains a sketch of the apparatus employed with exact details of how the author conducts the latter method.

The hydrogen is generated from drillings of pure iron or "mossy" zinc with dilute hydrochloric acid, and is passed successively through potassium hydroxide solution, concentrated sulphuric acid, over a roll of platinum gauze in a strongly heated silica tube, and finally over phosphoric oxide.

The finely divided borings (20—30 grams) are weighed into a platinum (or silica) boat introduced into the silica combustion tube, and after passing hydrogen until all air has been removed, the tube is rapidly heated to about 850°, maintained at this temperature during about thirty minutes, whilst the purified dry hydrogen passes at a rate of about 100 c.c. per minute; the apparatus is cooled in the stream of gas, and the tared absorption tube, which is charged with phosphoric oxide, re-weighed. A correction obtained by blank experiments must be employed to ensure accurate results. F. M. G. M.

**Estimation of Sulphur in Pyrites.** ARNOLD HECZKO (*Zeitsch. anal. Chem.*, 1911, 50, 748—753).—The following conclusions are arrived at. For a rapid and safe estimation of available sulphur in pyrites, Dennstedt's process (combustion in oxygen, absorption of the gases in sodium carbonate heated at 450°: *Abstr.*, 1905, ii, 761) is very suitable. Tubes made of quartz instead of Jena glass are, however, preferable, as they do not retain traces of sulphuric acid; this saves the trouble of rinsing the tube with hot water.

When precipitating the sulphate with barium chloride, double the theoretical quantity of the latter should be added. The results agree very well with those obtained by Lunge's process. L. DE K.

**The Phenolsulphonic Acid Method for the Estimation of Nitrates in Water.** ALFRED E. JOHNSON (*Chem. News*, 1911, 104, 235).—Attention is drawn to the necessity of heating the sulphuric acid and phenol together for eight hours (compare *Abstr.*, 1890, ii, 832) in order to obtain a reagent which will yield a red coloration with nitrates without any development of a green coloration.

W. P. S.

**Estimation of Nitrogen in Drainage Water and Rain Water by Schloesing's Method.** (Miss) ALIDA HUIZINGA (*Chem. Weekblad*, 1911, 8, 882—895).—The usual method of carrying out Schloesing's process gives inaccurate results, arising from the presence of air in the solutions employed, and of nitrites and carbonates in the samples examined. The author recommends evaporation of the water with potassium hydroxide instead of magnesium oxide, elimination of carbonic acid by boiling with acetic acid, and oxidation of the nitrite with acidified potassium permanganate. With these precautions, the error in the estimation of the nitrogen in an ordinary sample does not exceed 0.1 mg. of nitrogen. A. J. W.

**Bacteriological Methods for Estimating the Available Nitrogen in Fertilizers.** JACOB G. LIPMAN (*J. Ind. Eng. Chem.*, 1910, 2, 146—148).—That the formation of nitrates in organic substances bears a direct relationship to the proportion of nitrogen they contain, and generally also to the ease with which they undergo decomposition, has been demonstrated previously. From the fact that nitrate formation is preceded by the formation of ammonia, it would appear that a similar relationship should exist between ammonification and nitrification, and the present paper contains an account of preliminary experiments for the purpose of testing this hypothesis.

The nitrogenous material to be tested was mixed with 100 grams of soil and 1 gram of calcium carbonate, and maintained at its optimum moisture content (18%); a further quantity of water was added in the ammonification experiments to ensure an organic matter containing 75% moisture; the ammonia determination was made after six days, and the nitrate estimation after four weeks.

The results showed that, as a general rule, easily ammonifiable substances are also readily nitrifiable, the highest ammonia content being found in concentrated tankage, ground fish, solid and liquid

fresh manure, dried blood, and bone-meal, whilst the nitrate content followed the order concentrated tankage, cottonseed meal, ground fish, dried blood, and solid and liquid fresh manure.

The high position of cottonseed meal in the nitrate series, whilst possessing low availability in the ammonia series, is considered (from the result of other experiments) to be due to the depressing effect of soluble carbohydrates on ammonification. F. M. G. M.

**A Bacteriological Method for Estimating Available Organic Nitrogen.** J. M. McCAUDLESS and F. C. ATKINSON (*J. Ind. Eng. Chem.*, 1911, 3, 174—175).—An account of experiments to determine the available ammonia in two samples of fertilisers prepared from leather by a special process which rendered it soluble; cottonseed meal was employed for comparison.

The total nitrogen content in the initial materials, also in their filtered boiling water extracts, was estimated, the extracts shaken up with soil, the filtered solutions incubated at 38—40° under both aerobic and anaerobic conditions (the surface of the liquid in the latter being protected by a layer of oil), and the ammonia estimated at intervals.

After two hundred and ten hours, the experiments were stopped by exhaustion of the flasks; in the anaerobic experiments practically no reaction had taken place, but in the others considerable quantities of soluble organic nitrogen had been converted into ammonia; in one case (3.35% ammonia) the action was retarded probably by the toxic effect of excess of ammonia on the organism producing it.

The insoluble residues were treated with soil extract in the presence of a nutritive mixture (devoid of nitrogen), and after twenty-six days the extracts and residues separately examined, when it was found that a quantity of insoluble proteid matter had been converted into ammonia.

The author concludes that two distinct processes are involved: (1) the conversion of insoluble proteids into a soluble form, and (2) their subsequent change into available ammonia, but whether both these changes are the work of the same or of separate organisms has yet to be determined. F. M. G. M.

**Estimation of Phosphorus in Iron and Steel.** C. REICHARD (*Pharm. Zentr.-h.*, 1911, 52, 1314—1315).—Owing to the high molecular weight of the ammonium phosphomolybdate ("yellow") precipitate and the fact that even minute quantities of phosphorus in iron or steel still yield a precipitate that can be weighed with great accuracy, it is proposed to limit the amount of iron taken for analysis to 1 gram. L. DE K.

**Estimation of Inorganic Phosphorus in Animal Tissues.** A. C. WHITTIER (*J. Ind. Eng. Chem.*, 1911, 3, 248—250).—An account of various methods employed for the estimation of phosphorus in animal tissue, with a discussion on the difficulty (owing to the rapidity of subsequent chemical change) of determining the relative proportions in organic and inorganic combination at the time of death.

The conclusions drawn are: (1) that the determination of organic

phosphorus by the barium method gives high results with uncoagulated extracts, owing to barium phosphate passing through the filter.

(2) At the boiling temperature, water has very little hydrolysing action on organic compounds of phosphorus in animal tissue.

(3) Enzymes and bacteria have a greater hydrolytic action on organic phosphorus compounds than boiling.

(4) Coagulation of the proteins by boiling clears the solution, giving more complete precipitation, and also arrests the action of enzymes and bacteria.

F. M. G. M.

**The Quantitative Separation of Organic Phosphorus and Phosphates in Fodders.** GUSTAV FINGERLING and A. HECKING (*Biochem. Zeitsch.*, 1911, 37, 452—456).—In Stutzer's process, the inorganic phosphates are extracted from the material by dilute hydrochloric acid, and precipitated from the solution thus obtained by ammonia and calcium chloride. The precipitated phosphates are then dissolved in nitric acid, and precipitated from this acid solution as phosphomolybdate. The authors find that this process is in most cases satisfactory, but it is not applicable to those materials which contain phytin, which is precipitated with inorganic phosphates. As this substance is present in a large number of fodders, a new process is necessary for estimating phosphoric acid in materials of this character.

S. B. S.

**Comparison of Methods for the Estimation of Phosphates in Vegetable Substances.** A. PONTE (*Chem. Zentr.*, 1911, ii, 900; from *Staz. sperim. agrar. ital.*, 1911, 44, 459—461).—Incineration of the substance with the addition of calcium oxide yielded results which agreed with those obtained by electrolytic oxidation, whilst from 2 to 11% less phosphoric oxide was found by the ordinary method of incineration.

W. P. S.

**A Possible Fallacy in Fleitmann's Test [for Arsenic].** WALTER J. DILLING (*Pharm. J.*, 1911, [iv], 33, 811).—Arsenic having been found in a urine by the Fleitmann test when its presence was thought to be highly improbable, the author investigated the cause, and found that when applying this test, the test-tube containing the zinc and sodium hydroxide with the suspected material should be heated until a stream of hydrogen bubbles is being evolved and *no longer*; the tube should be removed from the flame, and the silver nitrate paper then placed over the mouth of the test-tube. If, as might be done unintentionally, the mixture is boiled, the steam escaping (which perhaps also contains volatile organic products) exerts a more or less strong reducing action, and the spot obtained may be mistaken for an arsenical one.

L. DE K.

**The Estimation of Arsenic in Insecticides.** E. B. HOLLAND (*J. Ind. Eng. Chem.*, 1911, 3, 168—171).—A review of numerous methods employed for the estimation of arsenic, with a discussion as to their adaptability to the analyses of insecticides in which arsenic tri- or pent-oxides are the active constituents. The Avory-Haywood

method (*Proc. Assoc. Off. Agr. Chem.*, 1905, 22, 27) is considered most trustworthy, and from it the author carries out the following modified procedure.

About 2 grams of the sample are boiled during five minutes with 50 c.c. of sodium acetate solution (1:2), cooled, shaken with about 60 c.c. of dilute hydrochloric acid (1:3), filtered from insoluble matter, and the volume made up to 500 c.c.

About 25—50 c.c. are neutralised with dry sodium hydrogen carbonate and treated with 25 c.c. of sodium potassium tartrate (10%) (to redissolve the copper), and titrated with *N*/20-iodine in the presence of starch.

For samples containing lead arsenate the following method is recommended: Two grams of the sample are boiled with 66 c.c. of nitric acid (1:3), cooled, filtered, and made up to 500 c.c. From 50 to 100 c.c. are removed, evaporated with 10 c.c. of diluted sulphuric acid (2:1), and, finally, heated to 150—200°; the residue is dissolved in water, treated with 10 c.c. of potassium iodide (165:1000), and boiled until free iodine is expelled; the solution is rapidly cooled, neutralised with sodium hydroxide, re-acidified with sulphuric acid, starch paste added, any remaining free iodine destroyed with sodium thiosulphate, the liquid rendered alkaline with sodium hydrogen carbonate, and titrated with *N*/20-iodine solution. F. M. G. M.

**Elementary Analysis.** RICHARD DOHT (*Zeitsch. anal. Chem.*, 1911, 50, 755).—The author thinks that it would have been better if Kurtenacker (*Abstr.*, 1911, ii, 823) had given analytical figures to prove why silver and iron are not suitable for the reduction of nitric oxides in the combustion of nitrogenous substances, for experiments conducted by himself and Epstein (*Abstr.*, 1908, ii, 132) led to a different view. L. DE K.

**Detection of Carbon Disulphide in Oils.** E. MILLIAU (*Compt. rend.*, 1911, 153, 1021—1023).—Vegetable oils employed as lubricants should be free from carbon disulphide. This substance may be detected by heating 25 grams of the oil with 10 c.c. of a concentrated potassium hydroxide solution, adding 150 c.c. of water, and a little sodium hydrogen carbonate. The mixture is then poured into 20 c.c. of hydrochloric acid, and the evolved gas tested for hydrogen sulphide by means of lead acetate paper.

A second method consists in distilling 50 grams of the oil with 10 c.c. of amyl alcohol. The first 4 c.c. of distillate are heated in a sealed tube on the water-bath with 1 c.c. of cottonseed oil and a few centigrams of sulphur. The presence of traces of carbon disulphide is recognised by the appearance of a red coloration. W. O. W.

**Estimation of Silica in Iron Ores.** FR. MOLDENHAUER (*Zeitsch. anal. Chem.*, 1911, 50, 754—755).—In order to obtain accurate silica estimations, it is advisable to use platinum dishes, as it is often impossible to remove the silica, rendered insoluble by evaporation, from porcelain basins. L. DE K.

**Rapid Estimation of Zinc.** K. VOIGT (*Zeitsch. angew. Chem.*, 1911, 24, 2195—2198).—The process is briefly as follows: One to three grams of the zinc ore are dissolved in a mixture of 10 c.c. of nitric acid (D 1·2) and 20—30 c.c. of hydrochloric acid (D 1·9), preferably in a porcelain dish, so that the siliceous mass may be broken up with a pestle. After boiling for a while on a sand-bath, the whole is rinsed into a 200 c.c. flask, 50—60 c.c. of ammonia are added, and the solution is again boiled for a short time. When cold, dilute ammonia (1:3) is added up to the mark, and the solution is well shaken and filtered. One hundred c.c. of the filtrate are mixed with a little bromine water to precipitate any manganese, and the turbid liquid is then boiled with about one gram of aluminium scrapings until the copper present is all precipitated. Five c.c. of sodium sulphite solution (1:4) and a few c.c. of dilute ammonia are added, the liquid is again heated to boiling, and at once filtered; the residue is washed with a hot dilute ammoniacal solution of sodium sulphite.

The filtrate is neutralised with hydrochloric acid, and an extra 10 c.c. of dilute acid (1:3) are then added. After diluting to 150 c.c. and heating to boiling, the zinc is at once titrated with ferrocyanide (21·63 grams of potassium ferrocyanide and 14 grams of crystallised sodium sulphite per litre), using ammonium molybdate solution (9 grams per litre) as external indicator. The end reaction is shown by the formation of a reddish-brown spot.

L. DE K.

**Estimation of Copper. Modification of the Iodide Method.** E. C. KENDALL (*J. Amer. Chem. Soc.*, 1911, 33, 1947—1952).—A modification of the iodide method of estimating copper is described, in which the nitrous acid, formed during the solution of the copper in nitric acid, is destroyed by the addition of sodium hypochlorite, the chlorine thus liberated being removed by treatment with phenol.

The solution of copper, of volume about 50 to 60 c.c., is placed in a flask, and the acidity rendered equivalent to about 4 or 5 c.c. of concentrated nitric acid. The temperature should not be above 25°. Solution of sodium hypochlorite is added, and about two minutes later 5% solution of phenol is quickly introduced. Sodium hydroxide is added in slight excess to prevent the formation of nitrophenol, and the solution is afterwards acidified with acetic acid. Potassium iodide solution is now added, and the iodine liberated is titrated with standard sodium thiosulphate. This modification gives accurate results, is more rapid, and requires less attention than the original method.

E. G.

**The Estimation of Manganese by the Sodium Bismuthate Method.** PAUL H. M. P. BRINTON (*J. Ind. Eng. Chem.*, 1911, 3, 237—239).—The author has repeated the work of Blair (*Abstr.*, 1904, ii, 683) and others on the estimation of manganese by the sodium bismuthate method, and corroborates the statement that for small amounts of manganese it is the most accurate method known. The following modifications are suggested: that pure Sørensen sodium oxalate should be used to standardise the potassium permanganate, and that the empirical factor 0·1656, instead of the theoretical factor 0·16024, should

be employed in the conversion of the sodium oxalate figure into that of manganese; this corrects the tendency of the method to give low results, although the author considers that gravimetrically standardised manganous sulphate is the most accurate standard that can be employed. The decomposition of ores by the hydrochloric and sulphuric acids method is suggested as being fully as accurate, more rapid, and possibly more convenient than the employment of hydrofluoric and sulphuric acids. Fusing the ore with sodium peroxide is also recommended in the case of refractory samples.

F. M. G. M.

**A New Rapid and Accurate Volumetric Method for the Estimation of Manganese and its Application to the Analysis of Iron and Steel.** FLOYD J. METZGER and L. E. MARRS (*J. Ind. Eng. Chem.*, 1911, 3, 333—335).—It has been observed that the presence of manganese disturbs the estimation of ferrous iron in rocks by the sulphuric-hydrofluoric acid method: the more hydrogen fluoride employed, the higher the percentage of iron found, a fact which pointed to the possibility that manganese and permanganic acid react together quantitatively in the presence of a sufficient quantity of this acid.

Solutions of carefully standardised manganous sulphate were titrated with *N*/30-potassium permanganate in waxed beakers in the presence of 50% sulphuric acid (1 vol.), hydrofluoric acid (2.5 vols.), and varying quantities of ammonium fluoride (which increased the speed of reaction), and when the experiments were repeated in the presence of ferric iron identical results were obtained.

The analysis of steel was conducted as follows: About one gram of the sample dissolved in nitric acid was treated with ammonium persulphate (1 gram) and boiled during a few seconds, evaporated to dryness, and dissolved in a mixture of 50% sulphuric acid (20 c.c.) and 30 c.c. of water; the solution was boiled until clear, transferred to a waxed beaker, and treated with 5 grams of ammonium fluoride and 25 c.c. of hydrofluoric acid, the volume made up to 100—150 c.c., and finally titrated with potassium permanganate.

The results of numerous experiments are tabulated, and the method is claimed to be simple, accurate, and rapid, and at the same time applicable to the cases of spiegels and other manganese ores.

F. M. G. M.

**Estimation of Ferrous Ions with Standard Iodine.** GYSBERT ROMYN (*Chem. Zeit.*, 1911, 35, 1300).—The process is more particularly intended for pharmaceutical preparations (Blaud's pills, syrup of ferrous iodide, etc.). The preparation is dissolved in so much dilute sulphuric or hydrochloric acid that the free acidity amounts to about 20 c.c. of *N*-acid. The solution is then added to a mixture of 20 c.c. of *N*/10-iodine solution and 5 grams of powdered sodium pyrophosphate, and the mixture is shaken until the latter has nearly dissolved. After five minutes, the excess of iodine is titrated with *N*/10-thiosulphate as usual; 1 c.c. of the latter = 27.8 mg. of crystallised ferrous sulphate.

L. DE K.

**Detection of Nickel and Cobalt in Mixtures.** ANGEL DEL CAMPO and JAIME FERRER (*Anal. Fis. Quim.*, 1911, 9, 201—213, 272—276. Compare Abstr., 1911, ii, 825).—The value of potassium methyl xanthate as a delicate reagent for nickel and cobalt (compare *loc. cit.*) has been examined in respect to delicacy, and in comparison with Tschugaëff's reagent for nickel (dimethylglyoxime) and Vogel's reagent for cobalt (ammonium thiocyanate and amyl alcohol).

In the case of nickel alone, both reagents display about equal delicacy, detecting nickel in 1 c.c. of a 1 in 200,000 solution, or in 4 c.c. of a 1 in 500,000 solution, which is the limit.

With mixtures of nickel and cobalt in the proportion of 1 to 100, Tschugaëff's reagent fails, but potassium methyl xanthate is trustworthy, and with care may be employed to recognise nickel in the presence of even higher proportions of cobalt.

In regard to cobalt the xanthate has about five times the delicacy of Vogel's reagent, being capable of recognising the metal clearly in 1 c.c. of a solution of 1 in 250,000. With mixtures of cobalt with excess of nickel (10 to 2000 times), the reagents display about equal value when working at the limits of sensibility of Vogel's test.

G. D. L.

**Separation of Nickel and Zinc in German Silver and Other Alloys.** LA VERNE W. SPRING (*J. Ind. Eng. Chem.*, 1911, 3, 255—256).—About 0.5 gram of the drillings is freed from tin with nitric acid, the lead removed as sulphate, copper by electrolysis, and the iron by means of ammonium hydroxide. Five grams of ammonium chloride are then added, and the solution just neutralised with hydrochloric acid and treated with 0.4 gram of dimethylglyoxime (dissolved in alcohol) for every 0.1 gram of nickel supposed to be present; ammonium hydroxide is added drop by drop until just ammoniacal, and the solution allowed to remain at just below boiling point during about half an hour. The precipitate is collected on a tarred filter, washed with hot water, dried at 105°, and weighed:  $C_8H_{14}O_{11}N_4Ni \times 0.2031 = Ni$ .

The filtrate is acidified with an excess of 10 c.c. of concentrated hydrochloric acid, boiled to decompose the excess of dimethylglyoxime, treated with 10 grams of microcosmic salt (in saturated solution), rendered exactly neutral with ammonia, and allowed to remain just below its boiling point until the precipitate has granulated; this is collected, washed with hot water, ignited, and weighed as zinc pyrophosphate.

F. M. G. M.

**Estimation of Tin in Canned Foods.** HERMAN SCHREIBER and W. C. TABER (*J. Ind. Eng. Chem.*, 1911, 3, 257—261).—A discussion of the difficulties experienced in obtaining accurate results by the wet combustion methods usually employed for estimating tin in canned foods.

The author gives a detailed description of an alkali fusion method, which he finds gives excellent results, the main procedure of which consists in mixing about 100 grams of the material, weighed into an iron crucible with 50 c.c. of an aqueous solution containing 150 grams

of sodium hydroxide, and 100 grams of sodium carbonate per litre, adding 75 c.c. of alcohol (95%), evaporating carefully to dryness with continual stirring, slowly raising the temperature to about 160°, and finally igniting in a muffle until all volatile matter is removed.

The fused mass is transferred to a beaker, and evaporated with 50 c.c. of concentrated sulphuric acid and 30 c.c. of nitric acid (D 1.42) until fumes of sulphur trioxide are apparent; the mixture is cooled, diluted, almost neutralised with ammonium hydroxide, and treated with hydrogen sulphide; the collected precipitate is washed with a mixture of ammonium acetate and dilute acetic acid, the tin re-dissolved by boiling with sodium hydroxide, and after separation from other substances which may be present, it is finally re-precipitated, collected, ignited, and weighed as stannic oxide. F. M. G. M.

**Separation of Zirconium from Iron and Aluminium and the Analysis of Ferrozirconium.** M. WUNDER and B. JEANNERET (*Zeitsch. anal. Chem.*, 1911, 50, 733—735).—*Separation of Zirconium, Iron, and Aluminium.*—About 1 gram of the mixed oxides is fused in a platinum crucible with 6 grams of sodium carbonate, the mass is taken up with water, and after addition of 1 gram of sodium carbonate, boiled for a few minutes. The filtrate contains the aluminium (also any chromium), from which the alumina may be precipitated by adding excess of ammonium nitrate. If much is present, it is advisable to submit the insoluble mass to a second fusion with sodium carbonate.

The iron is dissolved by hot dilute hydrochloric acid (1:1), and estimated as usual. The undissolved zirconium oxide is ignited, and weighed as such.

*Analysis of Ferrozirconium.*—The alloy is heated on the water-bath with hydrochloric acid and bromine, when the zirconium and the iron pass into solution, whilst the silicon is converted into oxide. After adding a little nitric acid, the whole is evaporated to dryness, and finally heated in an air-bath at 110°. The mass is then dissolved in dilute hydrochloric acid, and the silica is collected and ignited. From its weight should be deducted the small amount of zirconium oxide which is left after the usual treatment with hydrofluoric and sulphuric acid.

The filtrate from the silica is precipitated with ammonia, and the oxides are then submitted to the fusion with sodium carbonate as described. The process may be also applied to zirconium carbides.

L. DE K.

**A Volumetric Method for Estimating Antimony in Alloys.** GEORGE S. JAMIESON (*J. Ind. Eng. Chem.*, 1911, 3, 250—251).—An application of Andrews' (Abstr., 1903, ii, 686) iodate method to the estimation of antimony in alloys, especially "hard leads" and solders; it is claimed to be rapid, accurate, and admissible in the presence of copper and iron.

Two other methods have been studied comparatively by the author, the first, which is based on getting the antimony into the quinquevalent form in dilute hydrochloric acid solution, adding potassium iodide, and titrating with sodium thiosulphate, gave good results only in

the absence of copper or iron; the second method depends on getting the antimony into the tervalent condition in sodium hydrogen carbonate solution, and titrating with iodine gave unsatisfactory results in the presence of lead, owing to the co-precipitation of antimony which was found to take place even in the presence of tartaric acid.

About 1 gram of an alloy containing less than 2% of antimony is weighed into a 200 c.c. Erlenmeyer flask, and heated with 10 c.c. of concentrated sulphuric acid until decomposition is complete, boiled gently for about two minutes after the lead sulphate has become white, cooled, and diluted with 15 c.c. of water; 15 c.c. of dilute hydrochloric acid (1:1) are then added, the mixture vigorously shaken, and the lead sulphate collected on a Gooch crucible and washed with hydrochloric acid of the same concentration. The filtrate is transferred to a glass-stoppered bottle of about 250 c.c. capacity, 5 c.c. of chloroform, 15 c.c. of concentrated hydrochloric acid, and 5 c.c. of a solution of iodine monochloride added; the bottle is shaken, and after about five minutes the liberated iodine titrated with standard potassium iodate until the chloroform in just decolorised after a vigorous shaking (which should be repeated in about a minute to ensure obtaining the correct end-point); the liquid can be poured off, and the chloroform employed for further titrations.

The concentration of the hydrochloric acid in the solution is of importance, and the above quantities should be adhered to carefully. The iodine monochloride solution is prepared by dissolving 10 grams of potassium iodide and 6.44 grams of potassium iodate in 75 c.c. of water, adding 75 c.c. of concentrated hydrochloric acid and a globule of chloroform, and adjusting exactly to a faint iodine colour by shaking and adding minute quantities of potassium iodide or iodate until the required condition is obtained.

F. M. G. M.

**The Geo-chemical Interpretation of Water Analyses.**  
CHASE PALMER (*Bull. U.S. Geol. Survey*, 479; a Reprint, 31 pp.).—A record of a large number of analyses of waters from American rivers. The results, however, are not given in terms of definite salts, but as follows: First, the properties of the solution in % proportions [primary salinity, secondary salinity, tertiary salinity (acidity), primary alkalinity, secondary alkalinity]; second, the percentage of reacting values of co-ordinate radicles, from which the properties of reaction may be directly derived accompanied by a statement of concentration values in parts per million; third, the character formula (the percentage of reacting values of the individual radicles determined), together with a statement of the concentration value; fourth, the base analyses.

(1) Primary salinity (alkali salinity) is salinity not to exceed twice the sum of the reacting values of the radicles of the alkalis; (2) secondary salinity (permanent hardness) is the excess (if any) of salinity over primary salinity not to exceed twice the sum of the reacting values of the radicles of the alkaline earths group; (3) tertiary salinity (acidity) is the excess (if any) of salinity over primary and secondary salinity; (4) primary alkalinity (permanent alkalinity) is

the excess (if any) of twice the sum of the reacting values of the alkalis over salinity; (5) secondary alkalinity (temporary alkalinity) is the excess (if any) of twice the sum of the reacting values of the radicles of the alkaline earth group over secondary salinity. In distinguishing the special properties the values of radicles of the same sign are doubled; the positive and negative radicles, which together induce their special properties, thus receive their full value.

In the author's opinion this form of stating results is more comprehensive to the geologist than the expression in definite salts, which is always more or less hypothetical. L. DE K.

**Colorimetric Estimation of Phenols in Waste Liquors.** HERMANN BACH (*Zeitsch. anal. Chem.*, 1911, 50, 736—740).—The process is based on the fact that 10 c.c. of a very dilute solution of phenol (a few mg. only) when heated to boiling with 0.2 c.c. of Millon's reagent and 0.1 c.c. of nitric acid give, when allowed to cool, a liquid of a permanent rose or reddish colour, which may then be matched with a solution of phenol of known strength similarly treated.

In order to apply the process to waste liquors, 1 litre of the sample is mixed with 5—10 c.c. of strong aqueous potassium hydroxide and evaporated in a dish to 50 c.c. The contents are then transferred to a 500 c.c. Erlenmeyer flask having a mark at 150 c.c., a slight excess of sulphuric acid is added, and when cold the liquid is diluted up to the 150 c.c. mark; one hundred c.c. are then distilled off. To this distillate, which contains the phenol from one litre, is then applied the above colorimetric test; if the colour should be a dark red, it must be suitably diluted. L. DE K.

**The Estimation of Phenol and *p*-Cresol in Mixtures of the Two.** HUGO DITZ and FRIEDRICH BARDACH (*Biochem. Zeitsch.*, 1911, 37, 272—312).—The authors maintain, in opposition to Siegfried and Zimmermann and others, that the original method proposed by Ditz and Cedivoda, in 1899, for the estimation of phenol and *p*-cresol in mixtures of these substances gives accurate results, provided that the details given in the description of the process are strictly adhered to. The method depends on the principal of estimating the amount of bromine taken up by the mixture, and the success of the process depends on using the right excess of bromate and bromide mixture and of hydrochloric acid, and on other details. The paper is largely controversial, and the various points insisted on by the authors are illustrated by a large number of analyses of mixtures containing known quantities of the two phenols. S. B. S.

**Two Modifications of Fehling's Solution.** EDWARD FRANK HARRISON (*Pharm. J.*, 1911, [iv], 33, 746—747).—Benedict has suggested recently that in the use of Fehling's solution for the detection and estimation of dextrose, the actual reduction is effected by a substance resulting from the action of the alkali hydroxide on the sugar, and that this change may proceed further, especially in presence

of substances which retard the normal action, and give rise to non-reducing products.

The reducing substance is produced more slowly by alkali carbonates, but these have little or no further action, and consequently Benedict has proposed two modified forms of Fehling's solution for qualitative and quantitative use respectively, in which, among other changes, sodium hydroxide is replaced by sodium carbonate (*Journ. Amer. Med. Ass.*, 1911, Oct. 7). The preparation and application of these solutions to the detection and estimation of dextrose in urine are described and critically examined in this paper. The author considers that Benedict's claim that his first solution is a far more delicate reagent for dextrose in urine than Fehling's solution, is justified. The solution for quantitative use is shown to give good results with solutions of dextrose in water, but is less satisfactory when used for urine containing dextrose.

T. A. H.

**Rapid Volumetric Estimation of Sugar.** WALTER F. SUTHERST (*J. Ind. Eng. Chem.*, 1911, 3, 256).—The following is stated to be a convenient method of indicating the end-point when estimating sugar with Fehling solution. The Fehling solution is heated to boiling, and the sugar added until a faint blue colour is apparent at the edge of the porcelain vessel employed. As further sugar is added, a drop of the mixture is placed on the top side of a filter paper folded in half, the filtrate passes through, and the spot is treated with a drop of a dilute acetic acid solution of 1% potassium ferrocyanide; on holding up to the light, the faintest trace of copper ferrocyanide is plainly seen, and the end of the reaction readily indicated.

F. M. G. M.

**The Physiology and Pathology of Carbohydrate Metabolism [Colorimetric Estimation of Small Amounts of Sugar].** KARL REICHER and E. H. STEIN (*Biochem. Zeitsch.*, 1911, 37, 321—344).—A method for estimating colorimetrically small quantities of sugar by means of the Molisch reaction is described. Ten c.c. of concentrated sulphuric acid are placed in a graduated cylinder with glass stopper, and to this a tablet containing 0.05 gram of  $\alpha$ -naphthol is added, and then 2 c.c. of the solution to be investigated. Under these conditions, the correct temperature for the development of the colour is attained. After gently mixing, so that the colour is uniformly distributed, the mixture is allowed to cool, and is then diluted to 20 c.c. The colour is compared by means of a Plesch colorimeter, or a Stein chromoscope, with a solution prepared in a similar way with 0.02% dextrose solution. This is the most convenient strength when the sugar in blood is to be estimated. For the estimation of sugar in this fluid, 2 c.c. of serum are taken and diluted to 10 c.c. with water, and then 1—2 c.c. of concentrated potassium sulphate, 6 to 7% of dialysed ferric hydroxide solution (the method of preparing which is given in detail), and water up to the total volume of 20 c.c. are added. Two c.c. of this filtered solution are employed for each test.

S. B. S.

**The Estimation of Sugars in Natural Products.** CARL NEUBERG and MIGAKU ISHIDA (*Biochem. Zeitsch.*, 1911, 37, 142—169).—By precipitation with 50% mercuric acetate solution, followed by

precipitation with 25% phosphotungstic acid solution, all optically active derivatives of proteins, as well as the proteins themselves, nucleoproteins, lecithin, and other substances can be precipitated. The sugars remain in solution, and can be accurately estimated polarimetrically in the filtrate. Glycosamine as well as the other carbohydrates can also be estimated in this way. The method is illustrated by a large number of examples of analyses of mixtures of known sugar content, with different varieties of sugars. A method is also given for preparing the phosphotungstic acid reagent directly from sodium tungstate, phosphoric and sulphuric acids. S. B. S.

**Estimation of Sugar in the Blood.** DENGU TAKAHASHI (*Biochem. Zeitsch.*, 1911, 37, 30—33).—The sugar in dog's blood was estimated polarimetrically, and after yeast fermentation, both polarimetrically and by the methods of Bang and Bertrand. In all cases, no sugar was found after fermentation. The total sugar in dog's blood was also estimated polarimetrically and by the methods of Kumagawa-Suto, Bertrand, and of Bang. The results by the first two methods agreed well with another, and were always somewhat lower than the results obtained by Bang's method. S. B. S.

**The Estimation of Dextrose in Urine and Blood.** BERTHOLD OPPLER (*Zeitsch. physiol. Chem.*, 1911, 75, 71—134).—In order to estimate dextrose in the urine polarimetrically before and after fermentation, the urine was treated with phosphotungstic acid, lead acetate, and hydrogen sulphide; this excludes pigment, other reducing substances, and laevorotatory materials. Estimation by reduction gives too high a result. The existence of physiological glycosuria is very doubtful; any sugar found in normal urine probably arises from other sources, especially glycuronic acid. Similar conclusions are arrived at in respect to the best method for estimating dextrose in blood. W. D. H.

**[Detection and] Estimation of Dextrose in Urine.** G. A. STUTTERHEIM (*Pharm. Weekblad*, 1911, 48, 1201—1204).—The author uses an alkaline copper solution made as follows: 17.32 grams of copper sulphate, 100 grams of glycerol, 20 grams of sodium hydroxide, and water up to 250 c.c. This solution should be kept in brown bottles. When testing urine for dextrose, 5 c.c. of the reagent are diluted with 5 c.c. of water, heated to boiling in a test-tube, and set aside. Five c.c. of the urine mixed with 5 c.c. of water are also heated to boiling, and then at once added to the copper solution. If dextrose is present, the red copper reduction will be noticed at the top of the liquid within one-half to one minute; 0.5% of dextrose may thus be readily detected even when, as frequently occurs, the urine contains substances which interfere with the ordinary Fehling test.

When estimating dextrose in urine by the iodometric method, the author recommends making an allowance of -0.15% on account of dextrose occurring naturally. L. DE K.

**The Detection and Estimation of Sugar in the Urine.** A. C. ANDERSEN (*Biochem. Zeitsch.*, 1911, 37, 262—265).—It was found that the clarification of urine by charcoal in the presence of 5% hydrochloric acid, according to the method of Bang and Bohmannson, leads to errors in the estimation of sugar, owing to adsorption by the charcoal, especially when blood-charcoal is used. If, however, the clarification is carried out by charcoal in the presence of 10% of acetic acid (40 c.c. urine, diluted to 50 c.c. with 50% acetic acid, and the mixture shaken with 4 grams of blood-charcoal for ten minutes), a perfectly clear, colourless solution is obtained, which, on polarisation, gives the correct sugar values. S. B. S.

**Colorimetric Estimation of Sugar, Creatine, and Creatinine in Urine.** WILHELM AUTENRIETH and GERHARD MÜLLER (*Münch. med. Woch.*, 1911; Reprint, 12 pp.).—Whilst the process described by Autenrieth and Tesdorpf (Abstr., 1911, ii, 159) yields trustworthy results when applied to colourless urines, it is recommended that dark-coloured urine should be treated with blood-charcoal free from iron after the diluted urine has been boiled with Bang's copper solution. The blood-charcoal, when free from iron, does not retain any of the copper. W. P. S.

**Colorimetric Estimation of Lactose in Urine and Milk.** WILHELM AUTENRIETH and ALBERT FUNK (*Münch. med. Woch.*, 1911, Reprint, 8pp.).—The presence of lactose in urine may be ascertained by means of the test described by Wöhlk (Abstr., 1906, ii, 122); dextrose, when present to the extent of not more than 1%, does not yield a coloration with the test, neither does it interfere with the lactose reaction. For the estimation of lactose, 10 c.c. of the diluted urine (containing not more than 0.04 gram of the sugar) are boiled for three minutes with 50 c.c. of Bang's copper solution, cooled, diluted with potassium thiocyanate solution to a volume of 50 c.c., 0.5 gram of blood-charcoal free from iron is added, the mixture is shaken for five minutes, and filtered. The quantity of unreduced copper in the filtrate is then estimated by comparison with standard solution in a colorimeter (compare Abstr., 1911, ii, 159). In the case of milk, 25 c.c. of the sample are diluted with 400 c.c. of water, acetic acid is added, the mixture is boiled, and diluted, when cold, to a volume of 500 c.c. After filtration, 10 c.c. of the filtrate are boiled with 50 c.c. of Bang's solution as described above. W. P. S.

**Estimation of Sucrose, and the Detection of Dextrin in Foods.** ANDRÉ F. VOLLANT (*Ann. Falsif.*, 1911, 4, 504—509).—A method proposed by Lemeland (Abstr., 1910, ii, 1006), which is based on the destruction of the reducing and rotatory powers of arabinose, dextrose, lævulose, galactose, and lactose when these sugars are heated with manganese dioxide and alkaline hydrogen peroxide solution, whilst sucrose is not affected, may be employed for the estimation of sucrose in commercial sugars, syrups, confectionery, dried milks, and honey. The results obtained are trustworthy. It is pointed out that acetic acid should be used for neutralising the sugar solution after

treatment, and not nitric acid as prescribed in the original paper. After clarification, the solution must be acidified by acetic acid before being examined in the polarimeter. Dextrin may be detected when mixed with other sugars by inverting the sucrose present, and then subjecting the solution to the above-mentioned treatment; any optical activity exhibited by the resulting solution is due solely to the presence of dextrin.

W. P. S.

**Approximate Estimation of Starch by Iodine.** LESTER REED (*Chem. News*, 1911, 104, 271).—A quantity of the substance, containing about 0.1 gram of starch, is heated with 5 c.c. of glycerol to a temperature of 190° for five minutes; the mixture is then diluted to a volume of about 50 c.c., and filtered. To the filtrate when cold is added concentrated iodine solution (in potassium iodide), the precipitated starch-iodine compound is collected on a filter, washed with boiling 90% alcohol, and then rinsed into a platinum basin with a jet of boiling water. The contents of the basin are boiled to expel iodine, then evaporated, dried, and weighed. Allowance is made for mineral matter present. The process cannot be applied to bread or cocoa, or to substances in which the starch has been heated previously. In the case of cocoa, theobromine or some other substance is precipitated together with the starch.

W. P. S.

**Estimation of the Acidity of Wine.** FERNAND REPITON (*Ann. Falsif.*, 1911, 4, 578—580).—The following method is recommended for the estimation of the total acidity of red wines: Five c.c. of the wine are placed in a large beaker, 5 drops of a cold saturated alcoholic phenolphthalein solution and 3 drops of a 1.2% alcoholic fluorescein solution are added, and the mixture is heated just to boiling; 5 c.c. of cold water are then added, and the solution is titrated with *N*/20-alkali solution. The red colour of the wine changes gradually to green during the titration, and the end-point is taken when the red colour of the indicator appears in the green solution. This point is readily seen if a white tile is placed under the beaker.

W. P. S.

**Estimation of the Acidity of Milk.** O. RAMMSTEDT (*Chem. Zeit.*, 1911, 35, 1218—1219).—Soxhlet's method (titration of 50 c.c. of milk with *N*/4-sodium hydroxide solution, using phenolphthalein as indicator) is the most trustworthy of the many processes which have been proposed for the estimation of the acidity of milk. In the case of Thörner's method (titrating a mixture of 10 c.c. of the milk and 20 c.c. of water with *N*/10-sodium hydroxide), the results obtained are lower than those yielded by Soxhlet's method when both sets of results are calculated to the same basis; this lower result is due to the presence of the added water, and the loss increases with the quantity of water.

W. P. S.

**Estimation of Benzoic Acid.** EDUARD REMY (*Chem. Zentr.*, 1911, ii, 1379—1380; from *Apoth. Zeit.*, 1911, 26, 835—836).—An iodometric method is described. The benzoic acid is dissolved in 50% alcohol, and the solution is treated with 5% potassium iodide and

potassium iodate solutions; the benzoic acid is converted into moniodobenzoic acid, and an equivalent quantity of iodine is liberated. This free iodine is then titrated with thiosulphate solution; 1.22 grams of benzoic acid liberate 1.269 grams of iodine. W. P. S.

**Estimation of Cinnamic Acid in Aqueous Solutions by means of Bromine.** ANNE W. K. DE JONG (*Rec. trav. chim.*, 1911, 30, 223—224).—The cinnamic acid is obtained in a finely divided state by solution in sodium hydroxide and precipitation by hydrochloric acid. Bromine water (*N*/10) is then added until the solution does not decolorise after five minutes. Potassium iodide is added, and the liberated iodine estimated by titration. From this is calculated the amount of bromine used, and thus the amount of cinnamic acid in the solution. W. G.

**Estimation of Uric Acid by means of Iodine and the Action of Iodine on Creatinine.** C. J. REICHARDT (*Pharm. Zeit.*, 1911, 56, 922).—In the method described by Pizzorno (*Abstr.*, 1911, ii, 667) care must be taken in heating the urine with sodium carbonate, as uric acid is converted into glyoxylic acid when boiled with alkalis. When the urine contains creatinine, this is changed into creatine by the treatment prescribed. The author finds that creatinine is converted into creatine by the action of iodine; in this reaction the iodine at first combines with the creatinine, and, only after the lapse of some length of time, is hydrogen iodide liberated with the formation of methylguanidineacetyl iodide. W. P. S.

**Estimation of Formaldehyde.** ELIAS ELVOVE (*Amer. J. Pharm.*, 1911, 83, 455—471).—The cyanide process was found to be trustworthy provided that an excess of cyanide is employed; when this excess is not less than one-half equivalent, the reaction is not influenced by moderate variations in temperature, neither does the time during which the mixture is left appreciably affect the results obtained. This process is considered to be preferable to the hydrogen peroxide method both for dilute and concentrated formaldehyde solutions (compare *Abstr.*, 1904, ii, 98). W. P. S.

**Presence of Furfuraldehyde as an Indication of Adulteration in Some Fermented Alcoholic Beverages.** V. PASQUERO and A. CAPPA (*Gazzetta*, 1911, 41, ii, 349—358).—Beer or wine gives a distillate which usually contains traces of furfuraldehyde, as indicated by the coloration with aniline acetate. If, however, the beverage has previously been neutralised with magnesium carbonate, the distillate no longer shows a furfuraldehyde reaction. The distillate from a neutralised wine or beer to which caramel or commercial alcohol has been added does give the furfuraldehyde reaction, so that an indication of the presence of these adulterants can be obtained by neutralising the beverage with magnesium carbonate and testing the distillate with aniline acetate. R. V. S.

**Microchemical Analysis of Plants. III. Detection of Æsculin by Micro-sublimation in the Examination of Rhizoma Gelsemii.** O. TUNMANN (*Chem. Zentr.*, 1911, ii, 1384; from *Apoth. Zeit.*, 1911, 26, 812—814. Compare Abstr., 1911, ii, 669, 1022, 1023).—Æsculin may be detected in the bark of *Æsculus Hippocastanum* by means of the sublimation test described by the author (*loc. cit.*); the spring is the only time of the year when the bark contains the substance. The latter is more readily obtained from *Gelsemium sempervirens*. The temperature employed for the sublimation should be from 50° to 60°, when the glucoside is obtained in the form of prisms or rods with square ends. The crystals are soluble in warm water, alcohol, and ether, and the aqueous solution exhibits a bluish-green fluorescence which disappears on the addition of hydrochloric acid. Chlorine colours the aqueous solution light red, but the glucoside is best identified by dissolving the crystals in 2 drops of ammonia and adding 1 drop of nitric acid, when a bluish-red coloration appears at the point of contact. Æsculetin could not be detected in *Radix Belladonnae*, but the seeds of *Euphorbia Lathyris* yielded a granular sublimate which became crystalline after about ten days. The subterranean portions of *Gelsemium elegans*, which are sometimes sold as a substitute for *Rhizoma Gelsemii*, yielded neither æsculin nor gelsemic acid.

W. P. S.

**Detection and Identification of "Saccharin" and "Dulcin" in Beverages, Foods, Drugs, Cosmetics, etc.** STEFANO CAMILLA and C. PERTUSI (*Chem. Zentr.*, 1911, ii, 1269—1270; from *Giorn. Farm. Chim.*, 1911, 60, 285—293).—"Saccharin" (*o*-benzoic sulphinide) and "dulcin" (*p*-phenetolecarbamide) may be detected in solid substances by heating about 30 grams of the sample with 1 gram of barium hydroxide and 50 c.c. of water, filtering the mixture, and extracting the acidified filtrate with a mixture of ether and benzene. On evaporating the solvent, the two sweetening materials are obtained as a crystalline residue. Liquids must be evaporated before being tested. "Saccharin" and "dulcin" may be identified as follows: 100 c.c. of the liquid, or 10 grams of the solid substance, under examination are mixed with 5 grams of magnesium oxide (in the case of solid substances, 10 c.c. of water are also added), and the mixture is evaporated to dryness. The residue is extracted with acetone containing 10% of water, the extract is evaporated to remove the acetone, and the residual aqueous solution is shaken with ether; "dulcin" goes into solution in the ether. The "saccharin" is obtained by shaking the acidified aqueous solution with a mixture of ether and light petroleum after the "dulcin" has been removed. Should salicylic acid also be present in the sample, the residue of "saccharin" obtained on evaporating the ether-light petroleum solution is dissolved in dilute sulphuric acid, treated with an excess of potassium permanganate in order to destroy the salicylic acid, and the "saccharin" then separated by again shaking the solution with a mixture of ether and light petroleum.

W. P. S.

**Estimation of Carbamide.** ALEXANDRE DESGREZ and FEUILLÉ (*Compt. rend.*, 1911, 153, 1007—1010).—A modification of Bouchard's

method is described. The ureometer consists of a wide-stemmed pipette having the bulb near the point and a tap at the other end. The pipette is plunged into a narrow jar containing chloroform, when the lower part becomes filled, and then 1 c.c. of urine, 5 c.c. of water, and 8—10 c.c. of Millon's reagent are introduced through the tap. The chloroform is warmed to 30—35° by heating a metal collar passing round the jar. After twenty to twenty-five minutes, reaction is complete, the pipette is transferred to another vessel, and the liquid displaced by water, then by sodium hydroxide solution, and finally by water, after which the volume of the gas is measured. Under these conditions, the ammonium salts, uric acid, amino-acids, purine derivatives, and undialysable substances in the urine are not decomposed. Allantoin is slowly decomposed, but the amount of nitrogen from this source is insufficient to affect the accuracy of a urine analysis.

W. O. W.

**Estimation of Amino-nitrogen in Polypeptides by van Slyke's Method.** EMIL ABDERHALDEN and DONALD D. VAN SLYKE (*Zeitsch. physiol. Chem.*, 1911, 74, 505—508).—Determinations of the amino-acid nitrogen in a number of polypeptides have been made by van Slyke's method; these are in agreement with the theoretical values, except in those cases in which the amino-group is present as glycine. When the values for the amino-nitrogen in glyceryl polypeptides are multiplied by the factor 0.8, values more in accordance with the calculated are obtained.

E. F. A.

**The Toxicological Detection of Aconitine.** HERMANN FÜHNER (*Arch. exp. Path. Pharm.*, 1911, 66, 178—190).—Chemical methods for the detection of aconitine give results which are not altogether satisfactory in forensic cases; the taste is characteristic, but veratrine produces a very similar, although weaker, effect on the tongue. The alkaloid can, however, be identified with certainty by its action on the isolated frog's heart, and 0.0005 mg. gives the effect. The effect in question is a characteristic peristalsis of which some tracings are given.

W. D. H.

**Reaction of Quinine and Other Alkaloids with Calomel.** E. BARONI and O. BORLINETTO (*Chem. Zentr.*, 1911, ii, 392—393; from *Giorn. Farm. Chim.*, 1911, 60, 241—244).—Various salts of quinine give a brown colour when rubbed together with moist mercurous chloride. The free base does not give the reaction. Hydrastine and heroine hydrochlorides, pilocarpine, cocaine in the presence of ether, and heroine in the presence of dilute alcohol give the same reaction.

S. B. S.

**Estimation of Hydrastine in Hydrastis Extract.** A. W. VAN DER HAAR (*Pharm. Weekblad*, 1911, 48, 1302—1307).—After criticising the official methods, the author proposes the following process: 10 grams of the extract are mixed with 20 c.c. of water, and then boiled in a flask until the weight of the solution amounts to about 10 or 11 grams. Four c.c. of dilute hydrochloric acid are added, and, when cold, the liquid is diluted to 20 grams. The liquid is then shaken with

1 gram of talc and filtered. Ten grams of the filtrate are placed in a 100 c.c. flask, 7 c.c. of ammonia are added, and also 25 c.c. of ether, when the whole is shaken for two minutes. Twenty-five c.c. of light petroleum (b. p. 60—80°) are now added, and, after shaking for half a minute, two grams of powder of tragacanth are introduced, and the whole is again thoroughly shaken. Forty c.c. are now taken off, and after adding another 5 c.c. of light petroleum, the solution is submitted to distillation until 35 c.c. have passed over. The flask is then put for eighteen to twenty-four hours in a cool place, and after pouring off the liquid and washing the crystals with 2 c.c. of light petroleum, they are dried on the water-bath and weighed.

L. DE K.

**Alkaloid. Reactions (Hydrastinine).** C. REICHARD (*Pharm. Zentr.-h.*, 1911, 52, 1253—1260).—A large number of reactions for hydrastinine are communicated, of which the two following ones are the most characteristic, and establish the identity of the alkaloid. A few particles of the hydrochloride are triturated with a minute crystal of potassium ferro- or ferri-cyanide, and a drop of water is then added. With ferricyanide a splendid reddish-green precipitate is obtained, which is characterised by its dichroism. The crystals form elongated prisms, and are beautifully developed. When held up to the light, they appear bluish dark green, with total reflexion of the light; the colours are permanent. With the ferrocyanide, crystals are obtained resembling mother-of-pearl; these are particularly characteristic for hydrastinine. Sodium nitroprusside gives a compound not unlike the ferricyanide.

The behaviour of sulphuric acid is also noteworthy, as the yellow colour given on warming again disappears on cooling, and the test may be repeated over and over again.

L. DE K.

**Estimation of Morphine in Opium.** H. WIEBELITZ (*Chem. Zentr.*, 1911, ii, 1383—1384; from *Apoth. Zeit.*, 1911, 26, 824).—The alkaloid separated by the process described by Frerichs and Mannheim may be estimated volumetrically by dissolving the moist precipitate in 25 c.c. of *N*/10-hydrochloric acid, washing the precipitate until the filtrate and washings amount to 100 c.c., and titrating 50 c.c. of this solution in the usual way.

W. P. S.

**Colorimetric and Physiological Estimation of the Active Principle of the Suprarenal Gland.** WORTH HALE and ATHERTON SEIDELL (*Amer. J. Pharm.*, 1911, 83, 551—558).—Of the various colour reactions of adrenaline, that with iodic acid, which has been described by Krauss, and independently by Fränkel and Allers (*Abstr.*, 1909, ii, 628), is the most trustworthy for the colorimetric estimation of this substance. The addition of phosphoric acid, as recommended by Fränkel and Allers, is however, not, advisable, as it causes the colour to fade. With specimens of the gland containing from 0.2 to 0.8% of adrenaline, a quantity of 0.01 gram is heated just to boiling with 5 c.c. of dilute hydrochloric acid (2.5 c.c. of *N*/1-acid per 100 c.c.) and 5 c.c. of 0.2% potassium iodate solution. After fifteen minutes, the mixture is filtered, and the colour produced compared with a series of standards containing from 0.01 to 0.1 mg. of adrenaline per c.c. The standard solutions may also be prepared by mixing 1 volume of a solution

containing 20 grams of potassium platinichloride and 100 c.c. of hydrochloric acid per litre with 3 volumes of a solution containing 12 grams of crystallised cobaltous chloride and 100 c.c. of hydrochloric acid per litre; quantities of this mixture are diluted so as to yield colorations corresponding with those given by definite amounts of adrenaline. The results obtained by this colorimetric process are lower than those found by determining the relative rise in blood-pressure as compared with that produced by a given amount of the pure substance, when the solutions were injected into dogs. W. P. S.

**Catalytic Action of Light in the Oxidation of Phenolphthalin to Phenolphthalein.** GIUSEPPE ROSSI (*Chem. Zentr.*, 1911, ii, 1659; from *Giorn. Farm. Chim.*, 1911, 60, 433—436).—Phenolphthalein is reduced to phenolphthalin by the action of nascent hydrogen, whilst the reverse reaction takes place in the presence of hydrogen peroxide, and may be employed for the detection of blood. In the absence of the latter, the oxidation proceeds very slowly and may take days, but when blood is present the action is much more rapid. The test is carried out as follows: An alkaline solution of phenolphthalein is shaken with zinc dust until colourless, filtered, and the filtrate mixed with the solution to be tested, to which a few c.c. of 12% hydrogen peroxide have been added previously. If blood is present, a red coloration develops within three hours (compare *Abstr.*, 1909, ii, 195). Exposure to bright light, such as an arc-light, also increases the rapidity of the oxidation of phenolphthalin.

W. P. S.

**Estimation of Methæmoglobin.** JOSEPH BARCROFT and FRANZ MÜLLER (*Proc. physiol. Soc.*, 1911, xx; *J. Physiol.*, 43).—See this vol., i, 58.

**Use of Aniline Dyes as Reagents for Bile Pigments in Urine.** OTTO V. C. E. PETERSEN (*Chem. Zentr.*, 1911, ii, 1490; from *Deutsch. med. Woch.*, 1911, 37, 1891—1892).—Methyl-violet, methylene-blue, Nile-blue, as well as indigo-carmin and Prussian-blue, yield a green coloration when added to urine containing bile pigments. The green coloration is also obtained in the case of urine free from bile pigments, and the intensity of the colour increases with the quantity of urine used. The test is, therefore, not a chemical reaction, but the result of mixing blue and yellow colouring matters; it is not very sensitive, but as a rough test a dye solution containing 1 part in 10,000 may be employed. W. P. S.

**Detection of Albumoses in Urine.** EMIL HUGO FITTIPALDI (*Chem. Zentr.*, 1911, ii, 1489—1490; from *Deutsch. med. Woch.*, 1911, 37, 1890—1891).—Twenty c.c. of the urine are mixed with 120 c.c. of absolute alcohol, and, after the lapse of twenty-four hours, the precipitate formed is collected on a filter; the precipitate is then dissolved in the least possible quantity of 32% sodium hydroxide solution, and treated with freshly-prepared ammoniacal nickel solution (equal volumes of ammonia and 5% nickel sulphate solution). If albumoses or peptones are present in the urine, a reddish-orange coloration develops immediately. Other proteins, uric acid, cyanuric acid,

xanthine, hypoxanthine, sarcosine, and urobilin do not give a reaction. The test may also be used for the detection of albumoses in blood after the latter has been heated with animal charcoal, cooled, and filtered.

W. P. S.

**The Different Methods for Estimating Pepsin and Trypsin, with a Description of a New Simple Method.** WILHELM WALDSCHMIDT (*Pflüger's Archiv*, 1911, 143, 189—229).—The very numerous methods devised for the purpose are described, discussed, and classified. The new method is a modification of Grützner's carmine-fibrin process; if diphenylrosaniline (spirit-blue) is substituted for carmine, the fibrin so stained can be employed for the estimation of both pepsin and trypsin.

W. D. H.

**New Method for the Physical Analysis of Soil.** J. DUMONT (*Compt. rend.*, 1911, 153, 889—891).—The following method is stated to be rapid and accurate. Two to five grams of the dried soil are treated with about an equal weight of oxalic acid; the volume of carbon dioxide liberated gives the amount of carbonate present. The mixture is diluted until the solution contains 2% of acid, boiled for thirty minutes, filtered, the residue washed with dilute nitric acid, and finally with water. Calcium, etc., may be estimated in the filtrate. The residue is washed with 75—80 c.c. of dilute ammonia, and boiled with 20 c.c. of ammonia to remove humic acid. After two hours the liquid is decanted, the residue suspended in dilute ammonia, and the coarse sand separated by centrifugation and weighed. The colloidal clays in the decanted liquid are again centrifugated at two different speeds, in order to separate two deposits of different degrees of coarseness.

Colloids remaining in suspension are coagulated by ammonium carbonate and removed after a third centrifugation. The final liquid is employed for determination of soluble extract and ash.

W. O. W.

**The Application of Bio-chemical Methods in the Analysis of the Bilberry (Whortleberry).** (Mlle.) A. FICHTENHOLZ (*J. Pharm. Chim.*, 1911, [vii], 4, 441—446).—The glucosides arbutin and methyl-arbutin are estimated in the dried leaves of the bilberry (*Arctostaphylos Uva ursi*) by the changes in rotation and reducing power produced by the action of emulsin on an extract of the leaves, allowance being made for the reducing power of the quinol and methylquinol also produced by the hydrolysis. The dried and powdered material is repeatedly extracted with boiling 90% alcohol, and the extract, after evaporating off the alcohol and dissolving in water, purified with basic lead acetate, the excess of lead removed, and the liquid made to a known volume.

It is then treated with yeast invertase for several days to remove the sucrose, the amount of this substance present being determined by the change in rotation and reducing power which the liquid undergoes during this time. The invertase is then destroyed by boiling, a preparation of emulsin is added, and the rotation and reducing power determined at intervals of several days until hydrolysis is complete.

W. J. Y.

## General and Physical Chemistry.

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**Spectrochemistry of Unsaturated Compounds.** KARL AUWERS (*Ber.*, 1911, 44, 3679—3692. Compare Eisenlohr, this vol., ii, 2).—In part polemical. Eisenlohr has failed to acknowledge sufficiently the work of Brühl on the influence of conjugation on optical properties. Exception is taken to the statement that the introduction of several disturbing groups turns an optical exaltation into a depression, which is claimed to be especially the case in crossed conjugations; the experimental evidence is not considered sufficient to justify this view.

The optical effect when a simple conjugation is converted into a crossed conjugation depends on two factors: the depression produced by the influence of the entering group on the conjugation, and the exaltation due to the new double bond. The final result depends on the magnitude of each of the opposing factors. In the case of crossed conjugations with partial valencies the new valencies compensate to some extent for the disturbing influence of the substituent.

The original must be consulted for the further criticisms of Eisenlohr's argument. E. F. A.

**Refractive Indices of Mixed Liquid Crystals.** PAUL GAUBERT (*Compt. rend.*, 1911, 153, 1158—1160. Compare Abstr., 1911, ii, 949).—The refractive indices of optically positive mixed liquid crystals follow fairly closely the ordinary law of mixtures for isomorphous solids. *p*-Azoxyphenetole and *p*-azoxyanisole influence in the same way the values of the indices for cholesterol octoate. Anomalous results with optically negative crystals are explained by supposing that these two substances exist in a hitherto unknown negative phase, and that crystals of the latter form mixtures with negative crystals of cholesterol salts. W. O. W.

**Heterogeneous Structure of "Fluid Crystals" of Parazoxyphenetole.** HELENE DEISCHA (*Zeitsch. Kryst. Min.*, 1911, 50, 24—32).—The peculiarities of structure and the birefringence shown by fused parazoxyphenetole under the microscope are regarded as due, not to any crystalline structure, but to the capillary attractions and tensions in a colloidal solution forming a frothy mass or emulsion.

L. J. S.

[**Spectroscopy of Oxygen.**] WALTER STEUBING (*Ann. Physik*, 1911, [iv], 36, 1077—1080).—Polemical against Kayser (Abstr., 1911, ii, 785). H. M. D.

**Line Spectrum of Nitrogen in a Geissler Tube.** C. PORLEZZA (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 584—587).—The paper gives the results of the author's measurements of the line spectrum of nitrogen from the red to the green, the nitrogen being enclosed in Geissler tubes at a pressure of about 100 mm. R. V. S.

**Line Spectrum of Nitrogen in a Geissler Tube.** C. PORLEZZA (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 642—645. Compare preceding abstract).—The author concludes his tables of wave-lengths for this spectrum, giving here those of the blue and ultra-violet regions. R. V. S.

**Spectrum of Boron.** SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1911, A, 86, 36—41).—The spectrum of the spark passing between electrodes of crystalline boron has been examined. Certain lines on the photographs have been traced to calcium and aluminium, and when these are eliminated it is found that the ultra-violet spectrum of boron consists of three lines of wave-lengths  $\lambda = 3451.50$ ,  $2497.83$ , and  $2496.89$ . The fourteen other lines given by Eder and Valenta, and the five other lines recorded by Exner and Haschek, could not be detected on any of the photographs in spite of excessively long exposures. H. M. D.

**Spectrum of the Magnesium High-frequency Arc.** ELLEN O'CONNOR (*Phil. Mag.*, 1912, [vi], 23, 94—101).—The spectrum obtained from an arc between magnesium electrodes has been examined with a high-frequency oscillatory discharge consisting of undamped oscillations. Photographs have been obtained which show the influence of the inductance, capacity, and frequency on the nature of the spectrum. A comparison of these indicates that the spectrum becomes richer in lines as the frequency increases, and the continuous background, which is seen in the case of the low-frequency discharge, gradually disappears as the frequency is increased. H. M. D.

**Measurements of the Wave-lengths of Normal Lines in the Iron Spectrum.** P. EVERSHEIM (*Ann. Physik*, 1911, [iv], 36, 1071—1076. Compare *ibid.*, 1909, [iv], 30, 815).—Further measurements of wave-lengths of iron lines have been made between  $\lambda = 4282$  and  $\lambda = 3371$ . The data are in excellent agreement with the corresponding measurements made by Fabry and Buisson, the maximum difference amounting to 0.003 Ångström units. H. M. D.

**Influence of the Solvent on the Position of Absorption Bands in Solutions.** T. H. HAVELOCK (*Proc. Roy. Soc.*, 1911, A, 86, 15—20).—An attempt has been made to measure the effects which can be ascribed to the operation of Kundt's rule in reference to the displacement of the absorption bands of dissolved substances towards the longer wave-lengths in virtue of the refractive or dispersive power of the solvent. H. M. D.

**Absorption Spectra of Phosphorescent Substances.** BERNHARD WALTER (*Physikal. Zeitsch.*, 1912, 13, 6—11).—Photographs have been obtained of the absorption spectra of the phosphorescent alkaline earth metal sulphides containing bismuth as "active impurity." The spectra are characterised by strong absorption bands, and it has been found that only those lines which are absorbed are capable of producing a well developed phosphorescence effect.

By reference to Lenard's observations, it is shown that the wave-lengths of those rays which excite the phosphorescence of the alkaline earth metal sulphides are nearly independent of the nature of the active metallic impurity, but vary considerably according to the particular alkaline earth metal present. This cannot be reconciled with Lenard's electronic explanation of phosphorescence, but appears to favour the older chemical theory. H. M. D.

**The Fluorescence of Anthracene.** LOUISA STONE STEVENSON (*J. Physical Chem.*, 1911, 15, 845—865).—From a chemical point of view the fluorescence of anthracene may be due to the following circumstances: (1) A continuous reaction generating a small amount of light, the intensity or wave-length of which is sufficiently altered by incident light to render the emitted light invisible. (2) Tautomeric change, incident light being absorbed and fluorescent light emitted during the formation of one or both isodynamic forms. (3) Dissociation under the influence of light, fluorescent light being generated either in the dissociation or in the re-association of the molecule.

A number of highly fluorescent substances in solution failed to produce any effect on the photographic plate under the most favourable conditions. Hence the conclusion is drawn that explanation (1) is improbable, although the plate was also unaffected by the gradual dehydration of quinine sulphate in which, it is supposed, light of very low intensity is emitted.

The tautomeric hypothesis (2) in the form suggested by Hewitt is discredited by the fluorescence of dihydroanthracene, which has no para-bond. A consideration of all the known anthracene derivatives shows, however, that the meso-ring is undoubtedly concerned with the fluorescence. Anthraquinone and its derivatives are not fluorescent, but oxanthrol derivatives may exhibit fluorescence. A tautomerism due to the oscillation of an hydrogen atom or equivalent group between the  $\gamma$ -position and some other part of the molecule is considered improbable in the case of dichloroanthracene tetrachloride, where all the immediately available positions for chlorine atoms are filled.

Hypothesis (3) can be applied to all the known fluorescent derivatives of anthracene. The author finds that the chlorination of molten anthracene to  $\gamma$ -dichloroanthracene is accompanied by the emission of a bluish-white light. The marked fluorescence of  $\gamma$ -dichloroanthracene is well explained by the dissociation of the compound with absorption of light and its re-formation with emission of light of a different wave-length. Tesla rays and  $\beta$ -rays from radium excite anthracene, dichloroanthracene, and dihydroanthracene to luminescence, whilst even anthraquinone may be rendered fluorescent in a powerful cathode beam.

The formation of dianthracene under the influence of light probably has no connexion with the fluorescence of anthracene.

Anthracene derivatives which have no para-bond and which cannot polymerise to dianthracenes are often fluorescent. Light has no appreciable influence on the oxidation of anthracene at 140—150° by gaseous oxygen.

The chlorination of anthracene in the dark yields dichloroanthra-

cene. In presence of iron filings, dichloroanthracene tetrachloride is produced. In direct sunlight, with or without halogen carrier, the product is hexachloroanthracene tetrachloride. The same product is obtained in the dark with red phosphorus as catalytic agent.

R. J. C.

**Crystalline Liquids.** H. VON WARTENBERG (*Physikal. Zeitsch.*, 1911, 12, 1230. Compare Abstr., 1911, ii, 952).—The fact that crystalline liquids behave like uniaxial crystals when examined in an electrical field at right angles to the lines of force has also been demonstrated by Mauguin (*Compt. rend.*, 1911, 152, 1680).

H. M. D.

**Chemical Action of Ultra-violet Rays: Synthesis and Decomposition of Water.** IWAN I. ANDRÉEFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1342—1364).—After discussing recent work on the chemical effects of ultra-violet light, the author describes his own experiments, which have been carried out with a mercury lamp at various voltages and currents.

With a voltage of 220, hydrogen and oxygen combine to form water with moderate rapidity. The velocity of the reaction, which terminates in from five to twenty hours, is independent of the concentrations of the reacting substances, and is in good agreement with the expression  $dx/dt = C$ ; it increases almost proportionately with the intensity of the light. The mean value of the temperature-coefficient of the reaction is 1.1.

Also, water decomposes under the influence of ultra-violet light, in the field of action of which an equilibrium is established between hydrogen, oxygen, and water, this equilibrium differing from the thermal equilibrium at the corresponding temperature. When the initial product is a mixture of hydrogen (2 vols.) and oxygen (1 vol.), the final position of equilibrium is the same as when water is employed.

With increase of the intensity of the ultra-violet light, the equilibrium is displaced in the direction of the dissociation, and the percentage of water decomposed increases proportionately with the increase of intensity.

T. H. P.

**Action of Ultra-violet Light on Sodium Thiosulphate.** LOUIS MARMIER (*Compt. rend.*, 1912, 154, 32—33).—After exposing a solution of sodium thiosulphate to the rays from a quartz-mercury lamp for five minutes, sulphur is deposited, and the liquid found to contain sodium hyposulphite. The latter, however, is completely destroyed after a further exposure of seventy minutes. The formation of a hyposulphite can only be detected in solutions containing less than 0.6% of thiosulphate.

W. O. W.

**Biochemical Reactions in Light.** HANS EULER (*Arkiv. Kem. Min. Geol.*, 1911, 4, No. 8, 1—10).—The degradation of lactic acid to carbon dioxide and alcohol takes place in pure aqueous solution under the influence of ultra-violet radiations. The rate of decomposition of the lactic acid does not depend on the concentration of the acid within

the limits studied,  $0.25N$  to  $N$ . The condensation of acetaldehyde to aldol also takes place without a catalyst on exposure to ultra-violet light. The bearing of these results on the degradation and synthesis of plant acids is discussed.

E. F. A.

**The  $\alpha$ -Particles Emitted by the Active Deposits of Thorium and Actinium.** E. MARSDEN and T. BARRATT (*Proc. Physical Soc.*, 1911, 24, i, 50—61. Compare this vol., ii, 6).—Probability considerations have been applied to the  $\alpha$ -particles emitted by the  $C$ -members of the thorium and actinium active deposits. For a single disintegration, the probability of occurrence of a time interval of length between  $t$  and  $t + \delta t$  is  $\mu e^{-\mu t} \delta t$ , where the  $\alpha$ -particles are emitted at the mean rate of  $\mu$  per second. If more than one  $\alpha$ -particle is emitted simultaneously, or if a product of very short period exists, there will be an excess of short intervals above that calculated from the formula. The method of two observers simultaneously observing two zinc sulphide screens, between which the radioactive substance was placed, or, in the case of an emanation, diffused, was adopted, each observer recording the observations seen. For the actinium active deposit, the agreement between the observed and calculated intervals was good, the short intervals being only about 1% of the whole in excess.

With the thorium active deposit good agreement was also obtained, and, as before, only a slight excess, in this case about 2% of the whole, of short intervals occurred. It is possible that this may be explained by imperfections in the experimental arrangement. A determination of the number of scintillations from thorium- $C$  of ranges 4.8 and 8.6 cm. respectively showed that the number of the longer range is 0.646 of the total, so that thorium- $C_2$  gives 1.83 times the number of  $\alpha$ -particles given by thorium- $C_1$ . This ratio held unaltered as the active deposit decayed. The period of the change in which the longer range  $\alpha$ -particle is expelled, calculated from the range, is only  $10^{-12}$  second. The distribution of the time intervals shows that if thorium- $C_2$  succeeds thorium- $C_1$ , its period should be greater than a few seconds, and it should be separable by recoil methods, which, however, fail.

The conclusion is drawn that thorium- $C_1$  and - $C_2$  must be simultaneous products of thorium- $B$ . However, there is the possibility that the ratio in the number of  $\alpha$ -particles given by the two  $C$ -members should be as 2:1, but the assumptions necessary in this case to avoid the introduction of branch series seem out of the question. The conclusion of Geiger and Kovarik (*Abstr.*, 1911, ii, 954) that thorium- $D$  gives two  $\beta$ -particles per atom disintegrating depends on the assumption that thorium- $C_1$  and - $C_2$  give two  $\alpha$ -particles per atom disintegrating, and is therefore no longer justified.

F. S.

**The  $\beta$ -Rays of the Radium Family.** J. DANYSZ (*Compt. rend.*, 1911, 153, 1066—1068. Compare *Abstr.*, 1911, ii, 840; Baeyer, Hahn, and Meitner, *ibid.*, 567).—The speeds of the separate bundles of  $\beta$ -rays, from a tube containing the emanation, have been determined with the greatest possible accuracy, and many more have been recog-

nised. The table gives in the first line the number of the bundle, in the second its velocity in terms of that of light, calculated according to the Lorentz formula, and in the third the relative strength of the bundle ( $s$  = strong,  $m$  = medium,  $f$  = feeble,  $v.f.$  = very feeble).

1.	2.	3.	4.	5.	6.	7.	8.
0·615	0·634	0·660	0·682	0·705	0·718	0·735	0·748
<i>s.</i>	<i>f.</i>	<i>v.f.</i>	<i>s.</i>	<i>f.</i>	<i>v.f.</i>	<i>s.</i>	<i>m.</i>
9.	10.	11.	12.	13.	14.	15.	16.
0·760	0·786	0·790	0·862	0·882	0·897	0·920	0·940
<i>f.</i>	<i>s.</i>	<i>f.</i>	<i>s.</i>	<i>f.</i>	<i>f.</i>	<i>f.</i>	<i>s.</i>
17.	18.	19.	20.	21.	22.	23.	
0·943	0·946	0·949	0·957	0·962	0·988	0·996	
<i>f.</i>	<i>f.</i>	<i>m.</i>	<i>s.</i>	<i>f.</i>	—	—	

The seven strong bundles apparently correspond with those before measured, the velocities being more accurately determined. From Nos. 1 to 9 the bundles appear to consist of rays travelling at velocities differing by about 1% from the mean value on either side. The more rapid bundles are perfectly sharply defined. Bundle No. 22 consists of from three to five separate bundles travelling with velocities between 0·98 and 0·99. These extremely fast  $\beta$ -rays, like the  $\gamma$ -rays, only slightly affect the photographic plate. The last bundle, No. 23, is for this reason very little known. The value given for the velocity, 0·996, which corresponds with a value of  $H\rho$  ( $H$  = strength of magnetic field,  $\rho$  = radius of curvature) of 18,100, comprises certainly some rays with a value of  $H\rho$  26,000 and of the velocity 0·998. The emanation from 0·3 gram of radium chloride was employed.

F. S.

**Radiant Emission from the Spark.** ROBERT W. WOOD (*Physikal. Zeitsch.*, 1912, 13, 32—34. Compare Abstr., 1910, ii, 915). —Polemical against Steubing (Abstr., 1911, ii, 838). Further photographs are reproduced which confirm the view that the spectrum under discussion is due to a spectral radiant emission, and not to a scattering of the light from the spark discharge by condensed particles of the vapour of the metal as maintained by Steubing. H. M. D.

**Charges on Thermions Produced in Air and Hydrogen at Atmospheric Pressure.** J. C. POMEROY (*Phil. Mag.*, 1912, [vi], 23, 173—182).—The magnitude of the charge carried by the ions emitted by a strip of heated platinum has been examined by observations on the distribution of the ions when subjected to the action of a uniform electric field. At a temperature which is only just sufficiently high to give positive ions, some of the ions from a fresh strip carry charges which are double the atomic charge. When, however, the strip is heated for some time, a gradual change takes place, and as the positive leak diminishes, the proportion of ions carrying a double charge gets smaller and smaller, until a steady state appears to be reached when the average charge is nearly equal to the atomic charge.

No such change in the average charge occurs in the case of the

negative ions, and at temperatures which are sufficiently high to give negative ions, it is found that the average charge of the positive and negative ions is about the same. This result suggested that the negative ions might also be found to carry single charges only, if obtained from a strip at a sufficiently low temperature, and experiments in hydrogen showed that this is actually the case. H. M. D.

#### Ionisation Produced by Carbon at High Temperatures.

JOHN N. PRING and A. PARKER (*Phil. Mag.*, 1912, [vi], 23, 192—200).—The emission of ions by carbon has been investigated at temperatures between  $1300^{\circ}$  and  $2050^{\circ}$ , and at different pressures. The negative leak at a given temperature diminishes with the progressive purification of the carbon, and with reduction in the pressure.

The smallest ionisation current obtained at  $1300^{\circ}$  was  $1.5 \times 10^{-9}$  ampere per square centimetre of carbon surface, whereas Richardson found  $1.3 \times 10^{-4}$  at this temperature. Above  $1800^{\circ}$  the increase in the ionisation with the temperature is very small, and the lowest value of the current observed at  $2000^{\circ}$  was  $4 \times 10^{-7}$  ampere. The data obtained in these experiments are incompatible with Richardson's formula, and indicate that the large ionisation currents hitherto obtained with heated carbon cannot be ascribed to the emission of electrons from the carbon itself. They are probably due to some interaction between the carbon, or the impurities contained in it, and the surrounding gases, which involves the emission of electrons. H. M. D.

#### The Emission of Positive Charges by Heated Metals.

G. REBOUL and E. GRÉGOIRE DE BOLLEMONT (*Le Radium*, 1911, 8, 406—411).—Surfaces of copper and platinum separated to definite distances from one another are heated to various temperatures under various conditions. A black deposit forms on the platinum. If the copper surface is in the shape of a cross, the deposit on the platinum assumes the same form. The thickness of the deposit increases to a maximum, and then decreases as the time of heating is increased, so that after a certain time no deposit is left. The maximum deposit results in a time the shorter the higher the temperature. The deposit is most abundant in oxygen, but occurs and has a grey colour, turning black on heating in air, in nitrogen and carbon dioxide. The nature of the surface receiving the deposit is not of great importance, and the platinum may be replaced by other metals, and even by porcelain. In addition to copper, a projection of metallic particles occurs with silver, as may be put into evidence by opposing it with a gold plate, which becomes coated with a white deposit of silver of the form of the silver surface. The maximum in the amount of deposit with copper is explained by the "fatigue" of the copper. All metallic surfaces are regarded as projecting metallic particles when heated, due to the liberation of occluded gas, and the mechanical carrying away of the metal by the bursting of the bubbles, a process which accounts also for the positive ionisation from heated metals, which in every respect is analogous to the phenomena investigated. At first the projection from the copper surface to the opposed surface is regarded as greater than that of the projection of particles from this

surface, but afterwards, when the gas has been liberated, "fatigue" of the copper takes place, and the deposit on the opposed surface is again removed by the projection of particles from that surface.

F. S.

**Positive Thermions from the Salts of the Alkaline Earths.** CLINTON J. DAVISSON (*Phil. Mag.*, 1912, [vi], 23, 121—139).—The nature of the ions emitted at high temperatures and low pressures by the chlorides, fluorides, sulphates, and phosphates of barium, strontium, calcium, and magnesium has been investigated by the method employed by Richardson. From observations on the influence of a known magnetic field, it is found that the truly characteristic thermions emitted by the salts of these metals consist of single atoms of the elements carrying unit positive charges.

Experiments with zinc sulphate lead to the same conclusion.

H. M. D.

**The Rôle Played by Gases in the Emission of Positive Thermions from Salts.** CLINTON J. DAVISSON (*Phil. Mag.*, 1912, [vi], 23, 139—147. Compare preceding abstract).—The emission of positive ions by heated strontium chloride, strontium sulphate, and aluminium phosphate has been examined with reference to the part played by gases in the phenomenon. The results indicate that the increased emission of thermions, which is observed when the heated substance is in contact with air, carbon dioxide, or hydrogen, is not due to the emission of molecules of the gas which have been absorbed by the salt and emitted in a charged condition. In reference to the suggestion that the traces of carbon monoxide or dioxide which are sometimes emitted by heated salts are responsible for the observed ionisation, it has been found that the emitted gas is not electrically charged.

H. M. D.

**The Production of Chemically Active Rays in Chemical Reactions.** J. MATUSCHEK and NENNING (*Chem. Zeit.*, 1912, 36, 21).—A beaker containing zinc and sulphuric acid is placed on a photographic plate in a light-tight case, a tinfoil star being interposed. After several hours' exposure, a distinct image is obtained on development. The best results are obtained when the zinc is in the form of a sheet with ribs on the lower surface. Similar results are obtained with hydrochloric and nitric acids, and with copper, tin, and lead, the intensity of the photographic action varying considerably. Copper oxide and hydroxide and potassium hydroxide also give chemically active rays when dissolved in acids. Other active reactions are: the slaking of lime, the setting of Portland cement and plaster, the decomposition of calcium carbide by water, and the formation of ammonium amalgam. The most active reaction observed is that between sodium silicate and dilute hydrochloric acid, which gives a distinct image in less than an hour.

C. H. D.

**The Detection of Actinium Emanation in Minerals containing Actinium.** GEORG VON HEVESY (*Physikal. Zeitsch.*, 1911, 12, 1213—1214).—An investigation has been made of the point

noticed by Boltwood (Abstr., 1908, ii, 454) that actinium emanation cannot be detected in a uranium mineral by passing air through its solution into an electroscope. It was found that by the use of vessels of sufficiently small capacity, and by filling these as completely as possible with the solution or drying liquid employed, the actinium emanation could be readily detected from a solution of pitchblende. One gram of pitchblende in 2.5 c.c. of solution, contained in a washing-bottle of 3.5 c.c. capacity, gave, when an air stream of 0.4 c.c. per second was passed through, a leak in the electroscope, due to actinium emanation, of two divisions a minute.

F. S.

**The Solubility of Actinium Emanation in Liquids and Charcoal.** GEORG VON HEVESY (*Physikal. Zeitsch.*, 1911, 12, 1214—1224).—By means of the differences in the ionisations produced in an electroscope when the actinium emanation is passed through various liquids at various rates on its way to the electroscope, the solubility of the emanation has been indirectly calculated in various liquids. These show the same relative absorbing powers as in the case of the other emanations. In increasing order of absorbing power the liquids examined were: saturated aqueous potassium chloride solution, water, sulphuric acid, ethyl alcohol, amyl alcohol, acetone, benzaldehyde, benzene, toluene, petroleum, and carbon disulphide. The solubility coefficient of actinium emanation in water is 2, as compared with 1 for the thorium and 0.33 for the radium emanation. Coconut charcoal also absorbs the actinium emanation strongly at the ordinary temperature.

F. S.

**Radium Emanation Contained in the Air of Various Soils.** JOHN SATTERLY (*Proc. Camb. Phil. Soc.*, 1911, 16, 336—355. Compare Joly and Smyth (Abstr., 1911, ii, 1048).—The radium emanation contained in the underground air of various soils and at various depths in the neighbourhood of Cambridge has been found on the average to be 2500 times as great as that in the atmospheric air of the same locality. Low barometer usually decreases the amount in the air, probably because of the rainfall accompanying it, which chokes the pores of the soil. In the tests of the influence of depth, the greatest amounts of radium emanation were found at the greatest depths. Continuous withdrawal of the air from the ground did not exhaust the supply of emanation.

F. S.

**An Attempt made to Detect the Electric Conductivity of Radium-*D*.** LÉON KOLOWRAT (*Le Radium*, 1911, 8, 401—404).—If the radium emanation is stored in a vessel all of the same potential, it is to be expected that the radium-*D* formed will be deposited as a uniform film. From the manner in which the resistance of films of platinum or silver suddenly augments when the thickness is decreased between  $10^{-5}$  and  $10^{-6}$  cm., and on the assumption that the density and electric conductivity of radium-*D* are the same as that of lead, it is calculated that the emanation accumulating in six days from 0.25 gram of radium should produce in a capillary tube 5 mm.

long and 0.2 mm. diameter a film of radium-*D* about  $4 \times 10^{-6}$  cm. thick with a resistance of 40 ohms. Capillary tubes of this size provided with two platinum wire electrodes and silvered internally, except for the space between the ends of the electrodes, had an initial resistance greater than a megohm. Filled with the emanation from 0.27 gram of radium, the silvering was rapidly attacked and rendered transparent, which was ascribed to the presence of oxygen. In one experiment a ring of brown deposit midway between the electrodes, and brilliantly metallic when seen by reflected light, was seen three or four days after the emanation was introduced, but this deposit after three days more, gradually and completely disappeared, and was hardly visible even under the microscope. The deposit is supposed to have been radium-*D*, oxidised in course of time by the presence of a trace of oxygen. In the second experiment no deposit formed, but in a third, a non-uniform, discontinuous deposit appeared. In all cases the resistance of the tube remained greater than a megohm. The formation of the active deposit appears not to take place uniformly, but over certain areas determined by the position of the electrodes and the shape of the tube.

F. S.

**The Decay-constant of Polonium.** ERICH REGENER (*Ber. Deut. physikal. Ges.*, 1911, 13, 1027—1033; *Le Radium*, 1911, 8, 458—461).—The half-period of polonium, determined by counting the scintillations produced on a zinc sulphide or diamond screen, was 129.5 days, the total number of scintillations counted being 16,800. This period is less than that usually given, which varies in different measurements from 134.5 to 143 days. An examination was made of the effects of unsaturation on the period of decay in ionisation measurements. The ionisation of a strong polonium preparation was measured by a galvanometer at different voltages over a period of nearly a year. At insufficient voltage to produce saturation the period found was higher than when higher voltages were employed. The true half-period deduced from these measurements was 136 days ( $\pm 0.5$  day).

F. S.

**Radioactivity of Marsh Gas.** JOHN SATTERLY (*Proc. Camb. Phil. Soc.*, 1911, 16, 356—359).—The inflammable gas drawn from stagnant backwaters and ditches around Cambridge during a long spell of fine weather was rich in radium emanation, to the same extent approximately as the air drawn from depths of three to five feet in the soil of the same locality.

F. S.

**The Radium Content of Various Fresh and Sea Waters, and Some Other Substances.** JOHN SATTERLY (*Proc. Camb. Phil. Soc.*, 1911, 16, 360—364).—The amount of radium present in various fresh waters in the neighbourhood of Cambridge was usually less than  $10^{-12}$  gram of radium per litre, which is some hundreds of times less than accounts for the quantity of emanation found in the water in the case of the tap water and spring waters. The water of the Cam contains much less dissolved emanation than these. Three specimens of coastal sea water contained about  $10^{-12}$  gram of radium

per litre, which is in agreement with Eve's and much smaller than Joly's results. F. S.

**The Apparatus Used for the Determination of the Radioactivity of Springs.** FERDINAND HENRICH and FRITZ GLASER (*Zeitsch. angew. Chem.*, 1912, 25, 16—19).—The "fontaktoscope" of Engler and Sieveking, has been compared with its improved form, the "fontaktometer" of Mache and St. Meyer. Similar results were obtained with the two instruments, and it is held that the former is advantageous on account of its cheapness, its ease of working, and its transportability. F. S.

**Electrical Resistance of Special Steels.** OCTAVE BOUDOUARD (*Compt. rend.*, 1912, 154, 1475—1478).—The influence of different percentages of carbon on the electrical conductivity of nickel, manganese, chromium, and tungsten steels of varying composition is shown in tabular form. In nickel steels the coefficient of resistance increases with the percentage of carbon. The curve showing the variation of the coefficient with the proportion of manganese shows a maximum corresponding with the compound  $\text{NiFe}_{90}$ . In manganese steels the resistance shows a maximum when 12—13% of manganese is present, the amount of carbon having little influence on the value. The resistance varies in a very irregular way with chromium steels, whether they are rich or poor in carbon. Tungsten steels show an increase up to a certain concentration, then a minimum, followed by a further increase. Benedick's formula for the conductivities of steel, expressing the conductivity as a linear function of the sum of the concentrations of the different elements present expressed in terms of their carbon equivalents, is found to hold good for the special steels studied. W. O. W.

**Conductivity of Pure Ethyl Ether.** J. CARVALLO (*Compt. rend.*, 1911, 153, 1144—1145).—The author considers that the ether employed in Schröder's experiments (*Abstr.*, 1909, ii, 462) was not pure, and that his values for the conductivity were too high. With ether purified over sodium, and in the absence of air, a current of  $0.93 \times 10^{-10}$  amperes traversed the liquid on establishing a difference in potential of 425 volts, but this diminished progressively owing to the experiment being conducted in glass vessels. It will be necessary to employ metallic apparatus with paraffin insulation to obtain accurate values. W. O. W.

**Influence of Temperature on the Density and Electrical Conductivity of Aqueous Salt Solutions.** HEINRICH CLAUSEN (*Ann. Physik*, 1912, [iv], 37, 51—67. Compare Heydweiller, *Abstr.*, 1910, ii, 106, 398).—The influence of temperature on the increase of density due to the ionised and un-ionised portions of the electrolyte has been examined in the case of aqueous solutions of twelve salts and of nitric acid by measurements of density and electrical conductivity at 6°, 18°, and 30°. From these data the constants  $A_s$  and  $B_s$  in the formula  $\Delta_s = A_s i + B_s(1 - i)$  have been calculated,  $\Delta_s$  being the

difference between the density of the solution and that of water, and  $i$  the degree of ionisation.

The constant  $A_s$  decreases with rising temperature, whilst  $B_s$  also decreases for most of the salts examined, but to a much smaller extent. In the case of potassium chloride, bromide, and iodide, and of nitric acid,  $B_s$  increases as the temperature rises. From this it follows that the influence of the ionisation on the change in density diminishes as the temperature is raised, and the alteration is such that the values of  $A_s - B_s$  for the different electrolytes become more nearly equal.

H. M. D.

**Dependence of the Conductivity of Binary Normal Electrolytes on the Concentration.** PAUL HERTZ (*Ann. Physik*, 1912, [iv], 37, 1—28).—A theoretical paper in which the author deduces a relationship between the conductivity and the concentration of the form  $\lambda_0 - \lambda = \text{function of } \sqrt[3]{c}$ , where  $\lambda$  is the molecular conductivity of the electrolyte at concentration  $c$ , and  $\lambda_0$  the conductivity at infinite dilution. By suitable variation of the dimensions of the system of co-ordinates from case to case, it is shown that the relationship between conductivity and concentration can be represented for all binary electrolytes by a single curve.

H. M. D.

**Conductivity of Certain Salts in Methyl and Ethyl Alcohols at High Dilutions.** HENRY R. KREIDER and HARRY C. JONES (*Amer. Chem. J.*, 1911, 46, 574—585).—In continuation of earlier work (Abstr., 1911, ii, 362) on the conductivity of very dilute solutions of salts in methyl and ethyl alcohols, measurements have now been made of the conductivities at 0° and 25° of similar solutions of sodium bromide, lithium bromide, potassium thiocyanate, and cobalt bromide. The values of  $\mu_\infty$  were found in most of these cases. The ratio of the value of  $\mu_\infty$  for a certain salt in one solvent to that for the same salt in another solvent is nearly constant for salts which are solvated to approximately the same extent. When one salt is solvated very much more than another, the value of  $\mu_\infty$  is generally less for the former.

The ratios of  $\mu_\infty$  for certain salts in two different solvents deviate from the ratios of the fluidities of the solvents, since the value of  $\mu_\infty$  in the solvent which has the greater molecular mass is always less than would be expected from the ratio of the fluidities. The greatest difference between these ratios is shown by the most highly solvated salts.

E. G.

**Affinity Measurements in Alcoholic and Aqueous Alcoholic Solutions.** ERIK HÄGGLUND (*Arkiv. Kem. Min. Geol.*, 1911, 4, No. 11, 1—31).—By means of conductivity measurements, the author has investigated the ionisation of various acids and bases and the hydrolysis of certain salts in 80 and 99·8% alcoholic solutions. At 18°, the mobility of the ammonium ion was found to be 17·9 in 80% alcohol, that of the hydroxyl ion 26·1 in 80% alcohol and 16·5 in 99·8% alcohol. Conductivity data were obtained for salicylic, cinnamic, and acetic acids, and for *p*-nitrophenol; also for piperidine, ammonia,

piperazine, and diethylamine in both 80% and 99·8% alcohol. For small variations of concentration it is found that the ionisation of both acids and bases is in harmony with the requirements of the law of mass action. The degree of hydrolysis was examined in the case of aniline salicylate,  $\alpha$ -picoline salicylate, piperidine salicylate,  $\alpha$ -picoline acetate, ammonium acetate, and ammonium *p*-nitrophenoxide. The extent to which these salts are hydrolysed in aqueous alcoholic solutions increases with increase in the alcohol content of the solvent.

Conductivity determinations were also made in order to ascertain whether salt formation occurs when certain ketones and aromatic nitro-compounds are brought into contact with sodium hydroxide in alcoholic solution. In the case of  $\beta$ -nitrophenylethylene, salt formation takes place at a sufficiently slow rate to allow of the process being followed by means of conductivity measurements. The rate of progress in 80% alcohol indicates that the reaction is bimolecular, but in 99·8% alcohol the corresponding values of the velocity coefficient diminish appreciably as the reaction progresses.

H. M. D.

**Measurement of Electrical Conductivity.** ALFONS KLEMENC (*Chem. Zeit.*, 1911, 35, 1420).—A rapid and sufficiently accurate method is described of making up solutions containing 1 gram-equivalent or one mol. in 32, 64 . . . . . litres (the usual dilutions in which electrical conductivity data are tabulated).

G. S.

**Electric Properties of Substances in Relation to their Allotropic State.** NICOLAUS A. HESSEHUS (*J. Russ. Phys. Chem. Soc.*, 1911, 43, *Phys. Part*, 365—371).—Study of the three allotropic forms of carbon—diamond, graphite, and charcoal—is in accord with the view previously advanced (*J. Russ. Phys. Chem. Soc.*, 1901, 33, *Phys. Part*, 19; Abstr., 1911, ii, 13), and indicates that the differences between the contact electrifications of allotropic forms of a substance depend, not only on the surface density, but also on the capacity of the atoms for ionic dissociation.

T. H. P.

**Surface Effects between Mercury and Certain Solutions and an Electrochemical Method of Estimating Dissolved Oxygen.** SAMUEL W. J. SMITH and WILLIAM F. HIGGINS (*Trans. Faraday Soc.*, 1911, 7, 64—77).—The influence of sodium sulphide on the difference of potential between mercury and certain salt solutions has been investigated (compare Smith and Moss, Abstr., 1908, ii, 343). The cells are connected in turn with a constant electrode, and the *E.M.F.* of the combination determined with an electrometer. Using *N*/10-solutions of potassium chloride, bromide, sulphate and hydroxide, and pure water, a sudden change of slope of the *E.M.F.*-concentration curve occurs at about 0·0004 equivalent of sodium sulphide. This break slowly disappears, even when air is excluded from the solutions, and is replaced by one between 0·0005 and 0·0006 equivalent. This is the point at which oxygen is completely removed from the solution by the oxidation of sulphide to thiosulphate. This is confirmed by further experiments with old solutions. The method may be used for the estimation of dissolved oxygen.

The initial break observed at 0.0004 equivalent is attributed to the formation of mercury sulphide, which is a maximum at this concentration, further additions of sodium sulphide diminishing the thickness of the film. This is confirmed by observations of the colours of the tarnished films. The surface adsorption of sodium sulphide must be greater than that of oxygen. C. H. D.

**Anode and Cathode Falls of Potential and the Minimum Potential in Chlorine.** R. RAISCH (*Ann. Physik*, 1911, [iv], 36, 907—928).—Measurements of the fall of potential at the electrodes have been made in tubes filled with chlorine at different pressures, and provided with electrodes of aluminium, platinum, mercury, and magnetite. In the case of magnetite electrodes, which are only slowly acted on by chlorine, the observed potential differences are not much larger than those obtained with other gases. With these electrodes the fall of potential at the anode was found to be independent of the strength of the current, but increased slightly with increasing pressure. When such tubes were left filled with chlorine for several weeks in an undisturbed condition, the anode potential at a pressure of 2.41 mm. was found to have risen from 41 to 300 volts. On passing a current through the tube, the potential difference fell rapidly, however, to its original value. These observations indicate that the large potential falls, which are exhibited by tubes containing aluminium, platinum, or mercury electrodes, are due to the formation of a surface layer by the action of the chlorine on the metals. When such electrodes are pulverised by the passage of a strong current, the anode and cathode falls of potential are found to undergo considerable diminution as a consequence of the removal of the surface film. H. M. D.

**Deposits Obtained from Flames by Electricity.** BRUNO THIEME (*Zeitsch. physikal. Chem.*, 1912, 78, 490—499).—When two electrodes between which a considerable difference of potential subsists are brought near together in a coal gas or candle flame, carbon is immediately deposited on the cathode. In certain circumstances the deposited carbon forms long, narrow growths extending some distance into the flame. The smallest potential giving rise to these structures is 12 volts; they increase in size up to about 25 volts, and beyond that point do not undergo much further change. Similar deposits are obtained when the electrodes are connected with an induction machine giving a short spark. When the poles are reversed, the carbon separates in large flakes from the electrodes. It is suggested that very finely divided soot might be prepared in this way, and a continuous arrangement for this purpose is described.

By means of the following arrangement, metals can be deposited in small amount from their salts. Two iron wires were connected with the poles of an induction coil and held at right angles to each other in the flame. A platinum wire on which were some copper sulphate crystals was held so as to touch the positive pole, and after the spark had passed, metallic copper was found on the platinum wire. In a similar way minute amounts of mercury, and apparently also of sodium,

have been obtained from their salts in the flame. The investigation is being continued. G. S.

**Potentials of the Most Important Standard Electrodes.** FRIEDRICH AUERBACH (*Zeitsch. Elektrochem.*, 1912, 18, 13—18).—As zero for electrode potentials should be taken that of the normal hydrogen electrode at the same temperature as the electrode in question, and with a hydrogen partial pressure of 1 atmosphere. For the calculation of the electrode potentials,  $\epsilon_h$ , referred to the hydrogen electrode as zero, the temperature-coefficients of the calomel electrode found by Richards (compare Abstr., 1898, ii, 7) should not be used, more particularly as they are of uncertain value from the effect of thermo-*E.M.F.*'s, which cannot be accurately allowed for. The dependence of  $\epsilon_h$  on the temperature can be determined directly, or can be calculated from the heat of reaction by means of the Helmholtz formula. For the decinormal potassium chloride-calomel electrode,  $\epsilon_h$  is practically independent of the temperature between 0° and 30°.

The following are the most probable values of  $\epsilon_h$  for the more important standard electrodes (concentrations in gram formula weights per litre):

Electrode.	$\epsilon_h$ in volts at		
	0°.	18°.	25°.
Hg   Hg <sub>2</sub> Cl <sub>2</sub>   KCl 0.1 .....	+0.337	+0.337	+0.337
Hg   Hg <sub>2</sub> Cl <sub>2</sub>   KCl 1.0 .....	+0.289	+0.286	+0.285
Hg   Hg <sub>2</sub> SO <sub>4</sub>   H <sub>2</sub> SO <sub>4</sub> 0.1-0.5	—	+0.68	—
Hg   HgO   KOH 1.0 .....	+0.130	—	+0.107
Hg   HgO   NaOH 1.0 .....	+0.133	—	+0.111
Hg   HgO   NaOH 0.1 .....	+0.184	—	+0.166

G. S.

**Aluminium Anode-Films.** G. E. BAIRSTO and R. MERCER (*Trans. Faraday Soc.*, 1911, 7, 1—29).—An examination of the results of previous workers shows that the aluminium anode-film is made up of two layers, an outer thick conducting film which varies in thickness with the electrolyte, and an inner thin dielectric film, the thickness of which is independent of the electrolyte.

The electrolytes now studied include potassium ferro- and ferri-cyanide, ammonium arsenite and arsenate, and ammonium molybdate, of which only the last gives good results, giving a high resistance, very little affected by temperature. The capacity in sodium phosphate solutions decreases with rise of temperature, whilst in ammonium borate it increases considerably, a large part of the increase persisting after cooling. The addition of chlorides, bromides, and other salts which have little or no valve action, to a phosphate electrolyte, produce a very large increase in the leakage current.

The capacity decreases slowly with the time of formation. The higher the voltage at which the film is formed, the longer is the time required for the capacity to fall to its minimum value. The product of capacity and voltage of formation decreases with increasing voltage.

Experiments with alternating currents, using an oscillograph, show that the asymmetrical conductivity only becomes marked at high voltages. C. H. D.

**Configuration of Equipotential Lines in an Electrolyte.** ANDRÉ BROCHET (*Compt. rend.*, 1911, 153, 1150—1152).—Lines of equipotential surfaces in a copper sulphate solution have been determined, and are reproduced in the form of curves. The method employed in mapping them was to plunge a copper wire into the liquid to different depths; the sound being connected to a potentiometer was not traversed by a current so long as the fall of potential between it and the two electrodes was the same as the resistances of the two branches of the potentiometer. A Deprez-d'Arsonval galvanometer was found most suitable for the purpose. W. O. W.

**Configuration of Equipotential Lines in an Electrolyte.** J. DELVALEZ (*Compt. rend.*, 1912, 154, 1474—1475. Compare *ibid.*, 121, 492).—A claim for priority against Brochet (preceding abstract). W. O. W.

**Study of the Hydrogen Electrode, of the Calomel Electrode, and of Contact Potential.** N. E. LOOMIS and SALOMON F. ACREE (*Amer. Chem. J.*, 1911, 46, 585—620).—The methods usually employed for determining hydrogen ion concentration in the study of organic reactions, such as the hydrolysis of esters, present serious difficulties in their general application. A study of the hydrogen electrode has therefore been undertaken in order to ascertain whether it can be satisfactorily used for the purpose.

The relative efficiency of the various forms of apparatus hitherto used has been investigated, and new forms have been devised to eliminate various sources of error. As the accuracy of the work depends largely on the constancy and ease of reproduction of the calomel electrodes used with the hydrogen electrode, a large number of calomel electrodes have been prepared and measured against each other in order to obtain an average value of the potential. Many platinum electrodes have also been prepared and compared with one another. The hydrogen electrode has been compared directly with the calomel electrode, and experiments have been made to determine the efficiency of various solutions in eliminating contact potential. All the experiments were carried out at 25°. The following results were obtained.

Calomel electrodes,  $N/10\text{-KCl-HgCl-Hg}$ , can be prepared, of which the variation does not exceed 0.10 millivolt during the first three weeks, but afterwards slowly increases. Platinum electrodes can be prepared which when used as hydrogen electrodes in  $N/10\text{-hydrochloric acid}$  show a deviation from the mean value of less than 0.10 millivolt.

The *E.M.F.* of the system  $\text{H}_2\text{-Pt-}N/10\text{-HCl-}N/10\text{-KCl-HgCl-Hg}$  is 0.4266.

Potassium chloride was found to be by far the most efficient of the salts tried for eliminating contact potential. A saturated solution of this salt eliminates almost completely the contact potential of systems consisting of potassium chloride and hydrochloric acid.

The value of the potential of the electrode,  $N/10\text{-KCl-HgCl-Hg}$ , is 0.3390 if the dissociation of  $N/10$ -hydrochloric acid is 92.2%, as found by Noyes; it is 0.3372 if the dissociation of the acid is 86%, and 0.3355 if the contact potential is assumed to be 0.0284, a value calculated from Lewis and Rupert's data (Abstr., 1911, ii, 364).

E. G.

**Application of the Hydrogen Electrode to the Measurement of the Hydrolysis of Aniline Hydrochloride, and the Ionisation of Acetic Acid in the Presence of Neutral Salts.** N. E. LOOMIS and SALOMON F. ACREE (*Amer. Chem. J.*, 1911, 46, 621—637. Compare preceding abstract).—The hydrolysis of aniline hydrochloride has already been studied by means of the hydrogen electrode by Denham (*Trans.*, 1908, 93, 48). The results he obtained are now discussed, and an account is given of a further investigation.

It has been found that if the value of the electrode,  $N/10\text{-KCl-HgCl-Hg}$ , is taken as 0.339, the hydrolysis of a  $N/16$ -solution of aniline hydrochloride is 2.19% and that of a  $N/32$ -solution is 3.05%. If the value 0.3355 is employed, the hydrolysis becomes 1.81% for the  $N/16$ - and 2.56% for the  $N/32$ -solution; these values agree closely with those of Bredig (Abstr., 1894, ii, 229) and Tizard (*Trans.*, 1910, 97, 2492). It is evident, therefore, that the hydrogen electrode is of service for the accurate determination of the relations between conductivity and hydrolysis.

It is shown that the addition of  $N/10$ -potassium chloride to  $N/4$ -acetic acid increases the hydrogen ion conductivity by about 4.5% of its original value.

A bibliography is appended.

E. G.

**Difficulties in the Use of the Hydrogen Electrode in the Measurement of the Concentration of Hydrogen Ions in the Presence of Organic Compounds.** L. JUNIUS DESHA and SALOMON F. ACREE (*Amer. Chem. J.*, 1911, 46, 638—648. Compare preceding abstracts).—When an oxime is formed by the reversible reaction between a carbonyl compound and a hydroxylamine salt, the oxime may exist in the solution as the free oxime, oxime salt, and oxime cation. The concentration of the oxime cation can be measured by determining the amount of free hydrogen ions which disappear in its formation. Only two methods seemed likely to prove satisfactory for estimating the hydrogen ion concentration during the reaction, namely, sucrose inversion and the potential of the hydrogen electrode. The former method has given good results in experiments which will be described in a subsequent paper. An account is now given of the difficulties attending the use of the hydrogen electrode.

It has been found that some organic compounds are decomposed in presence of the hydrogen electrode, and especially when oxygen is present, and the *E.M.F.* observed may not correspond with the concentration of the hydrogen ions present. In several cases in which hydroxylamine hydrochloride and acetone were both present, the maximum potential obtained indicated a hydrogen ion concentration about twice as great as was possible if the hydroxylamine and acetoxime hydrochlorides had been completely hydrolysed.

In most experiments with the hydrogen electrode, the true *E.M.F.* can be ascertained within thirty minutes, but if the platinum electrode and the reacting liquid are previously saturated with hydrogen, the *E.M.F.* can be measured within a millivolt in five to ten minutes.

Ammonium nitrate does not entirely eliminate contact potential.

E. G.

**Capacities of the Electrolytic Valve Effect in Fused Salts and in Absolute Sulphuric Acid.** GÜNTHER SCHULZE (*Zeitsch. Elektrochem.*, 1912, 18, 22—29. Compare Abstr., 1911, ii, 365).—In continuance of the experiments on electrolytic valve action, the thicknesses of the active layers formed on aluminium and tantalum in the presence of fused salts have been calculated on the assumption that the dielectric constant is unity. The capacity measurements were made, by a method which is fully described, after the cells had been formed for thirty minutes at a potential of 50 volts.

The thickness of the layer formed on tantalum, which in aqueous solutions is independent of the nature of the electrolyte and the concentration attainable at 0°, increases regularly at higher temperatures as the proportion of water is further diminished until the fused salt is reached. The same phenomenon is observed in the transition from dilute to absolute sulphuric acid, both with tantalum and aluminium. For tantalum the thickness in dilute electrolytes at 0° is  $4.10\mu\mu$ , in absolute sulphuric acid at 10°  $6.69\mu\mu$ , in fused silver nitrate  $7.12\mu\mu$ , and in fused potassium nitrate  $11.1\mu\mu$ .

With the different fused salts the thickness of the layer is the greater, and the capacity the smaller, the higher the melting point of the salt, and when the capacities are plotted against the melting points a straight line is obtained, which on extrapolation cuts the axis at 510°, as if above this temperature no valve effect was possible.

G. S.

**The After-glow of Electric Discharge and Kindred Phenomena.** (Hon.) ROBERT J. STRUTT (*Proc. Physical Soc.*, 1911, 24, 1—8).—It has been found previously that the ozone obtained from a Siemens' ozoniser supplied with oxygen at atmospheric pressure does not give any after-glow when mixed with nitric oxide, although this effect is obtained when the ozone is obtained from a low pressure discharge. Further experiments have shown, however, that the absence of the after-glow in the first case is due to the very considerable dilution of the ozone by the oxygen, for if the ozonised oxygen from the Siemens' tube at ordinary pressure is concentrated by fractional distillation, the greenish-yellow after-glow is readily obtained. Under similar conditions, a blue glow appears when the ozone is mixed with hydrogen sulphide.

The increased brilliancy of the after-glow, which has been found when ordinary or fuming sulphuric acid or sulphur were present along with air in the discharge tube, is now shown to be due to the removal by these substances of organic matter which is prejudicial to ozone. When these organic impurities are removed, the sulphur compounds have no influence on the after-glow.

Pure dry oxygen exhibits no after-glow, and the white glow observed with imperfectly dried oxygen is probably due to the interaction of ozone with some substance produced by the action of the discharge on water vapour. This substance is not, however, hydrogen peroxide.

The luminosity which is emitted when spring water is shaken up with ozone has been traced to oxidation of the peaty matter present.

H. M. D.

**Decomposition of Nitrogen Peroxide in the Electrical Glow.** J. ZENNECK and B. STRASSER (*Physikal. Zeitsch.*, 1911, 12, 1201—1204. Compare this vol., ii, 16).—Spectral observations have been made of the light emitted by the differently coloured layers which are obtained when a current of nitrogen peroxide is passed through a long, narrow discharge tube. The orange-yellow, greenish-yellow, and bright red glows of the first, third, and fourth stages exhibit spectra which have been recognised as due to nitrogen peroxide, nitric oxide, and nitrogen respectively. In the fourth stage, some oxygen lines are also present. The violet-blue glow of the second stage is probably due to an intermediate labile oxide, its spectrum differing from that of the peroxide by the absence of the continuous portion, and from that of nitric oxide by a difference in the relative intensities of the lines. As a result of the investigation of the different regions for after-glow effects, it is found that these are readily observed in the case of the first, third, and fourth stages, but the second stage does not appear to show any after-glow.

H. M. D.

**Magnetic Temperature-coefficients of the Ferro-magnetic Elements in Corresponding States.** J. R. ASHWORTH (*Phil. Mag.*, 1912, [vi], 23, 36—45).—Experiments have been made on the variation of the residual magnetic intensity of magnets made of nickel, iron, and cobalt for variations of temperature between that of the room and the magnetic critical temperature. If the fractional magnetic intensity ( $I/I_0$ ), where  $I_0$  denotes the intensity at absolute zero, is plotted against the temperature measured as a fraction of the magnetic critical temperature, it is found that the experimental data for the three metals can be represented by a single curve. The critical temperatures of nickel and iron were found to be  $388^\circ$  and  $785^\circ$  respectively, and  $1090^\circ$  was adopted as the value for cobalt. From this result it follows that the characteristic temperature-coefficients of magnetic intensity of the pure annealed ferro-magnetic elements in corresponding states are inversely proportional to the absolute magnetic critical temperatures.

The law of variation of the magnetic intensity of the ferro-magnetic elements with temperature is therefore of the same kind as that which expresses the variation of the density of a liquid, and it is shown that the coefficients involved are of the same order of magnitude.

H. M. D.

**Dependence of the Coefficient of Expansion on the Temperature.** CHARLES L. LINDEMANN (*Physikal. Zeitsch.*, 1911, 12, 1197—1199).—The thermal expansion of rods of aluminium, copper,

zinc, silver, and lead has been measured at low temperatures over the separate ranges afforded by the use of liquid hydrogen, liquid air, liquid oxygen, and ordinary room temperatures.

When the mean expansion coefficients thus obtained are divided by the mean atomic heats, calculated from Nernst and Lindemann's equation (compare Abstr., 1911, ii, 466), numbers are obtained for each metal which are approximately independent of the temperature. This result is in accordance with the relationship anticipated by Grüneisen (*Verh. deut. phys. Ges.*, 1911, 13). H. M. D.

**The Linear Expansion of Solid Elements as a Function of the Absolute Melting Point.** A. STEIN (*Zeitsch. anorg. Chem.*, 1911, 73, 270—273).—If  $\alpha$  is the linear coefficient of expansion of a solid element, and  $v$  its atomic volume, the quantity  $\alpha\sqrt[3]{v}$ , may be considered as the linear expansion of the atomic volume. The product  $\alpha\sqrt[3]{v}T$ , where  $T$  is the absolute melting point, is practically constant over a large range of melting points, being, however, high for elements of very low melting point (P, K, Na, S) and low for the infusible platinum metals. The regularity becomes more pronounced when the expansion is measured at low temperatures, the coefficient of the more fusible elements being more variable. The relation may be expressed in the form that, the atomic heats of solid elements being equal, the force resisting the separation of the atoms with increase of temperature is proportional to the absolute melting point. C. H. D.

**Cubical Expansion of Fused Silica and the Variation of the Boiling Point of Aniline with Pressure.** FREDERICK J. HARLOW (*Proc. Physical Soc.*, 1911, 24, 30—39).—Measurements of the cubical coefficient of expansion of fused silica have been made by the weight thermometer method, the data being referred to the absolute coefficient of expansion of mercury. For the interval 0—100°, the cubical expansion coefficient is given as  $99.8 \times 10^{-8}$ , and for 0—184° as  $144.7 \times 10^{-8}$ . The former value is considerably smaller than that calculated from previous measurements of the linear expansion, but the fact that the coefficient has been shown to change in sign at about -80° points to its probable correctness.

From measurements of the boiling point of aniline at pressures from 74 to 78 cms. of mercury, it is found that the temperature rises 0.49° per cm. of mercury. H. M. D.

**Change of Volume Accompanying the Fusion of Crystals. The Thermal Expansion of Crystals and of their Products of Fusion.** HEINRICH BLOCK (*Zeitsch. physikal. Chem.*, 1912, 78, 385—425).—The changes of volume which occur in the fusion of crystals was determined by drawing the fused substance into a capillary tube not more than 1.5 mm. wide, sealing one end of the tube, and allowing the substance to solidify slowly at a temperature very little below its melting point, whereby the occurrence of air spaces is excluded. The position of the upper surface of the solid is then carefully noted, as is that of the upper surface after fusion. The tube is then carefully calibrated with mercury, and from the data thus

furnished the change of volume on fusion is obtained. When impure substances are used, the impurities rise to the surface of the liquid in the capillary tube and can be removed, after which the definite readings are taken. The thermal expansion of the crystals was obtained by determining the density at different temperatures by the floating method, and the density of the liquid was taken in a special form of dilatometer. These observations gave an alternative method of obtaining the change of volume on fusion, and the results are in very good agreement with those obtained directly. The physical constants in question were found for thirty-one substances (organic compounds, with one exception), and the results are given in tabular form. They are in most cases in good agreement with those of previous observers. The available data for changes of volume on fusion, including those for a number of inorganic compounds, are also tabulated.

No relationship has been found between the molecular weights of substances and the changes of volume on fusion. On the other hand, Tammann's formula  $\delta v = T_0(d_p v'/dT - d_p v''/dT)$ , where  $\delta v$  is the change of volume on fusion in c.c. per gram,  $T_0$  the absolute temperature of fusion and  $d_p v'/dT$  and  $d_p v''/dT$  the change in volume of liquid and solid respectively (in c.c. per gram) for a change in temperature of  $1^\circ$  (compare *Krystallisieren und Schmelzen*, Leipzig, 1903) is valid for the great majority of substances examined. G. S.

**Thermodynamics of the Equilibria in One Component Systems.** I. GUSTAV TAMMANN (*Ann. Physik*, 1911, [iv], 36, 1027—1054).—From a consideration of the theory of thermodynamic potential in its application to one component systems, it is shown that two forms of equilibrium curves are possible. One of the two groups of curves is characterised by a critical point, but such a point is absent in the second group. From this, it follows that the limits of existence of the two phases corresponding with an equilibrium curve of the first type are incompletely defined, whereas the conditions of existence of the phases corresponding with curves of the second type are completely determined by closed systems of curves on the equilibrium diagram. Similar results have already been obtained on the basis of molecular considerations, and the theoretical deductions are in agreement with experimental observations. H. M. D.

**A Correlation of the Elastic Behaviour of Metals with Certain of their Physical Constants.** JOHN JOHNSTON (*J. Washington Acad. Sci.*, 1911, 1, 260—267).—When pressure acts on a solid phase, but not on the liquid phase produced from it, the effect is always to lower the melting point. By means of a thermodynamical equation (Lewis, Abstr., 1908, ii, 465) the pressure required to produce melting at  $25^\circ$  is calculated for a number of metals for which the density and the latent heat of fusion are known. The values obtained increase from 64 atmospheres for potassium to 21300 for platinum. The order is found to be the same as that of decreasing ease of flow and compressibility, and of increasing Young's modulus and modulus of rigidity. This indicates that the flow of metals is due to conversion into liquid under the influence of pressure, in accordance with the views of Beilby (Abstr., 1904, ii, 647). C. H. D.

**Neutral Salt Action as Exhibited in the Freezing Points of Mixtures in Aqueous Solution.** ALBERT C. D. RIVETT (*Med. K. Vetensk. Nobelinst.*, 1911, 2, No. 9, 1—32).—Measurements of the freezing points have been made for aqueous solutions of fourteen different salts and mixtures of these with (1) ethyl acetate and (2) sucrose. The freezing-point depressions for the two series of mixtures are always greater than the sum of the individual depressions due to the salt and the non-electrolyte. This departure from additivity is attributed to mutual influences operating between the salt and the non-electrolyte, and in the absence of evidence as to the relative extents of these influences, the relative increases in the freezing-point lowering are calculated on the assumption that the effect is entirely due (1) to the action of the salt, (2) to the action of the non-electrolyte. The data thus obtained show that the influence of the salt (or non-electrolyte) is independent of the concentration of the non-electrolyte (or salt), and is, in general, directly proportional to its own concentration. The proportionality does not hold in the case of sucrose, and the more concentrated solutions of lithium chloride, magnesium chloride, and magnesium nitrate.

The order of the salts is not the same for the two non-electrolytes, and this is considered to furnish a strong argument against any explanation of the observations which is based entirely on the formation of hydrates.

In the case of sucrose, there appears to be no connexion between the influence of the different salts on freezing-point depression and on the velocity of inversion.

H. M. D.

**2:6-Dimethylpyrone as a Solvent.** G. POMA (*Gazzetta*, 1911, 41, ii, 518—538).—From determinations of its latent heat of fusion (56.0 calories), the cryoscopic constant of dimethylpyrone is found to be 58.7, whilst the mean deduced from cryoscopic measurements with stable organic substances (azobenzene, anthracene, phenanthrene, and phenanthraquinone) is 64.6. The molecular weights of benzoic acid and thymol in dimethylpyrone are slightly below the normal. The molecular weights of some electrolytes in dimethylpyrone solution were found to be much lower than the theoretical values. These results accord with those obtained from the measurement of the electrical conductivities of the solutions in some cases, but not in others. Measurements of the molecular surface energy and its temperature-coefficient show that dimethylpyrone is slightly associated. It also has considerable dissociating power, but this is not manifested in the same sense as that of water, so that in the series of alkali halides the degree of dissociation is greatest for sodium iodide and least for lithium chloride, the dissociation of lithium bromide being intermediate between these two.

The following other constants have been determined:  $D^{137}$  0.9953,  $D^{183}$  0.9483; specific heat 0—100°, (solid) 0.368; specific heat 152.3—183°, (liquid) 0.550; surface tension at 137° 30.76, at 183° 26.31; molecular surface energy at 137° 767.1, at 183° 677.5; coefficient of molecular association 1.21 (?).

R. V. S.

**Capillary Force of Evaporation.** CARLO DEL LUNGO (*Nuovo Cim.*, 1911, [vi], 2, ii, 425—430).—According to Laplace's theory the molecules of a liquid in the surface layer are subjected to an attractive force directed towards the interior. This force must naturally be greatest on the molecules quite at the surface. From considerations of the work done in evaporation, the author deduces mathematically the formula  $P = E\rho C/2$ , where  $P$  is the force at the extreme outermost layer,  $\rho$  is the density of the liquid,  $C$  is the internal heat of vaporisation, and  $E$  is the mechanical equivalent of heat. From this it is calculated that at  $0^\circ$ ,  $P$  for water is 11,928 atmospheres, for alcohol 3733 atmospheres, for ether 1320 atmospheres, and for carbon disulphide 2214 atmospheres. The results are in fair agreement with those obtained by van der Waals by an alternative method. At  $100^\circ$ , the calculated value of  $P$  for water is 9852 atmospheres.

In the second part of the paper an alternative deduction is given of Sir J. J. Thomson's formula connecting the saturation pressure of a vapour and the curvature of its surface. G. S.

**Relations between Critical Temperatures, Boiling Points, and Expansion Coefficients of Liquids.** PHILIPPE A. GUYE (*Trans. Faraday Soc.*, 1911, 7, 119—121. Compare Prideaux, *Abstr.*, 1911, ii, 368).—The formulæ of Mendeléeff and of Thorpe and Rücker (*Trans.*, 1884, 45, 126) are only approximations, and when several values of  $a$  are determined for the same liquid, the differences found are greater than the errors of observation. The absolute boiling point  $T_e$ , may be substituted for the critical temperature,  $T_c$ , and the relation,  $V_1/V_2 = D_2/D_1 = (a'T_e - T_2)/(a'T_e - T_1)$ , in which  $a'$  is a new constant = 3.09, gives good results over a wide range of temperature.

The formula of Avenarius expresses a more exact relation. The three constants in the equation  $\log V = c - d \log (A - t)$  may be found as shown by Mallet and Friderich (*Arch. Sci. phys. nat.*, 1902, 14, 50), and good results are obtained for temperature intervals of from  $150^\circ$  to  $300^\circ$ . The expansion coefficient may be found by the relation  $dv/dt = (d \log e)/(A - t)$ , and the results thus obtained are in close agreement with experiment.

The constant  $A$  is very nearly the observed critical temperature, exceeding it by  $5^\circ$  or  $10^\circ$ ;  $c$  represents the critical density, and  $c/d = 3.78$ . C. H. D.

**Energy Relationships in Vaporisation and Electrolytic Dissociation.** SVANTE ARRHENIUS (*Medd. K. Vetensk. Nobelinst.*, 1911, 2, No. 8, 1—34).—From a thermodynamic consideration of the changes in free and total energy which are involved in the process of vaporisation, it is found that the change in free energy,  $A$ , can be represented by the formula  $A = A_0 + BT + CT^2$ , in which  $A_0$  represents the molecular heat of vaporisation at absolute zero, and  $B$  and  $C$  are constants. The change in total energy,  $U$ , can similarly be expressed by  $U = A_0 - CT^2$ . In the case of water, the constants involved give rise to the special equation  $A = -11394 + 48.74T - 0.00927T^2$ , and it is shown that the values of  $A$  calculated from this are in excellent

agreement with the experimental data between  $-20^{\circ}$  and  $+250^{\circ}$ . At higher temperatures, deviations occur which are ascribed to wide divergences from the simple gas laws at the high pressures corresponding with these temperatures. A similar agreement between theory and experiment is exhibited in the case of *n*-hexane and acetic acid.

The constants  $A_0$ ,  $B$ , and  $C$  have been calculated for a large number of substances. It is further shown that the free energy changes associated with dissociation processes (electrolytic and non-electrolytic) can be represented by formulæ of the same type, and for these the corresponding constants are also tabulated. In all cases, the second term,  $BT$ , has a very important influence on the magnitude of the free energy change, and on the other hand, the formula for  $U$  indicates that  $dU/dT$  becomes very small in the neighbourhood of absolute zero.

A detailed examination of the values of  $U/T$  shows that Trouton's rule does not hold at all accurately in the case of a large number of liquids, and that it may lead to erroneous conclusions when applied to determine whether liquids are associated or not. H. M. D.

**Vapour Pressure of Nitrogen Peroxide.** F. E. C. SCHEFFER and J. P. TREUB (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 536—549).—Whilst liquids give the same vapour pressure by either the statical or the dynamical method, solids which dissociate on passing into vapour give different results by the two methods (Ramsay and Young, *Abstr.*, 1886, ii, 410, 965). The results obtained for nitrogen peroxide by Guye and Drouguine (*Abstr.*, 1910, ii, 1056) by a statical method differ considerably, however, from those found dynamically by Ramsay and Young, and the vapour-pressure curve also shows a point of inflexion, a character hitherto unknown.

In order to avoid contact with mercury, a glass manometer of the form devised by Jackson (*Trans.*, 1911, 99, 1066) is used. The statical measurements coincide almost exactly with those of Ramsay and Young, and the vapour-pressure curve is of normal form without inflexion. The under-cooled liquid has been compared with the solid, and the intersection of the two curves observed. The boiling point is found to be  $21.2^{\circ}$ , and the melting point  $-10.8^{\circ}$ . An approximate estimation of the degree of dissociation is also made. C. H. D.

**Composition and Vapour Pressure of Solutions.** V. Change of the Partial Pressures of Vapours of Solutions and Mechanical Mixtures with Temperature. M. S. VREVSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1446—1457. Compare *Abstr.*, 1911, ii, 256).—When the two liquids do not mix, the change of the ratio of their partial pressures with change of temperature is expressed by:

$$\frac{dy}{dt} \cdot \frac{1}{y} = \frac{dP_1}{dt} \cdot \frac{1}{P_1} - \frac{dP_2}{dt} \cdot \frac{1}{P_2},$$

where  $P_1$  and  $P_2$  are the vapour pressures of the two liquids at temperature  $t$  and  $y = p_1/p_2$ , that is, the ratio between the partial pressures. The same expression holds for the case when the liquids

mix, assuming that the addition of the second liquid to the first lowers the vapour pressure of the latter in the solution according to Raoult's law,  $p_1 = P_1 x$ ,  $x$  being the number of gram-mols. of the first liquid per 1 gram-mol. of the mixture.

When the formation of the solution of the two liquids is accompanied by a heat effect, the change in composition of the vapour with temperature is expressed by :

$$\frac{dy}{dt} \cdot \frac{1}{y} = \frac{dP_1}{dt} \cdot \frac{1}{P_1} - \frac{dP_2}{dt} \cdot \frac{1}{P_2} + \frac{dQ}{dx} \cdot \frac{1}{RT^2},$$

where  $Q$  is the heat-effect produced on mixing  $x$  gram-mols. of the first liquid with  $(1-x)$  gram-mols. of the second, and  $R$  is the gas constant in heat units; hence, in the general case, change of the equilibrium between vapour and solution is the result of the combined action of two factors, one of them physico-mechanical and the other physico-chemical. With solutions formed with either development or absorption of heat, these two factors act in the same direction in one region of concentration, and in opposite directions in another region, the limit between the two regions being the solution for which the heat of mixing is a maximum or minimum, that is,  $dQ/dx = 0$ .

In the first two cases considered above, if, between  $t$  and  $t'$ , the rate of increase of the vapour pressure of the first liquid does not change in the solution, the same will hold for the second liquid. But, in the general case, where a heat-effect is observed on mixing and the temperature-coefficient of the partial pressure of the vapour is not equal to the temperature-coefficient of the vapour pressure of the liquid in the free state, the change of composition of the vapour with temperature is expressed by :

$$\frac{y_1}{y} = \left( \frac{P_1^1}{P_1^2} : \frac{P_2^1}{P_2^2} \right) e^{\int_{t_1}^{t_2} \frac{dQ}{dx} \cdot \frac{dt}{RT^2}}.$$

Various pairs of liquids have been studied, the results confirming qualitatively the theoretical deductions. T. H. P.

**The Distillation of Difficult Boiling Substances.** HUGO DUBOVITZ (*Seifensied. Zeit.*, 1911, 38, 529—530).—An enquiry into the distillation of mixtures under varying pressures with superheated steam; the author suggests the following formula as a means of estimating the vapour tension of a contained substance of high boiling point:  $(M_2 P_2)/(M_1 P_1) = a$ , where  $M_1$  and  $P_1$  are the molecular weight and vapour pressure respectively of the substance of lower, and  $M_2$  and  $P_2$  the corresponding data for that of the higher, boiling point.

F. M. G. M.

**Heat of Formation of Titanium Dioxide.** WILLIAM G. MIXTER (*Amer. J. Sci.*, 1912, [iv], 33, 45—48. Compare Abstr., 1909, ii, 644).—The heat of formation of titanium dioxide has been redetermined by combustion of the finely divided metal in oxygen. The most trustworthy observations give  $\text{Ti} + \text{O}_2 = \text{TiO}_2$  (crystalline) + 218.4 Cal. This is about 1.1% higher than the value obtained previously by the sodium peroxide method. Both values are in complete disagreement

with that given by Weiss and Kaiser (Abstr., 1910, ii, 302), which is only 97.77 cal. H. M. D.

**Use of Dewar's Vessels in Calorimetry.** ALEXIS J. BOGORODSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1262—1268).—Dewar flasks, which have been used recently by Mathews and Germann (Abstr., 1911, ii, 187) and by Luginin and Dupont (Abstr., 1911, ii, 369) as calorimeters, were employed by the author for this purpose as long ago as 1901 (*Protokol Phil. Soc. Kazan Univ.*, 1901, No. 197). The values then obtained for the heats of solution of  $\text{KClO}_3$  and  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  were  $-10051$  ( $-10040$ ) and  $-26008$  ( $-25859$ ) cals. respectively, the numbers in brackets being those given by Thomsen. The apparatus used is described, and the results of further measurements made with it given.

For  $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$  the molecular heat of solution gave the values 22836—22925 cals., the mean being 22880 (22830). T. H. P.

**Heats of Solution of Mono- and Di-hydrated Lithium Chlorides.** ALEXIS J. BOGORODSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1268—1274).—The experiments here described were carried out by means of the apparatus mentioned in the preceding abstract.

The mean of the values obtained for the molecular heat of solution of  $\text{LiCl} \cdot \text{H}_2\text{O}$  at the mean temperature  $20.3^\circ$  is  $+4121$  cals., the value of  $\phi$  (Thomsen), the change of the heat of solution with temperature, being  $29.02$  cals. per degree. For  $\text{LiCl} \cdot 2\text{H}_2\text{O}$ , the mean value of the molecular heat of solution is  $+981$  cals. at the mean temperature  $22.2^\circ$ ,  $\phi$  having the value  $12.3$ . From these results, together with the value  $8444$  given by Thomsen for the heat of solution of  $\text{LiCl}$  at  $20.7^\circ$ , the following equations are deduced:  $\text{LiCl} + \text{H}_2\text{O} = \text{LiCl} \cdot \text{H}_2\text{O} + 4323$  cals.;  $\text{LiCl} \cdot \text{H}_2\text{O} + \text{H}_2\text{O} = \text{LiCl} \cdot 2\text{H}_2\text{O} + 3162$  cals. On account of the low transition temperature ( $-15^\circ$ ) of the trihydrate, the heats of formation and solution of this hydrate were not investigated. The existence of such a hydrate, if this were unknown, would be indicated by the positive sign of the heat of solution of the dihydrate.

The proposition advanced by Thomsen, to the effect that the heat of solution of haloid compounds in water is negative when they are completely saturated with water possesses no general significance.

T. H. P.

**A New Method of Determining Vapour Densities. IX.** PHILIP BLACKMAN (*J. Physical Chem.*, 1911, 15, 869—870. Compare Abstr., 1908, ii, 157).—The improved apparatus consists of a graduated tube closed by a ground-in stopper carrying a capillary U-tube. The tube is filled with mercury, and, after the weighed amount of liquid has been introduced, is closed and inverted. When the liquid has been vapourised, its volume and pressure can be read off. R. J. C.

**Simple Method for Vapour Density Determinations. XI. The Dehydration of Copper Sulphate Pentahydrate.** PHILIP BLACKMAN (*J. Physical Chem.*, 1911, 15, 871—873. Compare Abstr., 1909, ii, 643).—Experiments made with the author's apparatus

indicate that the dehydration of copper sulphate takes place progressively as a function of temperature and pressure, there being no sudden increase in stability as each molecule of water is removed from the hydrate. The dehydration was not carried as far as the monohydrate stage.

R. J. C.

**Dilatometric Researches. New Form of Dilatometer for Mixtures of Liquids.** FILIPPO BOTTAZZI and GIUSEPPE BUGLIA (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 623—627).—The authors describe a dilatometer intended for measuring the change of volume occasioned by the mixing of two liquids. The mixture of the two liquids is brought about by the removal of the partition separating them, the removal being due to the fusion of the wax which holds it in position. In its original form, the apparatus consists of a stomach-shaped glass bulb, which has two openings at the ends of the upper surface. To one of these a graduated capillary is fused, whilst the other aperture consists of a wide tubulure, ground on the inside. Into the tubulure fits a glass tube, which is open at the bottom and is closed at the top by a glass stopper. This tube serves to hold one of the liquids, whilst the main bulb contains the other. In filling the apparatus, a suitable quantity of one liquid is placed in the bulb. The tube just mentioned is closed at the bottom by means of a circular glass plate, attached to it by means of a little wax of suitable melting point. To facilitate the introduction of the stopper into this tube, the glass plate is provided with a small hole, which is kept closed with the finger during the filling, and is finally sealed with a spot of wax. The tube thus constructed is filled with the second liquid, a glass marble is introduced into it, the stopper is inserted, and the hole in the glass plate sealed as described. The whole is then inserted in the tubulure of the bulb as though it were a stopper. All the joints are well covered, externally, with wax of high melting point, and the apparatus is immersed in a thermostat. When a sufficient temperature is reached, the glass plate may be shaken off, and the change of volume due to the mixing of the liquids may then be observed.

A simplified form of the apparatus differs only in being cylindrical, and in having the graduated capillary attached to the top of the tube instead of a stopper, so that one of the ground surfaces is dispensed with. This form is recommended.

R. V. S.

**Dilatometric Researches. II. Preliminary Results Regarding Non-colloidal Solutions.** FILIPPO BOTTAZZI and GIUSEPPE BUGLIA (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 627—633. Compare preceding abstract).—The paper gives the changes of volume observed on mixing solutions of sodium chloride, sodium hydroxide, sulphuric acid, and hydrochloric acid with pure water. The changes in volume were always the same for the same liquids, and calculations in the case of sodium chloride solutions showed that the observed changes agreed with those calculated from the specific gravities before and after mixing.

R. V. S.

**Law of Molecular Attraction.** DAN TYRER (*Phil. Mag.*, 1912, [vi], 23, 101—113. Compare Kleeman, *Abstr.*, 1910, ii, 22, 492, 600, 932; 1911, ii, 34, 97).—According to Kleeman, the magnitude of the force of molecular attraction is dependent on the distance of separation of the molecules and on the temperature, but the author shows that, so far as latent heat considerations are concerned, it is unnecessary to assume that the law of attraction includes a temperature function. From the data for the specific heat of various substances at constant volume, it is found that the specific heat is considerably greater in the liquid state as compared with the gaseous, and from this the conclusion is drawn, that the change of energy which accompanies the isothermal expansion of a liquid is not entirely due to a change in the potential energy of molecular attraction, but that a liberation of intra-molecular energy must be involved. If it is assumed that the law of attraction can be represented by  $K^2/S^n$ , in which  $K^2$  is constant for a given pair of molecules, and  $S$  is the distance between them, then the author's reasoning leads to the result that  $n$  cannot be less than 5, and is probably greater than 7. It is, however, impossible to determine completely the law of attraction from the consideration of the energy changes which accompany the change of volume of a liquid or a gas. H. M. D.

**Internal, Molecular, or Intrinsic Pressure.** A Survey of the Various Expressions Proposed for its Determination WILLIAM C. MCC. LEWIS (*Trans. Faraday Soc.*, 1911, 7, 94—115).—The expressions proposed by various authors for the internal pressure are reviewed, and the assumptions underlying them criticised. It is shown that all involve one or other of the assumptions, (1) that the pressure  $K$  is independent of temperature, (2) that  $K$  may be represented by  $a/v_0^2$  in van der Waals' equation, and that  $a$  is independent of temperature, that is, that  $K/\delta^2$  is independent of temperature, where  $\delta$  is the density. Neither of these assumptions is justifiable, although the second is nearly true. The general thermodynamic equation does not allow  $K$  to be calculated, without some further assumption. Assuming that the fractional change of  $K$  per degree is the same as that of the latent heat per unit volume,  $L_i$  per degree, the relation is found:  $K = L_i/1 - (T'/L_i)(\delta L_i/\delta T)$ , by the use of which probable values are obtained for ether, ethyl alcohol, and carbon disulphide. C. H. D.

**Simplest Example of the Diagram of Hardness** [System KBr—KF]. NICOLAI S. KURNAKOFF and I. B. VRSHESNEVSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1392—1397).—The existence of eutectics for the melting curves of binary mixtures of the type MF—MX (where M = K or Na, and X = Cl, Br or I) was shown by the work of Ruff and Plato (*Abstr.*, 1903, ii, 588).

In order to obtain information concerning the composition of the solid phase separating on solidification of mixtures of potassium bromide and fluoride, the authors have investigated the cooling curve by means of the registering pyrometer previously described (*Abstr.*, 1905, ii, 10). The melting-point curve consists of two branches meeting in an eutectic point corresponding with the temperature 580°

and the composition, 40% mol. KF. The addition of as little as 3% of one salt to the other causes a marked eutectic arrest in the cooling curve, this indicating that solid solutions are either absent or of very low concentration.

In agreement with this conclusion are the results of the hardness measurements. It was found that potassium bromide and fluoride, like other halogen salts of the alkali metals, are plastic substances, so that the measurement of hardness was carried out by determining the pressure required to produce flow; it has been shown by Kurnakoff and Schemtschuschny (Abstr., 1909, ii, 855) that this method gives results in correspondence with those yielded by Brinell's ball test. Measurements of the pressures required to produce flow with potassium chloride, bromide, iodide, and fluoride give values diminishing with the atomic weight of the halogen. Similar measurement with mixtures of potassium bromide and fluoride give values lying almost exactly on a straight line, joining those for the separate salts, this curve exhibiting no peculiarity at a position corresponding with the eutectic point.

These results show that, when crystallised from the fused condition, the system KBr-KF yields only superposed mixtures of the two salts.

T. H. P.

**Fusion and Pressure of Flow of Mixtures of Isomorphous Salts.** I. B. VRSHESNEVSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1364—1392).—The investigations here described were made with the view of ascertaining how the hardness and the pressure necessary to produce flow (compare Kurnakoff and Schemtschuschny, Abstr., 1909, ii, 855) with salts vary with respect to their capacity of forming solid solutions, this being studied thermally.

The melting-point diagram of the system KCNS-NaCNS consists of two branches meeting in an eutectic point corresponding with 30% mol. NaCNS. An arrest occurs at 143°, owing to the conversion of the  $\alpha$ -modification of potassium thiocyanate—stable above 143°—into the  $\beta$ -form, this change being accompanied by considerable development of heat (compare Gossner, *Zeitsch. Kryst. Min.*, 1904, 38, 136). A number of inferior arrests occur between 10 and 40% mol. NaCNS, the most probable cause of these being the formation of a new solid phase, NaCNS,3KCNS. Calorimetric investigation of the heat of solution of these fused salts shows the maximum absorption of heat to take place with the composition NaCNS,3KCNS.

On solidification of their fused mixtures, potassium and ammonium thiocyanates form an uninterrupted series of solid solutions. Owing to the polymorphism of the ammonium salt, the cooling curve exhibits four arrests: (1) at 146°, corresponding with the conversion of the liquid to the  $\alpha$ -solid phase; (2) at 120°, indicating the change of the  $\alpha$ - into the  $\beta$ -form; (3) at 100°, an eutectic point, and (4) at 90°, this being accompanied by a marked heat-effect and corresponding with the transformation of the  $\beta$ - into the  $\gamma$ -modification (compare Gossner, *loc. cit.*). At high temperatures, these potassium and ammonium salts give a continuous series of isomorphous mixtures. In order to explain the origin of the two middle arrests, the cooling curves of mixtures of

ammonium thiocyanate with the isomeric thiocarbamide were investigated. The cooling curve of thiocarbamide also exhibits an arrest at  $100^{\circ}$ , this being similar in character to that occurring at the same temperature with mixtures of potassium and ammonium thiocyanates. The melting point diagram of ammonium thiocyanate and thiocarbamide is characterised by a eutectic point at  $100^{\circ}$  and by two other arrests at  $120^{\circ}$  and  $90^{\circ}$ , so that the salt undoubtedly exists in the three modifications referred to above.

Potassium and rubidium thiocyanates form an uninterrupted series of solid solutions, the system showing a minimum freezing point and being of Roozeboom's third type (Abstr., 1900, ii, 132).

The system KCl-KI, on passing from the fused to the solid condition, gives a continuous series of isomorphous mixtures, this being confirmed by calorimetric investigation. At the concentrations 10 and 70% mol. of the iodide, the cooling curve shows arrests indicating the breaking-down of the solid solutions, the curves characterising this process having the nature of waves.

The systems KCl-KBr and KBr-KI give continuous melting-point curves each exhibiting a minimum, which lies at  $716^{\circ}$  (60% mol. KBr) and  $589^{\circ}$  (50% mol. KI) respectively. In either case, the cooling curve shows only an arrest corresponding with the conversion of the liquid into the solid phase; hence when the fused mixtures are cooled, even to low temperatures, no decomposition of the solid solutions occurs. Calorimetric measurements show, however, that such decomposition does take place with lapse of time.

It is found that the pressure necessary to produce flow in the pure potassium halogen salts varies considerably with the rate at which they have been cooled. The rapid cooling referred to in the following table was effected by pouring the fused salt into a cold platinum dish and medium cooling by means of a platinum dish previously heated; for slow cooling, the platinum crucible containing the substance is placed in a wider clay crucible situate in a Fletcher furnace surrounded by asbestos cloth. The pressures are given in kilos. per sq. mm.:

	Rapid cooling. $P_1$ .	Medium cooling. $P_2$ .	Slow cooling. $P_3$ .	$P_3 : P_1$ .
KCl.....	28	35	50.5	1.8
KBr.....	36	38	40.5	1.13
KI .....	20.5	24	31.0	1.5

With fused mixtures of salts, the effect of variation of the rate of cooling is more complex; with KCl-KI, for example, this effect is opposite in direction to that obtained with the pure salts. In the following experiments, "rapid" cooling was always employed.

The maximum pressure required to cause flow corresponds, in the case of KCl-KBr, with 40% mol. KBr, and, in that of KBr-KI, with 60% mol. KBr. In both systems, this pressure is more than double that required by the constituent salt which flows the less readily. After the cooled masses have been kept at the ordinary temperature for five weeks, the pressures required are considerably less than the original ones. It is hence evident that, as the process of decomposi-

tion of the solid solutions approaches its final state, the curve of pressures approaches the straight line joining the pressures for the two constituent salts.

With KCl-KI, the pressure of flow curve shows two maxima and a minimum. The stability and slight amount of decomposition of the solid solutions of low concentrations condition a very rapid rise in the pressure in passing from 0 to 10% mol. KI and from 100 to 90% mol. KI. When the concentration of the solid solutions is increased, continuous decomposition of these solutions occurs until a state of mechanical mixture is approached, this corresponding with a rapid fall in the pressure of flow. It is remarkable that the minimum pressure, which corresponds with about 50% mol., is lower than the pressure for either of the two salts.

With KCNS-NH<sub>4</sub>CNS, the pressure of flow curve consists of two branches: (1) that from 0 to 20% mol. KCNS, being almost a straight line, which corresponds with mechanical mixtures of  $\gamma$ -NH<sub>4</sub>CNS with a definite concentration of the  $\beta$ -solid solution (20% mol. KCNS); (2) that from 20 to 100% mol. KCNS, showing a maximum at about 70% mol. KCNS and corresponding with solid solutions of the  $\beta$ -modifications of the two components.

With KCNS-RbCNS, the curve shows a maximum at 20% mol. KCNS, which greatly exceeds the pressure for either component.

Owing to the occurrence of the new solid phase mentioned above, the pressure diagram of the system KCNS-NaCNS is complicated by the presence of a maximum at 20% mol. NaCNS. Further increase of the latter results in the fall of the pressure to a minimum (intermediate to the values for the separate constituents) at 40% mol. NaCNS.

T. H. P.

**Chief Law of Adsorption Phenomena.** SVANTE ARRHENIUS (*Medd. K. Vetensk. Nobelinst.*, 1911, 2, No. 7, 1-44).—The recent work of Homfray (*Abstr.*, 1910, ii, 771, 1041) and Titoff (*ibid.*, ii, 1041) on the adsorption of gases by charcoal, and that of G. C. Schmidt (*ibid.*, ii, 1041) on the adsorption of acetic acid from its aqueous solutions by charcoal, indicates that the ordinary exponential formula,  $a = kc^n$ , cannot be valid between wide limits. The formula is devoid of theoretical foundation, and should be regarded, at most, as an empirical formula, the applicability of which is limited to a comparatively narrow range of concentrations. By taking into account the fact that the quantity of adsorbed substance reaches a maximum value, the adsorption is supposed to be determined by the equation,  $k \cdot dx/dc = (s - x)/x$ , which, on integration, gives  $\log_{10} s/(s - x) - 0.4343 \cdot x/s = 1/k \cdot c$ , where  $x$  represents the quantity of adsorbed substance per gram of charcoal,  $s$  the maximum value of  $x$ ,  $c$  the pressure of the gas or the osmotic pressure of the dissolved substance, and  $k$  a constant. For a given kind of charcoal, the values of  $s$  (expressed in gram-molecules) are of the same order of magnitude for different substances.

It is shown that the above formula affords a satisfactory representation of the adsorption of gases and of acetic acid by charcoal within wide limits of concentration. At high temperatures and small concentrations, deviations are found between the calculated and observed

results, which are ascribed to the variation in the heat of adsorption with the quantity of substance adsorbed.

From the fact that the adsorption of a gas increases with increase in the attraction between the gas molecules, the author infers that the phenomenon of adsorption is essentially determined by the attractive forces between the molecules of the adsorbed substance. In support of this view it is shown that the changes in volume which occur when a liquid is compressed can be represented by the above adsorption formula. In this case,  $\alpha$  represents the density of the liquid,  $c$  the pressure (internal plus external), and  $s$  the maximum density. By reference to the compressibility data for ethyl ether and ethyl alcohol, it is shown that experimental observations can be adequately represented by this formula.

In comparison with the exponential formula which contains two arbitrary constants, the author points out that this formula contains only one, for the quantity  $s$  is in every case directly determinable from experimental observations.

H. M. D.

**Absorption of Gases by Porous Materials.** JACQUES DUCLAUX (*Compt. rend.*, 1911, 153, 1217—1220. Compare Abstr., 1911, ii, 479).—An attempt to calculate the absorption coefficient of carbon for carbon dioxide on the basis of the hypothesis put forward in an earlier communication. Comparison of the result with the known value suggests that local differences in temperature have a greater effect on absorption than local differences in pressure within the minute cavities of which the porous material is composed.

W. O. W.

**Adsorption in Solution. II. Dualistic Nature of Adsorption Phenomena.** GEORG VON GEORGIEVICS (*Monatsh.*, 1911, 32, 1075—1087. Compare Georgievics and Pollak, Abstr., 1911, ii, 1070).—The adsorption of acids from solution by wool also includes the dissolution of acid in the wool analogous to that shown in the adsorption of gases by charcoal. Once equilibrium between acid and wool is attained, there is no slow further retention of acid.

The velocity with which equilibrium is attained depends, not only on the nature of the adsorbed and adsorbing substances, but also on the concentration of the solutions employed. Until a concentration of roughly 0.05 gram of acid per 250 c.c., hydrochloric and sulphuric acids are dissolved by wool; in more concentrated solutions the phenomenon is one of adsorption, it being impossible to say whether there is any diffusion into the interior of the thread. Sulphuric acid is somewhat more easily soluble in wool than hydrochloric acid, the ratio being approximately 9:7. The statement previously made that sulphuric acid is adsorbed more than hydrochloric acid in dilute solution and less in concentrated solution is now explained as owing to the excess of solubility of the sulphuric acid: actually hydrochloric acid is the more adsorbed.

The speed with which a substance is adsorbed is no criterion of adsorption, as it is shown that from concentrated solutions very rapid diffusion into the inside of the solid material takes place.

The facts mentioned afford an explanation of some anomalies in the

results obtained on dyeing silk with picric acid (Georgievics, Abstr., 1911, i, 537). In dilute solutions containing 0.01 gram of picric acid per 100 c.c. and less, the retention of picric acid is due to solution; in more concentrated solutions of picric acid, the retention is due to adsorption. In concentrations of 0.01 to 0.02 gram per 100 c.c., there is a rapid increase of the retention of acid which is regarded as due to chemical processes. Picric acid and silk afford a case of retention due to solution, chemical action, and adsorption in turn.

Similarly, solution of the dye in the fabric takes place in the case of dyeing in dilute solution; there is some chemical action between dye and fabric, but in stronger dye solutions the retention is chiefly caused by adsorption.

E. F. A.

**The Nature of Solvates and the Relationships between Adsorption and Dissociation.** KURT GEBHARD (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 263—265. Compare Ostwald, Abstr., 1911, ii, 1068).—The relationships between adsorption compounds and solvates are discussed from the point of view of a theory of partial valencies, with special reference to the explanation of the formation of complex compounds between dyes and fibres.

H. M. D.

**Mechanism of Osmosis.** EUGÈNE FOUARD (*Compt. rend.*, 1911, 153, 1152—1155. Compare Girard, Abstr., 1909, ii, 537; 1911, ii, 861).—A polemical paper against Girard and Henri, drawing attention to the importance of absorption by the membrane in the mechanism of osmosis. Osmotic pressure can only be measured when this absorption is complete, and when equilibrium has been established, the osmotic effect is independent of the nature of the membrane. Objection is raised against De Vries' definition of isotonic solutions, on the ground that the protoplasm of a vegetable cell maintaining constant volume in a solution, is in osmotic equilibrium, not with the external solution, but with a liquid between the two cell membranes, this liquid differing in composition from the first owing to the absorption of dissolved substance by the exterior envelope.

W. O. W.

**Behaviour of Edges and Corners in Certain Diffusion Experiments.** RAPHAEL E. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 296—298).—If irregularly shaped pieces of jelly, obtained by the solidification of a 10% solution of gelatin containing a small quantity of silver nitrate, are placed in a saturated solution of potassium dichromate, it is found that silver chromate is preferentially formed on those parts of the surface which are approximately plane. The portions of the surface in the neighbourhood of hollows and protuberances are unaffected by the surrounding reagent. The importance of this observation in connexion with certain processes employed by histologists is referred to.

H. M. D.

**Diffusion of Oxygen and Carbon Dioxide in Water.** TOR CARLSON (*Medd. K. Vetensk. Nobelinst.*, 1911, 2, No. 6, 1—8).—The coefficients of diffusion of carbon dioxide and oxygen in water at 18.2°

have been found to be 1.479 and 1.720 respectively. These values, when corrected for difference in temperature, are in fairly good agreement with the coefficients determined at 16° by Stefan and Hüfner. The ratio of the coefficients is 1.166, which approximates closely to that calculated from measurements of the rates of dissolution of the gases. The rates of diffusion are very nearly in the inverse ratio of the square-roots of the densities, which requires 1.173 instead of the observed ratio of 1.166.

H. M. D.

**Velocity of Diffusion and Size of the Particles in Disperse Systems.** II. THE SVEDBERG (*Arkiv. Kem. Min. Geol.*, 1911, 4, No. 12, 1—7).—The author has carried out further experiments to decide between the Sutherland-Einstein and the Smoluchowski formulæ for the rate of diffusion of a particle, using a colloidal gold solution for the purposes of experiment. The velocity of diffusion of the gold particles was measured by means of the apparatus used by Svedberg and Andreen-Svedberg (*Abstr.*, 1911, ii, 375), the concentrations being determined by measuring the extinction-coefficients of the solutions. From the velocities of diffusion so determined, the radii of the diffusing particles were then calculated by means of the above-mentioned formulæ, and found to be  $1.25\mu\mu$  and  $2.97\mu\mu$  respectively. The size of the particles was then determined by Zsigmondy's "nucleus method" (*Keimmethode*), and found to be  $1.33\mu\mu$ , which agrees with the first of the above two values. The Sutherland-Einstein formula may, therefore, be taken as the correct one.

T. S. P.

**The Alleged Colour of the Ions.** GAETANO MAGNANINI (*Gazzetta*, 1911, 41, ii, 425—429).—The author re-asserts his views on this subject (see *Abstr.*, 1893, ii, 570; 1894, ii, 226; 1897, ii, 14).

R. V. S.

**Systematics of the Aggregated States of Matter.** P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1477—1502).—Principally a discussion of the author's orientation or vectorial theory of matter (compare *Abstr.*, 1910, ii, 1048, and elsewhere).

T. H. P.

**The Dependence of the Brown-Zsigmondy Movement on Temperature.** M. SEDDIG (*Zeitsch. anorg. Chem.*, 1912, 73, 360—384).—If the molecular explanation of the Brownian movement is correct, the displacements should be proportional to the square-root of the absolute temperature, and inversely proportional to the square-root of the internal friction of the liquid used (Einstein, *Ann. Physik*, 1905, [iv], 17, 549). The values hitherto obtained from visual observation differ widely from theory, owing to errors of measurement and to the relatively long time of observation, which allows currents in the liquid to form. An arrangement for preparing kinematographic records at a magnification of 3000 is described, but quantitative measurements have not been made satisfactorily.

The best results are obtained by using an ultra-microscope in which the rays are focussed in the object by an oblique, concave mirror, and are prevented from reaching the eye-piece by a small, lateral stop.

Two successive short exposures are made by means of a special shutter, and the distance separating pairs of images is measured. The stage is electrically heated to a constant temperature, which is measured by a thermo-couple, placed in a layer of paraffin immediately below the thin glass carrying the liquid under examination. The suspensions used are cinnabar and freshly-prepared lamp black, both of which give good contrasts and are uniform in size.

As the displacements thus observed are only projections of the actual displacements on a horizontal plane, the absolute values are only found with difficulty, but relative values for a range of temperature from  $5.5^{\circ}$  to  $90^{\circ}$  are obtained, and show divergences which do not differ from those calculated by Einstein's formula by more than 6%, being always too high, probably owing to absorption of heat from the source of light during the short exposure. C. H. D.

**The Brownian Movement of Particles in Colloidal Solutions.** III. THE SVEDBERG and KATSUJI INOUE (*Arkiv. Kem. Min. Geol.*, 1911, 4, No. 19, 1—20).—The method of measuring the Brownian motion of colloidal particles, referred to in a previous paper (compare Abstr., 1910, ii, 772, 1047), is now described in detail. It consists in tracing the movements of individual particles over a considerable period of time (five to twenty seconds), and registering the positions occupied at successive times during such periods on a moving photographic plate. From the records obtained for a number of particles, the displacements which occur as the result of the Brownian motion can be calculated. Experiments made with gold hydrosols, prepared by direct reduction of gold chloride solutions with hydrazine, show that the movements are in agreement with Einstein's molecular kinetic formula. For Avogadro's constant, the data obtained with such hydrosols, consisting of small sized particles, give the value  $6.2 \times 10^{23}$ . H. M. D.

**Determination of the Dimensional Distribution of the Colloidal Particles in a Disperse System.** THE SVEDBERG and KNUD ESTRUP, (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 259—261).—The degree of uniformity in the size of the colloidal particles in various dispersoid systems has been investigated by microscopic observations of the changes which occur in the spacial distribution of the particles when these are allowed to fall under the influence of gravity. Experiments were made with aqueous suspensions of mercury and gamboge, with the milk juice of *Chelidonium laciniatum*, cow's milk, cream from cow's milk, and cocoanut milk. Curves are plotted which show the numerical distribution of the particles according to their dimensions. In this way curves are obtained which are more or less symmetrical and convex to the dimensional axis, and the closeness with which the symmetrical branches of the curve approximate affords a measure of the degree of uniformity of the size of the particles. H. M. D.

**Coagulation of Prussian-Blue.** NICOLA PAPPADÀ (*Gazzetta*, 1911, 41, ii, 454—460. Compare Pappadà and Sadowski, Abstr., 1910, ii, 593).—Ferric ferrocyanide differs from silicic acid in that

its coagulation is instantaneous, so that the effect of different coagulating agents has to be measured by comparing the minimum quantities of them required to produce coagulation. The results obtained are identical with those for silicic acid. Undissociated organic substances do not cause coagulation. Coagulation is produced by electrolytes, and the colloid has a negative charge. The coagulating action of the salts of univalent cations increases with increase in the atomic weight of the cation, whilst a comparison of univalent, bivalent, and trivalent cations shows that the coagulating power increases with the electrical charge of the cation. R. V. S.

**Stability of Emulsions of Water in Hydrocarbon Oils.** ERICH GROSCHUFF (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 257—259).—Observations relative to the stability of emulsions of water in benzene, petroleum (D 0.792), machine oil (D 0.864), and paraffin oil (D 0.882) have shown that the stability is not determined by the difference in density between the disperse phase and the dispersive medium, or by the solubility of water in the hydrocarbon. It is more probable that the stability is to a large extent dependent on the surface tension at the surface of separation of the two phases, increasing as the surface tension diminishes. The water emulsions examined increase in stability in the order: benzene, petroleum, paraffin oil, machine oil, and the pronounced difference in the stability of the two last emulsions is attributed to the presence of colloidal impurities in the machine oil. H. M. D.

**Plant Colloids. I. The Solution Swelling of Starch in Presence of Crystalloids.** MAX SAMEC (*Koll. Chem. Beihefte*, 1911, 3, 123—160).—Measurements have been made of the temperatures at which starch granules lose their characteristic form by a process of swelling, in which highly viscous globules of a starch solution are formed, when the starch is heated in contact with water or aqueous solutions. An optical method is described, by means of which the accompanying change in the transparency and refractive index of the granules can be employed for the accurate determination of this temperature. For a given solution, the separate observations agree to about 0.2—0.4°. In all experiments the same sample of starch was used, the swelling solution temperature of this being 59.7°.

This temperature is altered in presence of salts, acids, bases, and non-electrolytes, and the effect of these different substances is qualitatively the same as in the case of the swelling of gelatin. Whether the temperature is raised or lowered is essentially determined in the case of salts by the anion, the cation having a much smaller influence. At low concentrations, bases exhibit the largest effect in lowering the swelling temperature, and in accordance with this it is found that salts formed by a strong base and a weak acid have in general a depressant effect at moderate concentrations. In certain cases, such as chloral hydrate and carbamide, the influence of non-electrolytes on the swelling temperature is very considerable.

H. M. D.

**The Ultramicroscopic Structure of Jellies.** WILHELM BACHMANN (*Zeitsch. anorg. Chem.*, 1911, 73, 125—172).—The internal structure of organic jellies may be studied by means of the cardioid condenser, whilst the finer structure of silicic acid gels requires the ultramicroscope.

The process of gel-formation is the same in gelatin, agar-agar, and silicic acid gels. The amplitude of the movements of the ultramicroscopic particles diminishes, and the size of the particles increases during the ageing of the gel. The process resembles that of the separation of two liquid phases from a solution (Lepkowski, *Abstr.*, 1911, ii, 95). Solutions containing less than 1% of gelatin, which do not set on cooling, show a gradual formation of separate flocculent particles or aggregates of submicrons. With increasing concentration, the structure becomes less distinct, and at last ultramicroscopically homogeneous, owing to the closeness of packing of the "jelly-elements." There is no evidence of a honeycomb or foam structure, and these structures, where previously observed, are due to diffraction effects in the microscope, and are much coarser than the submicronic structure. After treating with alcohol or chromic acid, a new, coarser structure is obtained, due to the formation of capillary cracks following on partial coagulation.

The clearest colloidal silica is obtained by dialysis with a collodion membrane. The mass, dried over sulphuric acid, polarises light when viewed in the ultramicroscope, indicating a very minute heterogeneity. The changes observed during the passage through the opaque stage, after immersion in benzene, correspond with those described by Zsigmondy (*Abstr.*, 1911, ii, 880). C. H. D.

**Application of the Kinetic Theory of Gases to Chemical Problems.** OTTO SACKUR (*Ann. Physik*, 1911, [iv], 36, 958—980).—A theoretical paper in which the relationship between the entropy of a system in a given condition and the "probability" of this condition is applied to the consideration of irreversible chemical changes. This leads to the conclusion that molecules of different substances, which are contained in an adiabatically closed space, will only react together if the reaction leads to an increase in the "probability" of the system. The condition of equilibrium is characterised by a maximum value of the "probability." H. M. D.

**Equilibrium in the Adsorption by Graham's Ferric Oxide Hydrosol.** P. MAFFIA (*Koll. Chem. Beihefte*, 1911, 3, 85—122).—The relationship between the quantity of chloride adsorbed by colloidal ferric hydroxide, prepared by Graham's method, and the chloride concentration of the aqueous solution in equilibrium with it has been investigated by two series of experiments, in one of which the colloidal solution was filtered through a membrane of collodion, and in the other was subjected to dialysis. The results obtained by each method indicate that the adsorbed chloride varies with the chloride concentration of the dispersive medium in accordance with the requirements of the exponential equation  $x/m = \beta \cdot c^{1/2}$ . H. M. D.

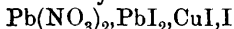
**Reduction of Mercuric Chloride by Phosphorous Acid and the Law of Mass Action.** JAMES B. GARNER (*Amer. Chem. J.*, 1911, 46, 648).—Garner, Foglesong, and Wilson's interpretation of the data obtained in their study of the reduction of mercurous chloride by phosphorous acid (Abstr., 1911, ii, 972) was erroneous. New calculations are being made, and will be presented in a subsequent communication.

E. G.

**A Special Case of Heterogeneous Equilibrium.** P. P. FEDOTÉEFF (*Zeitsch. anorg. Chem.*, 1911, 73, 173—199).—Following on the study of the cuprous iodide equilibrium (Abstr., 1911, ii, 42), the equilibrium  $\text{Cu}(\text{NO}_3)_2 + \text{PbI}_2 \rightleftharpoons \text{Pb}(\text{NO}_3)_2 + \text{CuI} + \text{I}$  has been investigated. Neither cuprous iodide nor iodine reacts with lead nitrate, but a mixture of the two readily forms lead iodide.

The solubility of lead iodide in pure water at 20° is 0.015 mol. per litre, and this is increased to 0.216 in a saturated solution of iodine, owing to the formation of the tetraiodide. In a solution saturated with copper and lead nitrates, the concentration of copper nitrate is almost the same as in pure water, but that of the lead nitrate is reduced from 1.523 to 0.052 mol. per litre.

When  $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CuI}$  are both present in the solid phase, an irreversible reaction sets in, with the formation of oxides of nitrogen and a basic salt. The system with solid phase



is realisable.

The value of  $K = \Sigma \text{Cu} / \Sigma \text{Pb}$  is not constant, but varies with the total concentration  $\Sigma(\text{NO}_3)_2$ , increasing with the dilution.

The equilibrium has also been studied electrolytically by means of the cell  $\text{Pt} \mid \text{solid PbI}_2, \text{I} \mid \text{Pb}(\text{NO}_3)_2 \text{ solution} \mid \text{KNO}_3 \text{ solution} \mid \text{Cu}(\text{NO}_3)_2 \text{ solution} \mid \text{solid CuI}, \text{I} \mid \text{Pt}$ , the solutions used being, in different experiments, 3N/2, N/1, and N/2 as regards  $\Sigma(\text{NO}_3)_2$ . The observed *E.M.F.* is in good agreement with the calculated. The results are applied to the theory of fractional precipitation, as in the addition of a soluble iodide to a mixture of lead and copper nitrates.

C. H. D.

**Colorimetric Investigation of Neutral Salt Action.** BOHDAN VON SZYSZKOWSKI (*Zeitsch. physikal. Chem.*, 1912, 78, 426—489. Compare Abstr., 1908, ii, 761).—The measurements were not made in a colorimeter, but with two glass cylinders, which for comparison were held in the hands and examined with a background of white paper some cms. away. Methyl-orange was exclusively used as indicator.

When solutions of acetic acid and of hydrochloric acid are compared, the former acid gives the deeper tint with methyl-orange up to a  $\text{H}^+$  ion concentration of  $1 \times 10^{-3}$  mols. per litre, but with higher concentrations hydrochloric acid gives the deeper colour. The tints produced by the two acids are not quite identical.

Neutral salts enter into reaction with methyl-orange, and render it more sensitive to  $\text{H}^+$  ions. This effect is mainly due to increased dissociation of the indicator as an acid, and partly to the formation

of complex compounds with the salts. That the latter is not the sole factor is shown by the observation that sodium chloride is much more effective than potassium chloride in intensifying the colour. The interpretation of the results is complicated by the fact that methyl-orange is an amphoteric electrolyte.

The effect of salts in deepening the colour of solutions containing acetic acid and methyl-orange is due partly to an increase in the dissociation of the acid and partly to increased sensitiveness of methyl-orange. The "neutral salt action" of sodium salts is greater than that of potassium salts, and that of bromides greater than that of chlorides. Non-electrolytes are practically without influence on the sensitiveness of methyl-orange. An estimate of the influence of potassium and sodium chlorides on the degree of dissociation of hydrochloric acid is given, but the results are only approximate.

Aqueous solutions of methyl-orange alter slowly in sensitiveness for some hours after preparation, but then remain constant for weeks. Solutions of methyl-orange containing acids and salts slowly undergo an irreversible chemical change, whereby the colour becomes much paler.

G. S.

**Hydrolysis of Esters of Substituted Fatty Acids.** WILLIAM A. DRUSHEL (*Amer. J. Sci.*, 1912, [iv], 33, 27—31).—From measurements of the rate of hydrolysis of ethyl acetate, chloroacetate, and cyanoacetate in presence of 0.1*N*-hydrochloric acid at 25°, it is found that the velocity coefficients are in the ratio 67.7, 45.8, 10.25. The rate of hydrolysis of the cyanoacetate is smaller than would be expected from the relative ionisation constants of the three acids. The relative amounts of hydrolysis for a given time interval were also compared in a series of experiments with 0.1 molar solutions of the three esters in the absence of acid. The data show that the chloroacetate and cyanoacetate are hydrolysed much more quickly than ethyl acetate, and the velocity for the chloroacetate is considerably greater than for the cyanoacetate, although cyanoacetic acid is a stronger acid than chloroacetic. It is suggested that the observations may be explained if it is assumed that the cyanoacetic acid is to some extent polymerised in its aqueous solutions.

H. M. D.

**Configuration of Ring Systems.** JACOB BÖESEKEN and A. VAN ROSSEM (*Rec. trav. chim.*, 1911, 30, 392—406. Compare Abstr., 1911, ii, 197).—Magnani (Abstr., 1890, 1357; 1891, 251) has studied the behaviour of boric acid in solution towards mannitol and dulcitol by determining the conductivities of solutions of various strengths of mixtures. The authors have extended the research to nine other alcohols and phenols.

Glycerol, pentaerythritol, catechol, and pyrogallol are found to increase the molecular conductivity of boric acid, whilst the other alcohols and phenols studied either have no action or else cause a diminution of the conductivity. Comparison of the enormous influence of catechol with the indifference of ethylene glycol shows that it is not sufficient that the hydroxyl groups should be in the ortho- or  $\alpha$ -position to one another, but that these two hydroxyl groups should be in the

same plane, thus permitting the formation of ring combinations with the boric acid

W. G.

**Velocity of Saccharification of Starch.** VI. HENRI VAN LAER (*Bull. Acad. Roy. Belg.*, 1911, 795—830. Compare Abstr., 1910, ii, 839; 1911, ii, 28, 478).—This part deals with Kjeldahl's law of proportionality and the retarding action of the products of reaction on the activity of diastase. The results obtained by previous investigators are first critically considered, notably those of Kjeldahl (*Med. Carlsberg Lab.*, 1878, French edition), Brown and Heron (*Trans.*, 1879, 35, 596), Ling (*Abstr.*, 1902, ii, 636), Ford (*Trans.*, 1904, 85, 980; 1906, 89, 76), and Wohl and Glimm (*Abstr.*, 1910, i, 799), and a large number of new results are recorded. From all the results available, the following conclusions are drawn. Even in feeble concentrations maltose exerts a small but nearly negligible inhibiting action on the activity of diastase, but this retardation does not mask the appreciable rise in the coefficient of velocity of saccharification. The adsorption of diastase by maltose appears to result in the combination of minute quantities of the enzyme with a large excess of the sugar. All the peculiarities of the reaction appear to be explained by the adsorption compounds formed by the ferment with (a) starch, (b) the dextrins, and (c) maltose; thus the increase or decrease in the velocity of saccharification depends on the adsorption or release of new quantities of ferment by non-hydrolysed material. When the conditions are such that the enzyme is all adsorbed by the maltose at the moment of its formation, the reaction follows the logarithmic law.

Observations on the reaction should not be made near the limits of saccharification. Kjeldahl's law is followed in the reaction, below and above the limit of 45% of maltose laid down by its author. Apart from the inhibiting action of maltose, there are a series of retarding and accelerating influences capable of altering the limits within which the law holds; of these, the most important is that due to the rapid lowering of concentration of starch in liquids containing much diastase. The effect of the quantity of diastase used on the velocity of saccharification is expressed by the equation  $K = nF^m$ . In reactions in which the logarithmic law for unimolecular reactions is followed,  $m = 1$ , but it becomes greater, although always remaining nearly 1, when any departure from this law is made. Such increases in the value of  $m$  are not occasioned by greater adsorption of enzyme in solutions rich in diastase. In hydrolysis of starch by acids, the velocity depends on the number of ions per unit of volume, whilst in hydrolysis by diastase it depends at each instant on the relation between the mass of enzyme adsorbed and that of the maltose which remains to be formed.

T. A. H.

**Dependence of the Influence of Neutral Salts on the Concentration of the Acid in Catalytic Reactions.** HARALD LUNDEN (*Medd. K. Vetensk. Nobelinst.*, 1911, 2, No. 3, 1—5).—To express the influence of neutral chlorides on the catalytic action of hydrochloric acid in the inversion of sucrose, the formula  $k = A.[H]\{1 + a[H] + b[K] + c[Cl]\}$  is suggested. In this  $k$  is the velocity coefficient,  $[H]$ ,  $[K]$ ,

[Cl] the concentration of the hydrogen, salt cation, and chlorine ion respectively, and  $A$ ,  $a$ ,  $b$ , and  $c$  are constants. It is shown that the experimental data obtained by Trey for the influence of sodium and potassium chloride can be satisfactorily represented by means of this formula. The constants  $a + b$  and  $b + c$  represent respectively the influence of the acid and of the neutral salt on the catalytic activity of the hydrogen ions. Since these have the same value for varying concentrations of the catalysing acid, it follows that the relative neutral salt action is independent of the concentration of the acid. Since this is also independent of the concentration of the hydrolyte, it seems probable that the neutral salt action is dependent on physical rather than on chemical factors.

H. M. D.

**A New and Simple Method for Comparing Molecular Weights.** I. PHILIP BLACKMAN (*J. Physical Chem.*, 1911, 15, 866—868. Compare Thovet, *Compt. rend.*, 1902, 134, 564).—The method is based on Riecke's theory which requires that the rate of diffusion should be inversely proportional to the square-root of the molecular weight. When solutions of equal (weight) concentration of the two substances, the molecular weights of which are to be compared, are connected by a tube of pure solvent, the position in the tube at which the diffusing solutes meet enables their relative diffusion velocities, and hence their relative molecular weights, to be calculated. A suitable apparatus is described for use with pairs of solutes which give a coloration or precipitate when they meet in the tube. The result is independent of the state of ionisation of the solutes.

R. J. C.

**Determination of the Molecular Weight of Crystalline Substances.** GUSTAV TAMMANN (*Ber.*, 1911, 44, 3618—3628).—From a consideration of the pressure-temperature ( $p, T$ ) curves the author divides crystalline substances into two classes, which are distinguished by use of the term "crystal group." Substances of the first class, which correspond with monotropic substances, form only one crystal group, but to each crystal group there belong a stable and a series of unstable, thermally different forms. Substances belonging to the second class, which correspond with enantiotropic substances, form two crystal groups, and each of these groups consists of a stable and a series of unstable forms.

Comparison of the association of different liquids, as measured by the Eötvös-Ramsay and Shields method, shows that the normal liquids on crystallisation give only one crystal group, whereas the associated liquids often give two crystal groups. From this the author draws the conclusion that the molecular weight of normal liquids does not alter during crystallisation, and consequently that gas, liquid, and crystals have the same molecular weight. Further considerations lead him to the conclusion that the molecular structure of a crystal deposited from an associated liquid is simpler than that of the liquid itself.

Rules are given by means of which, from a consideration of the specific volumes and heats of fusion of unstable forms, the crystal group to which they belong may be determined.

T. S. P.

**The Effect of Continued Grinding on Water of Crystallisation.** C. E. GILLETTE (*Chem. News*, 1911, 104, 313—314. Compare Bleeker, *Abstr.*, 1910, ii, 238).—On continued grinding of 3 grams of the salt in an agate mortar, barium chloride lost from 0.01 to 0.51% of water, the loss being lessened by recrystallisation. The loss is chiefly due to superficial water, which is again taken up when the ground salt is exposed to air. Potassium and ammonium alum lost over 2% of water on continued grinding. Strontium chloride lost 1.5—2%, borax 3.3—3.7%, manganous chloride 1.92%, and disodium hydrogen phosphate 28—30% of water. C. H. D.

**An Electrical Laboratory Furnace Wound with a Non-noble Metal.** LEO UBBELOHDE (*Chem. Zeit.*, 1911, 35, 1403—1404).—The disadvantage of a furnace wound with nickel wire is, that after a time the nickel changes its structure and readily oxidises. The author prevents this oxidation by imbedding in charcoal the wire, which is previously protected with a fire-resisting, but porous, insulating layer made from kaolin, alumina, and asbestos. At the temperature of the furnace, a small quantity of the charcoal burns, giving a mixture of carbon monoxide and dioxide, which protects the wire from oxidation. An arrangement is made for adding charcoal from time to time to replace that which burns away.

The wire used in the furnace is an alloy (the composition is not given), the resistance of which at 1000° is only slightly higher than at 20°. The furnace may, therefore, be directly connected with the heating voltage without it being necessary to insert rheostats, and thus offers many advantages over furnaces supplied with platinum resistances (Heraeus furnaces). T. S. P.

**Two Simple Forms of Gas-Pressure Regulators.** EDGAR STANSFIELD (*Trans. Faraday Soc.*, 1911, 7, 116—118).—A glass cylinder, open below, is fixed in an outer vessel containing water. A beaker moves easily within this as a float, and carries a glass rod, at the upper end of which is, in one form of apparatus, a glass bulb, in the other a cap, to serve as a valve. The seating for the bulb is provided by an outer short glass tube with ground top, whilst the cylindrical cap of the second form nearly fits the inlet tube. The delivery pressure is equal to the difference of level in the inner and outer vessels when the valve is just on the point of closing. The first form is the more sensitive, but is occasionally liable to set up a continuous vibration. C. H. D.

**A New Funnel.** III. PHILIP BLACKMAN (*Chem. News*, 1911, 104, 312. Compare *Abstr.*, 1911, ii, 796, 1081).—The funnel has a wide lower aperture and no stem, so that the cone of the filter-paper projects freely. C. H. D.

**Exact Reading Device for the Mohr-Westphal Balance.** VON HEYGENDORFF (*Chem. Zeit.*, 1912, 36, 5—6).—In order to facilitate bringing the point of the swinging arm of the specific gravity balance into coincidence with the stationary point, two glass microscope slides,

each with an etched horizontal line, are attached to the stationary arm by rubber bands, so that the swinging point lies between them.

C. H. D.

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## Inorganic Chemistry.

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**Derivatives of Hydrogen Peroxide.** JOH. D'ANS and W. FRIEDERICH (*Zeitsch. anorg. Chem.*, 1912, 73, 325—359).—The hydrogen atoms of hydrogen peroxide may be replaced by metals or acid radicles, yielding derivatives which resemble the corresponding compounds of water in constitution and properties.

Pure hydrogen peroxide is prepared by Ahrle's method (Abstr., 1909, ii, 395). It reacts in ethereal solution with sodium, forming a white product, sodium hydrogen peroxide,  $2\text{NaHO}_2, \text{H}_2\text{O}_2$ . This compound is shown to be identical with the compound obtained from sodium ethoxide and hydrogen peroxide by Wolfenstein and Peltner (Abstr., 1908, ii, 180), whilst the sodyl hydroxide obtained by Tafel (Abstr., 1894, ii, 448) from sodium peroxide and absolute alcohol below  $0^\circ$  has the composition  $\text{NaHO}_2$ , and yields the former compound with hydrogen peroxide, or on further treatment with alcohol. The compound containing an additional molecule of hydrogen peroxide is the more stable.

Potassium reacts more vigorously with ethereal hydrogen peroxide than sodium, and there is much decomposition. The potassium hydrogen peroxide obtained has the composition  $2\text{KHO}_2, 3\text{H}_2\text{O}_2$ . Another compound,  $2\text{KHO}_2, \text{H}_2\text{O}_2$ , identical with that prepared by Schöne (*Annalen*, 1878, 193, 276, 289), crystallises on mixing absolute alcoholic solutions of potassium hydroxide and hydrogen peroxide.

Calcium does not react with dry ethereal hydrogen peroxide, but in presence of a little water the action is vigorous, and a mixture of compounds, including calcium peroxide and calcium hydroxide, is obtained.

The compound formed by the action of alcoholic acetic acid on sodium peroxide or sodium hydrogen peroxide, and regarded by Tafel as derived from a peracetic acid, is shown to have the composition  $2\text{CH}_3 \cdot \text{CO}_2\text{Na}, \text{H}_2\text{O}_2$ .

Nitrogen pentoxide reacts with cooled hydrogen peroxide, and the product oxidises aniline to nitrosobenzene, and shows other reactions of a per-acid, but pernitric acid has not been isolated. The preparation of Caro's acid and persulphuric acid has been described (Abstr., 1910, ii, 706). Attempts have been made to prepare salts of Caro's acid, but the products are impure, although the aniline salt,  $\text{C}_6\text{H}_5 \cdot \text{NH}_2, \text{H}_2\text{SO}_5$ , is precipitated from ethereal solution as a white salt, containing 88.7% of the persulphate. Fluorosulphonic acid and hydrogen peroxide yield only a mixed product. Caro's acid in aqueous solution has a molecular weight corresponding with  $\text{H}_2\text{SO}_5$ , and it may

be obtained quantitatively from persulphuric acid by the reaction  $\text{H}_2\text{S}_2\text{O}_8 + \text{H}_2\text{O}_2 = 2\text{H}_2\text{SO}_5$ .

Acetyl chloride reacts with pure hydrogen peroxide, yielding peracetic acid,  $\text{CH}_3\cdot\text{CO}_3\text{H}$ , a volatile, highly explosive liquid, or, with a larger quantity of acetyl chloride, diacetyl peroxide,  $\text{Ac}_2\text{O}_2$ , is formed.

C. H. D.

**The Weight of a Normal Litre of Hydrogen Chloride and the Atomic Weight of Chlorine.** FRANK P. BURT and ROBERT WHYTTLAW-GRAY (*Trans. Faraday Soc.*, 1911, 7, 30—41).—The density of hydrogen chloride found by Scheuer (Abstr., 1909, ii, 991) being higher than that obtained by the authors (*Trans.*, 1909, 95, 1644), fresh determinations have been made, and the sources of error have been examined. Some gas is dissolved by the grease used for the taps, and is released when the vessel is exhausted. A pure paraffin lubricant gives better results than rubber grease. The adsorption by glass surfaces has been determined by displacing gas at constant pressure by means of mercury, when the adsorbed film remains between the glass and mercury, and can afterwards be collected by lowering the mercury and so producing a Torricellian vacuum. The adsorption with hydrogen is negligible, whilst for hydrogen chloride the quantity condensed is very nearly directly proportional to the pressure. The correction, however, only amounts to 1 part in 10,300.

A new apparatus has been used, in which, as the gas is absorbed by charcoal, mercury is allowed to enter the bulb so as to keep the internal pressure constant and approximately atmospheric. Traces of mercury vapour are condensed by solid carbon dioxide or absorbed by gold wire. The gas is prepared from pure ammonium chloride and syrupy phosphoric acid, and dried over re-di-tilled aluminium chloride. Pure hydrogen chloride does not react with mercury, but the mercury is attacked in presence of traces of air. The final result obtained for the weight of a normal litre of hydrogen chloride is  $1.63915 \pm 0.00004$  grams, identical with that previously obtained. This gives the value 35.460 for the atomic weight of chlorine, identical with the International Committee's value.

C. H. D.

**Formation and Decomposition of Anhydrous Substances; Case of Iodic Anhydride.** MARCEL GUICHARD (*Compt. rend.*, 1911, 153, 1226—1229. Compare Abstr., 1909, ii, 136).—The temperature at which iodic anhydride begins to decompose has been determined by heating the substance in a silica tube in a vacuum and measuring variations in pressure by the MacLeod gauge. After forty-eight hours at  $200^\circ$  there is no appreciable decomposition, the slight evolution of gas (0.08 c.c. from 10 grams) being partly from the walls of the apparatus and partly due to occlusion. After heating further at  $205^\circ$  for two hundred and fifty-seven hours, practically no more gas was evolved. At  $259^\circ$  gas evolution was proportional to duration of heating. Baxter and Tilley (Abstr., 1909, ii, 225) heated the anhydride for four hours at  $240^\circ$ , when it still retained a trace of water. Dehydration can be pushed further by heating for one

hundred hours at 250°, decomposition occurring to the extent of only 0.0002—0.0003 of the weight of material. W. O. W.

**Chemically Active Modification of Nitrogen Produced by the Electric Discharge.** II. (Hon.) ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1911, 4, 86, 56—63. Compare Abstr., 1911, ii, 482, 678).—The chemically active modification of nitrogen, which is produced by the passage of the electric discharge through tubes containing pure nitrogen, is not acted on by hydrogen. Oxygen destroys it, but this change is not accompanied by the formation of any oxides of nitrogen. The same greenish-yellow flame with a continuous spectrum is obtained by the action of (1) ozone on nitric oxide and nitrogen peroxide, (2) active nitrogen on the two oxides of nitrogen, and (3) when the two oxides of nitrogen are introduced into a Bunsen flame. Nitrogen peroxide is formed in the action of active nitrogen on nitric oxide. This reaction can be used to estimate the percentage of active nitrogen in the gas issuing from the discharge tube. The numbers obtained in this way show that about 2.5% of the active modification is present. The electrical conductivity of glowing nitrogen is very high, a large deflexion being obtained with a single battery cell and an ordinary high resistance galvanometer. The ions are formed in the glow, and the ionisation process does not appear to be much altered when metals or other substances are introduced between the electrodes so as to give rise to the corresponding spectra. The intensity of these spectra is not diminished when large potential differences are applied to effect the removal of the ions.

When a current of nitrogen carrying phosphorus vapour is introduced into glowing nitrogen there is no immediate action, but after the glow has disappeared, a further glow effect is observed, indicating that the nitrogen gets into a state in which it can react with phosphorus.

Experiments with ozone show that this can in some cases give rise to metallic spectra when mixed with metallic vapours at comparatively low temperatures. H. M. D.

**Colloidal Arsenic Trisulphide.** A. DUMANSKI (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 262—263).—The properties of colloidal arsenious sulphide are described. The particles, which are negatively charged, can be slowly segregated by rapid centrifuging. From measurements of the density and electrical conductivity of the colloidal solution and the dispersive medium, it is found that the density of the colloidal sulphide is 2.938, and the specific conductivity  $136 \times 10^{-6}$ . The solution is coagulated by various electrolytes, whilst others react with the sulphide. With an iodine solution, reaction takes place according to  $\text{As}_2\text{S}_3 + 10\text{I} + 5\text{H}_2\text{O} = \text{As}_2\text{O}_5 + 10\text{HI} + 3\text{S}$ ; with a solution of potassium permanganate which has been decolorised by hydrogen peroxide, the sulphide is also converted into arsenic acid, and in this case, also, there is no coagulation. Solutions of alkali hydroxides and potassium cyanide have no coagulating action; with silver nitrate and copper sulphate coagulation occurs, but the precipitated substance contains

considerable quantities of silver or copper. Lead acetate, on the other hand, coagulates the colloid without formation of lead sulphide.

H. M. D.

**The Proportion of Carbon Dioxide in the Air of Antarctic Regions.** ACHILLE MÜNTZ and E. LAINE (*Compt. rend.*, 1911, 153, 1116—1119).—In cold regions the dissociation pressure of hydrogen carbonates in the sea being low, the proportion of carbon dioxide in the air should be below normal if Schloesing's theory of the distribution of this gas is correct. Samples of air collected over the sea at latitudes of 64—70°, at temperatures between 1 and -2°, gave a mean value of 2.0524 parts of carbon dioxide per 10,000 by volume, a distinctly smaller proportion than is met with in warmer regions.

W. O. W.

**Action of Atmospheric Moisture on the Moisture Content and on the Velocity of Combustion of Black Powder.** CARL KULLGREN (*Arkiv. Kem. Min. Geol.*, 1911, 4, No. 17, 1—20).—Varying weights of black powder ( $\text{H}_2\text{O}$ , 1.10;  $\text{KNO}_3$ , 74.0; C, 15; S, 9.8%) were placed in glass dishes in a desiccator, through which was passed air of varying moisture content (38 and 86% of the saturation content), the temperature being 16.5°. The glass dishes were weighed from time to time. According as the powder was dried or not, the equilibrium was approached from different sides. It was found that with air containing 38% of moisture, the percentage of moisture in the powder when equilibrium was attained was 0.91%, whilst with air containing 86% of moisture the equilibrium percentage was 1.38%.

The results are treated theoretically by the author, and it is shown that the rate of absorption (or loss) of moisture by the powder is given by the expression  $dx/dt = k/x$ .

The velocity of combustion of the powder diminishes as the moisture content increases.

T. S. P.

**The Solubility of Alkali Salts in the Corresponding Acids.** WALTER HERZ (*Zeitsch. anorg. Chem.*, 1911, 73, 274—276).—The solubility of  $\text{LiCl}$ ,  $\text{H}_2\text{O}$ , of  $\text{NaCl}$ , and of  $\text{KCl}$  in hydrochloric acid is less than that in water, by an amount which is directly proportional to the concentration of the acid. Hydrobromic acid depresses the solubility of potassium chloride less than hydrochloric acid. The solubility of sodium acetate is only very slightly lowered by acetic acid, whilst sodium and potassium sulphates are more soluble in sulphuric acid solutions than in water.

C. H. D.

**The Capacity of Potassium Halides for Forming Solid Solutions in Relation to Temperature.** II. MARIO AMADORI and G. PAMPANINI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 572—577. Compare this vol., ii, 48).—In the present paper the authors record the results obtained by the application of the method of thermal analysis to fused mixtures of these salts, and compare the results thus obtained at high temperatures with those previously arrived at for mixtures in the solid state. Potassium chloride and potassium bromide are miscible in all proportions, both at low and at high

temperatures. In the case of potassium bromide and potassium iodide the miscibility is complete at a high temperature, but limited at a low temperature. Potassium chloride and potassium iodide are miscible at a low temperature only to a very limited degree, but at a high temperature the miscibility is much greater, although not complete (0—49 mol.% KCl in KI, 0—9 mol.% KI in KCl). It is pointed out that this is in accord with the differences between the halogens in other respects.

R. V. S.

**Symmetry of Crystals of Potassium Dichromate.** A. SCHUBNIKOFF (*Zeitsch. Kryst. Min.*, 1911, 50, 19—23).—Crystals were grown from a slightly supersaturated solution (containing 1.4—3 grams per 100 c.c. in excess of the amount given by the solubility), and the vessel containing the solution was immersed in a thermostat with a large volume of water at 20.8°. Small crystals of the salt were introduced to form nuclei for the growth. The crystals are tabular in habit, parallel to (001), and when they have grown on the floor of the vessel there is an appreciable difference in their form according to whether the face (001) or parallel face (00 $\bar{1}$ ) was uppermost. The differences are such that they cannot be due to the influence of gravity and the consequent convection currents in the liquid. These effects are, however, eliminated by growing the crystals suspended in a vessel rotating on a horizontal axis. A crystal grown under these conditions has the face (001) bright and smooth, and (00 $\bar{1}$ ) dull and rough; and in the case of other forms the parallel faces are not of the same size, or one may be absent. Crystals of potassium dichromate therefore belong to the asymmetric class of the triclinic system.

L. J. S.

**Mercury-Sodium Alloys.** ERNEST VANSTONE (*Trans. Faraday Soc.*, 1911, 7, 42—63. Compare Schüller, Abstr., 1904, ii, 657).—The alloys are prepared by melting sodium in carbon dioxide and allowing it to flow into a weighed tube, when the shell of oxide remains in the first tube. Mercury is then added from a burette. The sodium may also be cleaned by dipping in ether containing alcohol, and melted under paraffin. The thermal analysis shows the existence of the compounds Na<sub>3</sub>Hg, Na<sub>3</sub>Hg<sub>2</sub>, NaHg, Na<sub>7</sub>Hg<sub>8</sub>, NaHg<sub>2</sub>, and NaHg<sub>4</sub>, the formula Na<sub>7</sub>Hg<sub>8</sub> being more probable than Na<sub>12</sub>Hg<sub>13</sub>, given by Schüller, which is not consistent with the range of the transformation temperature.

The specific volumes of alloys liquid below 237° have been determined by drawing up the alloys into graduated pipettes in carbon dioxide by means of a hand pump. The specific volumes determined at 110° lie on a smooth curve, and almost smooth curves are also obtained at 184° and 237°. The alloys near to NaHg<sub>2</sub> (m. p. 353°) have not been investigated, but this compound probably exists in the liquid in an undissociated condition (Bornemann and Müller, Abstr., 1910, ii, 924). The specific volumes of the solid alloys have also been determined. The maximum contraction occurs at 48 atomic % Na. A relation cannot be traced between the specific volumes and the sum of the valencies in the compounds present. Microscopical examination shows that the compounds Na<sub>3</sub>Hg, Na<sub>3</sub>Hg<sub>2</sub>, NaHg, Na<sub>7</sub>Hg<sub>8</sub>, NaHg<sub>2</sub>, and NaHg<sub>4</sub> occur in distinct crystals.

C. H. D.

**The Hydrates of Sodium Carbonate.** RUDOLF WEGSCHEIDER (*Zeitsch. anorg. Chem.*, 1911, 73, 256—258).—The hydrate considered to have the composition  $\text{Na}_2\text{CO}_3 \cdot 2.5\text{H}_2\text{O}$  is probably the monohydrate. The apparent difference in crystalline form (Morel, *Bull. Soc. franç. min.*, 1889, 12, 546) is due to an error in the angles recorded, and the range of stability is quite consistent with the compound observed by Morel being the monohydrate. C. H. D.

**Reciprocal Solubility of Sodium Carbonate and Sodium Hydrogen Carbonate in Water.** DÉSIRÉ DE PAEPE (*Bull. Soc. chim. Belg.*, 1911, 25, 413—419. Compare Abstr., 1911, ii, 489).—Polemical. A reply to Herzen (Abstr., 1911, ii, 724). W. G.

**The Differentiation of True Peroxy-salts from Salts with Hydrogen Peroxide of Crystallisation.** ERNST H. RIESENFELD and W. MAU (*Ber.*, 1911, 44, 3589—3595).—The authors maintain the thesis that the true percarbonates can be distinguished from carbonates containing hydrogen peroxide of crystallisation by the fact that the former give a quantitative liberation of iodine from a neutral solution of potassium iodide, whereas the latter liberate practically no iodine (compare Abstr., 1910, ii, 33, 203, 290, 774, 952). Even when hydrogen peroxide is added to a solution of potassium percarbonate in the proportion of 2 mols.  $\text{H}_2\text{O}_2$  : 1 mol.  $\text{K}_2\text{C}_2\text{O}_6$ , the liberation of iodine is very little affected.

At  $15^\circ$  a solution of potassium percarbonate, after keeping for an hour, still liberates iodine in quantity from a solution of potassium iodide, whereas the so-called sodium percarbonate does not liberate iodine from such a solution either at room temperature or at  $0^\circ$ , even when added as the solid. Tanatar has supposed (Abstr., 1910, ii, 774) that part of the oxygen in the compounds prepared by the action of hydrogen peroxide on the alkali carbonates is, at all events, firmly combined. The salt  $\text{Na}_2\text{CO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}$ , described by Tanatar, must, however, be either wholly a percarbonate, or else wholly a hydrogen peroxide additive product,  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ , since it contains only one active oxygen atom per molecule. The authors find that it gives no appreciable liberation of iodine from potassium iodide, so that Tanatar's supposition is incorrect.

The so-called rubidium percarbonate prepared by Peltner (Abstr., 1909, ii, 574) must be considered to have the formula  $\text{Rb}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ .

Persulphates and sulphates with hydrogen peroxide of crystallisation (Willstätter, Abstr., 1903, ii, 537) react towards potassium iodide in a similar way to the compounds just mentioned, so that the reaction may be considered a general one for differentiating between true peroxy-salts and hydrogen peroxide additive products. T. S. P.

**Isomeric Percarbonates.** ERNST H. RIESENFELD and W. MAU (*Ber.*, 1911, 44, 3595—3605).—In the light of the experience gained in the differentiation of true percarbonates from carbonates containing hydrogen peroxide of crystallisation (compare previous abstract), the authors have investigated the compounds prepared by the action of carbon dioxide on sodium peroxide (Wolffenstein and Peltner, Abstr.,

1908, ii, 180). They find that the four supposedly different salts prepared by Wolffenstein and Peltner are really salts of two different acids only, namely, monoperoxycarbonic acid,  $\text{H}_2\text{CO}_4$ , and monoperoxycarbonic acid,  $\text{H}_2\text{C}_2\text{O}_6$ . The salts to which was given the formulæ  $\text{Na}_2\text{CO}_5 \cdot \text{H}_2\text{O}$  and  $\text{NaHCO}_4$  are to be considered as  $\text{Na}_2\text{CO}_4 \cdot \text{H}_2\text{O}_2$  and  $\text{Na}_2\text{C}_2\text{O}_6 \cdot \text{H}_2\text{O}_2$  respectively. This was proved by comparison of the reactions of  $\text{Na}_2\text{CO}_4$  and  $\text{Na}_2\text{CO}_5 \cdot \text{H}_2\text{O}$ , and  $\text{Na}_2\text{C}_2\text{O}_6$  and  $2\text{NaHCO}_4$  respectively with potassium iodide; in all cases the iodine liberated, which is due to percarbonate oxygen and not to hydrogen peroxide of crystallisation, corresponded with the formulæ  $\text{Na}_2\text{CO}_4$ ,  $\text{Na}_2\text{CO}_4 \cdot \text{H}_2\text{O}_2$ , and  $\text{Na}_2\text{C}_2\text{O}_6$ ,  $\text{Na}_2\text{C}_2\text{O}_6 \cdot \text{H}_2\text{O}_2$ . It was also found that each of the last-mentioned pair of compounds could be transformed into the other by addition or withdrawal of hydrogen peroxide. The substance having the composition  $\text{Na}_2\text{CO}_4$  was shown to be a true compound, and not a mixture of  $\text{Na}_2\text{O}_2 + \text{Na}_2\text{C}_2\text{O}_6 (= 2\text{Na}_2\text{CO}_4)$  by comparing its action on potassium iodide with that of the mixture mentioned;  $\text{Na}_2\text{CO}_4$  liberated iodine, whereas the mixture did not.

It follows that the carbonates containing peroxidic oxygen can be classified as follows: (1) Carbonates containing hydrogen peroxide of crystallisation, for example,  $\text{Na}_2\text{CO}_4 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$ ; (2) monoperoxycarbonates, for example,  $\text{Na}_2\text{CO}_4$ ; (3) percarbonates (monoperoxycarbonates), for example,  $\text{Na}_2\text{C}_2\text{O}_6$ .

The compound  $\text{Na}_2\text{C}_2\text{O}_6$  behaves towards potassium iodide solution differently from the potassium percarbonate ( $\text{K}_2\text{C}_2\text{O}_6$ ) prepared by electrolysis, in that only about 50% of its active oxygen liberates iodine, whereas the potassium salt gives a quantitative liberation. This may be due to a difference in constitution, and in order to settle the question the authors have prepared a compound,  $\text{K}_2\text{C}_2\text{O}_6$ , from potassium peroxide and carbon dioxide by a method similar to that used for making the sodium compound (Wolffenstein and Peltner, *loc. cit.*). This compound behaves towards potassium iodide solution, whether added as the solid or as a solution, differently from ordinary potassium percarbonate, and similarly to the compound  $\text{Na}_2\text{C}_2\text{O}_6$ . It is therefore isomeric with ordinary potassium percarbonate, and its constitution may perhaps be represented as  $\text{K}\cdot\text{O}\cdot\text{O}\cdot\text{CO}\cdot\text{O}\cdot\text{CO}\cdot\text{OK}$ , as distinct from  $\text{KO}\cdot\text{CO}\cdot\text{O}\cdot\text{O}\cdot\text{CO}\cdot\text{OK}$ . The constitution of the compound  $\text{Na}_2\text{CO}_4$  would then be  $\text{NaO}\cdot\text{O}\cdot\text{CO}\cdot\text{ONa}$ , so that the percarbonates show similar relations to the persulphates (permono- and persulphates).

The authors point out that there is no trustworthy evidence for the assumption that the sodium hydrogen peroxide ( $\text{NaO}_2\text{H}$ ) prepared by the action of sodium peroxide on ethyl alcohol is different in constitution from that obtained by the action of hydrogen peroxide on sodium ethoxide (compare Wolffenstein and Peltner, *loc. cit.*).

T. S. P.

**Colloidal Silver.** NICOLA PAPPADÀ (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 265—270).—The mechanism of coagulation of colloids by electrolytes is discussed, and experiments are described which show the relative coagulating powers of different electrolytes for colloidal silver. The silver particles are negatively charged and coagulation is

effected by the cations. In the series of the alkali metal ions, the coagulating power increases with increasing atomic weight. The hydrogen ion is still more active, and it appears that the coagulating capacity is determined by the velocity of diffusion of the active ions. Non-electrolytes are without action, but for multivalent ions the effectiveness increases with the valency.

Colloidal silver is chemically active towards a number of substances. It reduces mercuric chloride, ferric chloride, and an acid solution of potassium permanganate. With a solution of iodine in 0.1*N*-potassium iodide, a slow reaction takes place, silver iodide being precipitated, and the solution becomes alkaline. With a solution of potassium nitrate, reduction to the nitrite occurs to a small extent. It reacts with hydrogen cyanide and alkali metal cyanides, and with the halogens to form the corresponding silver salts. H. M. D.

**Constitution of the Photo-halides.** II. ADRIAAN P. H. TRIVELLI (*Chem. Weekblad*, 1912, 9, 2—11. Compare Abstr., 1911, ii, 281).—Polemical. A reply to Reinders's criticism (Abstr., 1911, ii, 490). A. J. W.

**Formation of Complex Compounds of Salts of Silver and Mercury.** BICE FINZI (*Gazzetta*, 1911, 41, ii, 538—543).—Freshly precipitated silver chloride is soluble in an aqueous solution of mercuric sulphate. The solubility increases (but not in proportion) with the amount of mercuric salt present, but it is increased more by dilution, so that the greatest amount of silver chloride is dissolved by a large excess of mercuric salt at considerable dilution. When to such a solution hydrochloric acid is added in quantity equivalent to the silver present, the metal is not all precipitated. Similar results are obtained when hydrochloric acid is added to a solution of silver sulphate and mercuric sulphate. The amount of silver chloride remaining dissolved increases with the amount of mercury present, but not proportionately. When the precipitated silver chloride has been filtered, the filtrate gives a further precipitate with hydrochloric acid or chlorides, and with silver nitrate, whilst sulphates, nitrates, and alkali acetates cause no precipitation. Similar phenomena are observed when other mercuric salts, such as the nitrate or acetate, are employed. R. V. S.

**Some New Basic Silver-Mercury Compounds.** BICE FINZI (*Gazzetta*, 1911, 41, ii, 543—549).—Yellow mercuric oxide is soluble in solutions of silver nitrate, silver sulphate, and silver acetate, especially in the warm. The solubility increases with the dilution of the silver solution. When a boiling solution of silver sulphate (saturated in the cold) is treated with yellow mercuric oxide until no more dissolves, and filtered, in a few days a pale yellow substance,  $\text{Ag}_2\text{SO}_4 \cdot \text{HgO}$ , is deposited; it crystallises in aggregates of very small, rhombic tablets. When a twice normal solution of silver nitrate is similarly treated, a reddish-yellow substance,  $\text{AgNO}_3 \cdot 2\text{HgO}$ , is obtained; it forms tufts of acicular crystals. R. V. S.

**The Freezing-point Diagram of the Binary System Silver Sulphide-Iron Sulphide.** P. SCHOEN (*Metallurgie*, 1911, 8, 737—738).—Ferrous sulphide, prepared by heating crystalline pyrites, mixes with silver sulphide in all proportions in the molten state. The freezing-point curve of the system is a simple one, with an eutectic point at  $615^{\circ}$  and 11% FeS. The transformation of silver sulphide at  $175^{\circ}$  occurs at constant temperature throughout the series. The two sulphides do not combine with one another. C. H. D.

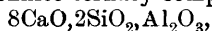
**Molecular Weight of Calcium Oxide. Atomic Weight of Calcium.** WILLIAM OECHSNER DE CONINCK (*Compt. rend.*, 1912, 154, 1479—1480).—In four experiments pure calcium formate was ignited, and the oxide weighed. In another, calcium oxalate was converted into the oxide by ignition. The mean of the five determinations gives 56.06 as the molecular weight of calcium oxide, or 40.02 for the atomic weight of calcium. W. O. W.

**The Reduction of Calcium Sulphate by Carbon Monoxide and by Carbon, and the Oxidation of Calcium Sulphide.** H. O. HOFMANN and W. MOSTOWISCH (*Bull. Amer. Inst. Mining Eng.*, 1910, 917—939).—Calcium and barium sulphates can be conveniently and quantitatively reduced by a stream of dry carbon monoxide at a temperature of  $900$ — $950^{\circ}$ ; the sulphate is first rendered anhydrous by heating until the weight is constant; the reduction commences at  $680$ — $700^{\circ}$ , becomes vigorous at  $750$ — $850^{\circ}$ , and is practically finished at  $900^{\circ}$ ; the heating is continued until there is no further loss of weight. The reduction with carbon in an atmosphere of nitrogen begins at  $700^{\circ}$ , is vigorous at  $800$ — $900^{\circ}$ , and completed at  $1000^{\circ}$ ; at low temperatures the carbon is converted into carbon dioxide, at higher into carbon monoxide.

The oxidation of calcium sulphide is carried out by heating in a stream of pure dry air; the action starts at  $800^{\circ}$ , and yields 73% calcium sulphate and 27% calcium oxide. F. M. G. M.

**The Constitution of Portland Cement Clinker.** ERNST JÄNECKE (*Zeitsch. anorg. Chem.*, 1911, 73, 200—222. Compare Shepherd and Rankin, *Abstr.*, 1911, ii, 725).—A part of the quaternary system  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3$  has been studied by means of thermal analysis. The ferric oxide appears to occur only in combination with lime, and solid solutions are not formed.

The mixtures are heated by means of an oxygen blowpipe in an iridium crucible, which can be unwrapped to remove the mass after solidification. After powdering, the mixture is re-melted, and a cooling curve taken. A single definite ternary compound is found,



with a melting point of  $1382^{\circ}$ , which is lowered by the addition of its components. This compound, which was not observed by Shepherd and Rankin, is regarded as being identical with alite, the principal crystalline constituent of Portland cement clinker. The existence of such a ternary compound explains why the presence of alumina is necessary in cements, its properties being different from those of the

binary calcium silicates. Microscopical examination confirms its homogeneity.

Belite, celite, and felite are probably the compounds  $2\text{CaO}, \text{SiO}_2$ ,  $3\text{CaO}, \text{Fe}_2\text{O}_3$ , and  $\text{CaO}$  respectively, the latter being often absent.

C. H. D.

**Fusion Experiments with Metasilicates and Titanates.** S. SMOLENSKY (*Zeitsch. anorg. Chem.*, 1912, 73, 293—303).—Mixtures of silicates and titanates have been examined by thermal analysis in graphite crucibles in an electric furnace.

Calcium silicate and calcium titanate form solid solutions, and the freezing-point curve has a minimum at  $1420^\circ$  and 33.4 mol. %  $\text{CaTiO}_3$ . At a lower temperature the solid solution is resolved into its components, the transformation curve rising to a maximum at  $1350^\circ$  and again falling. The transformation is confirmed microscopically. Mixtures of manganese silicate and titanate form a eutectiferous series, with the eutectic point at 22.3 mol. %  $\text{MnTiO}_3$  and  $1120^\circ$ . Solid solutions are formed from 38.3 to 100 mol. %  $\text{MnTiO}_3$ , but not at the other end of the series. A decomposition of this solid solution takes place at about  $1050^\circ$ . Barium silicate and titanate form a complicated system, of which the curve of initial freezing points only has been determined.

Synthetic titanite,  $\text{CaSiTiO}_5$ , forms blue crystals, m. p.  $1221^\circ$ , this colour being shown by all synthetic titanates. The crystals enclose small crystals of perowskite,  $\text{CaTiO}_3$ .

C. H. D.

**Thermal Analysis of Binary Mixtures of the Chlorides of Bivalent Elements.** CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 646—653. Compare Ruff and Plato, Abstr., 1903, ii, 588; Menge, Abstr., 1911, ii, 982; Sandonnini and Scarpa, Abstr., 1911, ii, 984; and this vol., ii, 162).—In the present paper the results are given of the thermal analysis of the bivalent systems formed by strontium chloride with the chlorides of barium, cadmium, lead and magnesium, and by barium chloride with the chlorides of cadmium and lead. Strontium chloride and barium chloride form mixed crystals in all proportions; there is a minimum at  $854^\circ$ , corresponding with about 35 mol. % of barium chloride. Strontium chloride and cadmium chloride are miscible only in the liquid state; the eutectic lies at  $502^\circ$ , corresponding with 58 mol. % of cadmium chloride. Strontium chloride and lead chloride give mixed crystals in all proportions. Strontium chloride and manganous chloride are miscible only in the liquid state; there is an eutectic at  $499^\circ$  (45 mol. % of manganous chloride). The system  $\text{BaCl}_2\text{--CdCl}_2$  is similar to the preceding; the eutectic lies at  $450^\circ$  (57 mol. % of  $\text{CdCl}_2$ ). Barium chloride and lead chloride give mixed crystals in all proportions.

The author dissents from Menge's conclusions in regard to the system  $\text{CaCl}_2\text{--CdCl}_2$ . His results give a simple curve of mixed crystals with a minimum.

R. V. S.

**The Reaction between Concentrated Solutions of Barium Acetate and Aluminium Sulphate.** JULIUS F. SACHER (*Chem. Zeit.*, 1911, 35, 1447).—Concentrated solutions of barium acetate and aluminium sulphate react together very slowly, and barium sulphate is not at first precipitated. Vigorous stirring or shaking, heating, or dilution with water brings about precipitation. Barium acetate and magnesium sulphate behave similarly, but precipitation is much more rapid, in accordance with the greater dissociation of magnesium sulphate. Saturated solutions of lead acetate and aluminium sulphate give a precipitate immediately. C. H. D.

**Distillation of Binary Mixtures of Metals in a Vacuum. I. Isolation of a Compound of Magnesium and Zinc.** ARTHUR J. BERRY (*Proc. Roy. Soc.*, 1911, A, 86, 67—71).—Mixtures of magnesium and zinc, containing the latter in excess of the ratio  $1\text{Mg} : 2\text{Zn}$ , have been distilled in highly exhausted glass tubes at temperatures somewhat lower than the temperature at which the glass began to soften. Analysis of the residual alloy gives numbers which correspond closely with the formula  $\text{MgZn}_2$ . Since the existence of a definite compound of this composition is indicated by the freezing-point diagram, it appears that this compound can be isolated by distilling off the excess of the more volatile component from a mixture of the two metals. Further experiments are described which show that this compound can be distilled without change.

H. M. D.

**Solubility of Magnesium Ammonium Sulphate.** ATHERTON SEIDELL (*Pharm. J.*, 1911, [iv], 33, 846).—Lothian (*Abstr.*, 1910, ii, 504) gave determinations of the solubility of crystallised magnesium ammonium sulphate much higher than those on record. The author calls attention to a mistake in Lothian's calculations, and shows that when this is corrected there is really a good agreement at the higher temperatures ( $15-27.22^\circ$ ). At the lower temperatures ( $1.11-10^\circ$ ), Lothian's results are probably incorrect, since his solubility curve for these temperatures is very irregular and abnormal in its course.

T. S. P.

**Action of Distilled Water and of Distilled Water Containing Electrolytes on Metallic Lead.** MARGHERITA TRAUBENGARINI and ALBERTO SCALA (*Mem. R. Accad. Lincei*, 1911, [v], 8, 576—598).—In contact with distilled water quite free from oxygen, metallic lead passes rapidly into colloidal solution at room temperature. In contact with oxygen from the air the colloiddally dissolved metal is rapidly transformed into the colloidal hydrated oxide, the particles of which slowly aggregate to form crystals of various forms. Electrolytes, above a concentration characteristic for each, prevent the corrosion of lead; below this concentration, corrosion continues, but the colloid is coagulated and deposited on the surface of the metal.

It is considered that the colloidal state is an ionised combination of a colloid with water, and it is shown that this theory affords a satisfactory explanation of the behaviour of colloids.

All metals dissolve more or less easily in water in the colloidal state. Lead dissolves most readily, zinc and iron also dissolve colloiddally in water in the absence of oxygen, and the results with these metals will be described in a later communication. Platinum comes at the other extremity, dissolving only with very great difficulty.

G. S.

**The Formation of Lead Carbonate from Metallic Lead in Presence of Metallic Aluminium.** C. REICHARD (*Pharm. Zentr.-h.*, 1911, 52, 1395—1396).—Aluminium number plates on the wooden vessels of a brewery were fixed on a backing of lead, held in an iron-frame. After a time, the plates became covered with a laminated deposit, consisting of lead acetate and lead carbonate, in which thin laminæ of lead and aluminium were also to be distinguished.

C. H. D.

**Thermal Analysis of Binary Mixtures of the Chlorides of Univalent Elements.** CARLO SANDONNINI and P. C. AUREGGI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 588—596. Compare Sandonnini, Abstr., 1911, ii, 800).—The paper deals with the thermal analysis of six more binary mixtures of the chlorides of these elements. Lithium chloride and thallous chloride are completely miscible in the liquid state. There is an eutectic at  $342^{\circ}$  corresponding with about 62 mol. % of thallous chloride, and the two substances do not give mixed crystals in any proportion. The eutectic point of the system NaCl-TlCl lies at  $412^{\circ}$  (about 85 mol. % of thallous chloride), and probably the two substances are not miscible in the solid state. Potassium chloride and thallous chloride are miscible in all proportions both in the solid and in the liquid state. The system RbCl-AgCl shows an eutectic point at  $253^{\circ}$  (60 mol. % of silver chloride); this is analogous to the system KCl-AgCl (compare Scheemtschuschny, Abstr., 1907, ii, 259), and here also thermal analysis does not reveal the compounds which are known to exist. Rubidium chloride and thallous chloride are completely miscible within wide limits. Thallous chloride gives with silver chloride a compound,  $2\text{AgCl}, 3\text{TlCl}$ , which decomposes on melting, and is revealed by a pause at  $252^{\circ}$ . There is an eutectic at  $210^{\circ}$  (41 mol. % of thallous chloride).

R. V. S.

**Europous Chloride.** GEORGES URBAIN and FRANÇOIS BOURION (*Compt. rend.*, 1911, 153, 1155—1158).—The action of chlorine and sulphur chloride vapour on europium oxide leads to the formation of a black mass containing less chlorine than europic chloride. To obtain the latter in the anhydrous state it is necessary to employ the hydrated chloride dried at  $100^{\circ}$ . Europous chloride,  $\text{EuCl}_2$ , is best prepared by reducing the higher chloride in a current of hydrogen at  $400\text{—}450^{\circ}$ . It is a colourless, amorphous substance, forming a neutral solution in water. When the latter is concentrated at  $100^{\circ}$ , oxidation occurs, in accordance with the equation  $12\text{EuCl}_2 + 3\text{O}_2 = 8\text{EuCl}_3 + 2\text{Eu}_2\text{O}_3$ .

Europous chloride is more stable than the corresponding chloride of samarium, the only other metal of the group known to form a lower chloride.

W. O. W.

**Atomic Weight of Holmium.** OTTO HOLMBERG (*Arkiv. Kem. Min. Geol.*, 1911, 4, No. 10, 1—4).—The holmium material previously obtained by the author (Abstr., 1911, ii, 286) has been further purified by a long series of fractional crystallisations. After 250 fractionations of the nitrate, 10 chief fractions were obtained, which contained only traces of erbium; these were further fractionated by repeated partial precipitation with ammonia, until finally an oxide was obtained which gave a value for the atomic weight of holmium which was not altered by further fractionation. As a mean of six determinations the atomic weight is found to be 163·5. Spectral examination of 2*N*- and 0·5*N*-solutions of the nitrate prepared from this oxide showed that only the merest traces of erbium and dysprosium were present.

Examination of the atomic weights of the rare-earth metals shows that they may be divided up into pairs, for example, lanthanum and cerium, praseodymium and neodymium, etc., in which the atomic weights are very close together; dysprosium (= 162·5) and holmium (= 163·5) form such a pair.

Holmium oxide is pale yellow in colour; the salts are yellow, with a slight tinge of orange.

T. S. P.

**Solubility of Aluminium Hydroxide in Sodium Hydroxide.** ROLAND EDGAR SLADE (*Zeitsch. Elektrochem.*, 1912, 18, 1—2. Compare *ibid.*, 1911, 17, 261; Herz, Abstr., 1911, ii, 728).—In a recent paper (*loc. cit.*) Herz, who had previously from solubility measurements found the ratio Na:Al as 3:1 for solutions of aluminium hydroxide in sodium hydroxide, criticised the author's statement, based mainly on freezing-point determinations, that the solutions in question contain only  $\text{NaAlO}_2$ . The author has now carried out further solubility measurements and finds that the ratio Na:Al varies from 2:1 to 10:1 according to the conditions of precipitation and the mode and duration of drying of the hydroxide. The observation of Herz that the ratio Na:Al is always 3:1 is erroneous, and there is no evidence that the solutions in any circumstances contain  $\text{AlO}_3'''$  ions. The gelatinous aluminium hydroxide is always an unstable phase under these conditions.

G. S.

**Solubility of Aluminium Hydroxide in Ammonium Sulphate Solution: Artificial Production of Alumian.** ROBERT KREMMANN and K. HÜTTINGER (*Zeitsch. Kryst. Min.*, 1911, 50, 85; from *Jahrb. k.k. geol. Reichs.*, 1908, 58, 637—658).—Starting with a concentrated solution of aluminium sulphate, the solubility of aluminium hydroxide increases with decreasing concentration, reaching a maximum for 38%  $\text{Al}_2(\text{SO}_4)_3$  at 60°, 32% at 20°, and 28% at 40°; the solid in contact with the solution has now the composition  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$ . The solubility of the hydroxide then decreases slowly with decreasing concentration to 7·5%  $\text{Al}_2(\text{SO}_4)_3$  at 60° and 40°, when the precipitate has the composition of alumian,  $\text{Al}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 12\text{H}_2\text{O}$ . Corresponding basic sulphates with  $10\text{H}_2\text{O}$  and  $11\text{H}_2\text{O}$  were also obtained.

L. J. S.

**Some Artificial Aluminosilicates of the Type  $\text{RO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ .** A. S. GINSBERG (*Zeitsch. anorg. Chem.*, 1912, 73, 277—292).—The

method of thermal analysis has been applied to mixtures prepared by heating alumina and silica with the carbonates of other metals in graphite crucibles in a kryptol furnace.

Synthetic anorthite,  $\text{CaAl}_2\text{Si}_2\text{O}_8$ , solidifies at  $1440^\circ$  when slowly cooled, the readings being sharp. The value  $1532^\circ$ , obtained by Day and Allen (Abstr., 1906, ii, 177) for the melting point, is probably high owing to superheating. The synthetic product is optically identical with the natural mineral. Synthetic nepheline,  $\text{Na}_3\text{Al}_2\text{Si}_2\text{O}_8$ , tends to form a glass unless the fused mass is heated to  $1500$ — $1600^\circ$  before cooling, when crystallisation occurs readily, the freezing point being at  $1223^\circ$ . The glass is slowly devitrified, forming nepheline crystals, at  $900^\circ$ .

Anorthite and nepheline are isomorphous, the freezing-point curve of their mixtures being continuous, with a minimum at  $1130^\circ$  and 70% nepheline. Mixtures near to the anorthite end of the series have a tendency to form glasses. The polymorphic transformation of anorthite at  $1150^\circ$  can be detected in the mixtures.

Kaliophilite,  $\text{K}_2\text{Al}_2\text{Si}_2\text{O}_8$  (potassium nepheline), crystallises with difficulty, and the freezing point has not been determined. Eucryptite,  $\text{Li}_2\text{Al}_2\text{Si}_2\text{O}_8$ , crystallises readily, forming twinned crystals. The freezing point is  $1307^\circ$ .

C. H. D.

**The Freezing-point Diagram of the Binary System Manganese-Arsenic.** P. SCHOEN (*Metallurgie*, 1911, 8, 739—741).—Alloys of manganese and arsenic, prepared by adding the compound  $\text{MnAs}$  to manganese, give a freezing-point curve which has a maximum at  $1029^\circ$  and 59.5% Mn, corresponding with the compound  $\text{Mn}_2\text{As}$ , and another at  $955^\circ$ , corresponding with  $\text{MnAs}$ . Eutectic points occur at  $932^\circ$  and 78% Mn, and at  $880^\circ$  and 50% Mn respectively. A reaction in the solid state, accompanied by the development of heat, reaches a maximum at  $752^\circ$  and 52.5% Mn, and probably indicates the formation of a third compound,  $\text{Mn}_3\text{As}_2$ . Alloys in the neighbourhood of this composition become magnetic on quenching from  $850^\circ$ , whilst those containing from 45 to 47.2% Mn are even magnetic when slowly cooled.  $\text{MnAs}$  and  $\text{Mn}_2\text{As}$  are not magnetic (compare Wedekind and Veit, Abstr., 1911, ii, 985).

C. H. D.

**Reduction of Neutral Potassium Permanganate Solutions in Presence of Normal Sulphates in Various Concentrations.** P. A. TSCHESHIWILL (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1402—1420. Compare Abstr., 1911, ii, 43).—The author has examined the action of a number of normal sulphates on potassium permanganate in neutral solutions, these being subsequently filtered through washed, ignited asbestos, and the permanganate estimated by titration. With all the sulphates employed except chrome alum, a slow reducing action on the permanganate was observed, and in some cases the percentage of the permanganate reduced was less after, say, eight months, than after three months. Chrome alum exerted a far more rapid action, as much as 80—90% of reduction occurring in twenty-four hours and 100% in a month; this result is probably due to the conversion of the chromic oxide into chromium trioxide,

$\text{Cr}_2\text{O}_3 + \text{O}_3 = 2\text{CrO}_3$ . A solution of permanganate in distilled water alone showed no reduction after eight months.

The general conclusion drawn from the results is that, in many cases, mineral salts play the part of positive or negative catalysts towards the reduction of permanganate in neutral solution. This action not only depends on the chemical nature of the constituent ions of the salts, but varies widely with the physical conditions of the surrounding medium. Concentration of the salt also influences the intensity of the catalytic action, which appears always to increase with increase of the concentration. T. H. P.

**The System Iron-Carbon.** ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 530—536; *Zeitsch. Elektrochem.*, 1912, 18, 51—54).—Although cementite is metastable when found as a constituent of alloys of iron and carbon, it may be formed by heating iron containing graphite at or above  $720^\circ$  (Royston, *J. Iron and Steel Inst.*, 1897, 1, 166) and cooling rapidly. It may be supposed that the liquid phase, and also the solid solution which separates from it, contain carbon dissolved both as graphite and as carbide, the equilibrium being  $3\text{Fe} + \text{C} \rightleftharpoons \text{Fe}_3\text{C}$ . An increase in the concentration of carbon shifts the equilibrium towards the right. When the solid solution is cooled rapidly from  $1030^\circ$ , the greater concentration of carbon in the solid phase may shift the internal equilibrium so far to the right that the solid solution becomes supersaturated with respect to carbide, which is therefore deposited. C. H. D.

**The Polyhedral Structure of Iron-Carbon Alloys.** N. J. WARK (*Metallurgie*, 1911, 8, 731—736. Compare this vol., ii, 52).—Martensite in quenched steels often forms large polyhedra. Quenching experiments with carbon steels almost free from other elements show that this structure is probably that of the original austenite solid solution, although it has not been found possible to obtain it, in low-carbon steels, entirely free from martensite, owing to the difficulty of undercooling such alloys. Steel etched with hydrogen chloride at high temperatures within the austenite region shows a polyhedral structure, whatever the proportion of carbon may be. C. H. D.

**Action of Heat on the Ochres. Allotropic Modifications.** A. BOUCHONNET (*Bull. Soc. chim.*, 1912, [iv], 11, 6—12. Compare Abstr., 1911, ii, 495).—The author describes the properties of some modified ochres. The density increases from the natural yellow ochre upwards through the various modifications to the black, obtained at  $1600^\circ$ . The plasticity diminishes with rise in temperature, and seems to have entirely disappeared at  $800$ — $850^\circ$ . The yellow and red ochres are soluble in acids, but the so-called " $\alpha$ -variety," obtained at  $950^\circ$ , and the other modifications are insoluble in all acids except hydrofluoric, even on heating. The  $\alpha$ -variety is highly magnetic. This property, however, disappears on prolonged heating, only to reappear at  $1600^\circ$ . W. G.

**A Compound of Ferric Sulphate and Alcohol. Constitution of Ferric Sulphate.** ALBERT RECOURA (*Compt. rend.*, 1911, 153, 1223—1226. Compare Abstr., 1909, ii, 552, 693).—The yellow

compound,  $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 3\text{H}_2\text{O}$ , obtained by dehydrating the hexahydrate at  $108^\circ$ , forms an alcoholic solution in which barium chloride fails to produce a precipitate of barium sulphate. The compound with alcohol,  $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 2\text{H}_2\text{O} \cdot 2\text{C}_2\text{H}_5\text{O}$ , previously described, loses half its water at  $105^\circ$  without changing in appearance; the remainder is lost simultaneously with the alcohol at  $115^\circ$ , the material becoming temporarily black. The alcohol does not appear to be united to sulphuric acid, since it is removed by solution in water, unlike the combined alcohol in ethyl ferrisulphate. These and other observations are explained by supposing that the trihydrate has the constitution  $\text{Fe}_2(\text{SO}_3)_3(\text{OH})_6$ , the salt in a manner resembling the green pentahydrate of chromic sulphate. W. O. W.

**The Form of Certain Silicate Precipitates.** RAPHAEL E. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 298—300).—The various forms assumed by the colloidal precipitates of ferric silicate are described. These different forms arise when drops of concentrated solutions of ferric chloride are brought into contact with a solution of sodium silicate under varying conditions. H. M. D.

**Red and Blue Cobaltous Hydroxide.** ARTHUR HANTZSCH (*Zeitsch. anorg. Chem.*, 1912, 73, 304—308).—Blue cobaltous hydroxide is generally regarded as a basic salt. It is found that when precipitated from a solution of the sulphate by an insufficient quantity of alkali, and washed with cold water until no more sulphuric acid is removed, the residue always contains much sulphate. Repeated boiling with water free from air, however, gradually removes most of the sulphate without altering the blue colour.

The red hydroxide is obtained by precipitating with an excess of alkali, washing with hot water in an atmosphere of hydrogen, and finally washing with alcohol and ether. It retains some water even after prolonged heating in nitrogen at  $300^\circ$ , whilst the blue hydroxide is completely dehydrated at  $170^\circ$ ; on the other hand, acetyl and benzoyl chlorides react much more vigorously with the red than with the blue compound.

The case is regarded as one of "chromo-isomerism," and the formulæ  $\text{Co}(\text{OH})_2$  and  $\text{H}_2\text{O} \cdots \text{CoO}$  are suggested for the red and blue compounds respectively. C. H. D.

**Solubility of Uranous Oxide in Certain Acids.** ALBERT RAYNAUD (*Compt. rend.*, 1912, 154, 1480—1482).—The uranous oxide employed was obtained by the ignition of uranyl oxalate. The oxide is readily soluble in nitric acid with formation of uranyl nitrate; aqua regia also dissolves it readily. It is less soluble in the other common acids, requiring 3100 grams of hydrochloric acid (D 1.17), 4650 grams of hydrobromic acid (D 1.52), 2200 grams of sulphuric acid (D 1.79), and over 12,000 grams of acetic acid to dissolve 1 gram of the oxide at  $17^\circ$ . The solubility is slightly greater in the boiling acids.

W. O. W.

**Pure Vanadium.** OTTO RUFF and WALTER MARTIN (*Zeitsch. angew. Chem.*, 1912, 25, 49—56).—Vanadium trioxide, melting at

about 2000°, gives better results in the preparation of pure vanadium than the pentoxide, on account of the ready fusibility of the latter, which causes it to pass into the slag. Vanadium trioxide, prepared by reducing the pentoxide in hydrogen below 550°, is mixed with aluminium and 2% of powdered carbon, and pressed into a crucible lined with magnesia. The crucible is covered and heated to redness after adding a layer of ignition mixture. The product contains 95% of vanadium. Reduction with carbon in an arc gives a less pure product. Products containing 95 to 97% of vanadium are obtained by moulding mixtures of the trioxide and carbon with starch into rods, sintering in an electric furnace at 1750°, and finally fusing in an arc. The impurity consists of carbon or oxygen, according to the proportions employed.

Vanadium carbide, VC, prepared in the resistance furnace, has m. p. 2750°,  $D^{18.7}$  5.405, and is silvery-white, highly crystalline, and extremely hard. When 6 grams of the powdered carbide are mixed with 4.76 grams of vanadium trioxide and a little starch solution, pressed into a zirconia crucible, and heated at 1950°, the metal is fused, and then contains V 98.11% and C 1.92%.

The melting points of different specimens of vanadium have been determined by heating in the electric vacuum furnace. Either oxygen or carbon raises the melting point of vanadium, and by extrapolating the two curves obtained from mixtures containing varying quantities of carbon and of oxygen, pure vanadium is found to melt at 1715°. The raising of the melting point is due to the formation of solid solutions with the oxide, VO, and the carbide. The density is also found by extrapolation, being lowered by impurities. The pure metal has  $D^{18.7}$  5.688. The heat of combustion of 1 gram to the pentoxide is 2456 cal.

C. H. D.

**Hetero-poly-acids containing Vanadic Acid.** WILHELM PRANDTL [and MAURICE HUMBERT] (*Zeitsch. anorg. Chem.*, 1911, 73, 223—238. Compare Düllberg, *Abstr.*, 1903, ii, 733; Prandtl and Lustig, *Abstr.*, 1907, ii, 477).—The complex vanadiselenites may be regarded as derived from a hexavanadic acid, and may then be formulated in accordance with Werner's theory. One molecule of a hexavanadate can combine with up to 12 mols. of selenious acid. The vanadiselenious acid,  $3V_2O_5, 4SeO_2, 4H_2O$ , which forms hydrates, may be represented as 1:4-hexavanadiselenious acid,  $H_4V_6O_{17}, 4H_2SeO_3$ , with  $4H_2O$  and  $8H_2O$ . The sodium, potassium, and ammonium salts are obtained by adding a 20—25% solution of selenious acid in excess to solutions of alkali vanadates. The following salts are described:  $Na_2H_2V_6O_{17}, 4H_2SeO_3$ , orange prisms;  $Na_2H_2V_6O_{17}, 4SeO_2, 2H_2O$ , dark red prisms;  $Na_2H_2V_6O_{17}, 4H_2SeO_3, 6H_2O$ , a bulky precipitate;

$K_3HV_6O_{17}, 4SeO_2$   
or  $K_2H_2V_6O_{17}, 4SeO_2$ , a bulky, orange precipitate;

$K_3HV_6O_{17}, 4SeO_2, 2H_2O$ ;  
 $K_2H_2V_6O_{17}, 4H_2SeO_3$ ;  $K_2H_2V_6O_{17}, 4SeO_2, 2H_2O$ ;  
 $(NH_4)_3HV_6O_{17}, 4SeO_2, H_2O$ ,

a yellow, pulverulent precipitate;  $(NH_4)_2H_2V_6O_{17}, 4SeO_2$ , an orange

precipitate. Higher proportions of  $\text{SeO}_2$  were found in some of the compounds prepared by Prandtl and Lustig (*loc. cit.*).

Ammonium 1:12-hexavanadiselenite,  $(\text{NH}_4)_3\text{HV}_6\text{O}_{17}\cdot 12\text{SeO}_2$ , 2 or  $4\text{H}_2\text{O}$ , forms red, transparent crystals with blue surface lustre, and the potassium salt is quite similar. The 2:5-hexavanadiselenites have the formula  $2\text{M}_4\text{V}_6\text{O}_{17}\cdot 5\text{H}_2\text{SeO}_3\cdot x\text{H}_2\text{O}$ , where  $\text{M} = \text{NH}_4, \text{K}, \text{Li}, \text{Na}$ .

The yellow vanadiselenites have the formula  $\text{M}_2\text{O}\cdot \text{V}_2\text{O}_5\cdot 2\text{SeO}_2\cdot x\text{H}_2\text{O}$ .

The complex vanaditungstates and vanadimolybdates described in the literature are reviewed and formulated as derivatives of hexavanadic acid.

C. H. D.

**Tantalum and Columbium Pentafluorides, and the Preparation of Pure Tantalic and Columbic Acids.** OTTO RUFF and EMIL SCHILLER (*Zeitsch. anorg. Chem.*, 1911, 72, 329—357).—Tantalum pentachloride is best prepared from the oxide by heating in a quartz tube to redness in a stream of chlorine and carbon tetrachloride. The chloride reacts with anhydrous hydrogen fluoride in a freezing mixture in a platinum apparatus (Abstr., 1907, ii, 268), and the resulting pentafluoride is purified by distillation under reduced pressure.

Tantalum pentafluoride forms large, colourless, doubly refracting prisms,  $D^{19.5} 4.744$ , m. p.  $96.8^\circ$  (corr.), b. p.  $229.2$ — $229.5^\circ/760$  mm. (corr.). The vapour pressure has been determined in a modified apparatus of Smith and Menzies (Abstr., 1910, ii, 1036) constructed of copper. The fluoride is inactive towards oxygen and most metals and non-metals up to its boiling point. It is rapidly decomposed by water, acids and alkalis, alcohol and ether. It forms potassium tantalum heptafluoride when fused with potassium fluoride.

Columbium pentafluoride is prepared in a similar manner, and forms colourless, refractive prisms,  $D^{18} 3.2932$ , m. p.  $75.5^\circ$  (corr.), and b. p.  $217$ — $220^\circ/760$  mm. (corr.). It is somewhat more reactive than the tantalum compound.

In order to improve the method of separation of tantalum and columbium by fractional crystallisation of their alkali double fluorides, determinations of the solubility of these salts in presence of varying quantities of hydrofluoric acid and potassium fluoride have been made, using pure hydrofluoric acid prepared by dissolving the anhydrous compound in water. The solubility of both fluorides diminishes rapidly with increasing concentration of potassium fluoride and decreasing concentration of hydrofluoric acid. The solubility increases rapidly with the temperature, and is always greater for the columbium salt than for the tantalum salt. A method of fractionation is described, based on these results, and suitable for the treatment of large quantities of material.

For the quantitative separation of tantalum and columbium, 0.5—1 gram of the mixed oxides is dissolved in hydrofluoric acid, the quantity of acid corresponding with an excess of 4.3%. Sufficient potassium fluoride is then added to combine with the columbium, the solution is evaporated, and the residue boiled with 0.75% hydrofluoric acid. After filtering the hot solution, the residue is washed twice with 10 c.c. of hot water. The filtrate is then evaporated, the residue

dried at  $120^{\circ}$  and dissolved in hot water, and *N*/10-potassium hydroxide is then added until the precipitate formed just dissolves. The solution is evaporated, the residue dissolved in 10 c.c. of hot water, and again evaporated. This is twice repeated, until the tantalum double salt remains. The united tantalum fluorides are then converted into oxides, and the columbium is estimated in the filtrate.

Tantalum is not carried off as vapour by hydrogen fluoride or ammonium fluoride, and the supposed acid fluorides of tantalum and columbium do not exist. The separation of titanium from the two other earths is best carried out by heating in a stream of chlorine and carbon tetrachloride, when titanium tetrachloride is first volatilised.

C. H. D.

**Interpretation of the "Protective Action" of Gelatin on Colloidal Gold.** GEORGE R. MINES (*Proc. physiol. Soc.*, 1911, xxii—xxiv; *J. Physiol.*, 43).—The experiments recorded confirm the view that the explanation of the "protective action" of gelatin is due to the formation of a thin coating of gelatin over the gold particles; this protects them from the action of electrolytes. W. D. H.

**Colloidal Gold and Platinum.** NICOLA PAPPADÀ (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 270—275. Compare this vol., ii, 157).—As a general rule, the influence of electrolytes on the coagulation of gold and platinum hydrosols is exactly the same as on the coagulation of colloidal silver. In regard to chemical activity, however, silver is much more active than either gold or platinum. Colloidal gold is not coagulated by mercuric chloride in the cold, neither is there any chemical action. When the solution is heated, coagulation takes place, but the mercuric salt is not reduced. When aqueous solutions of hydrocyanic acid or potassium cyanide are added to the gold hydrosol, its colour changes from dark violet to yellow. The yellow solution is not coagulated when active multivalent metal ions are added. When acted on by the halogens, colloidal gold is converted into the corresponding auric salts. Towards these chemical reagents the behaviour of platinum hydrosol is similar to that of gold.

H. M. D.

**Absorption of Hydrogen by Palladium at Small Pressures and Low Temperatures.** S. VALENTINER (*Ber. Deut. physikal. Ges.*, 1911, 13, 1003—1022).—The absorption of hydrogen by spongy palladium has been examined at  $-190^{\circ}$ ,  $-78^{\circ}$ , and the ordinary temperature for small values of the gas pressure. A glass tube of about 100 c.c. capacity was filled with purified hydrogen, and after its pressure had been determined by means of a McLeod gauge, the gas brought into contact with a known weight of palladium contained in a capillary tube. After equilibrium had been reached, the pressure in the apparatus was again determined by means of the gauge, and from the dimensions of the various parts of the apparatus, the amount of hydrogen absorbed by one gram of palladium could be calculated. By admitting successive quantities of hydrogen into the apparatus, it was possible to obtain the quantities of hydrogen absorbed for a series of pressures.

The data obtained in this way show that the absorption capacity of palladium for hydrogen increases very rapidly with falling temperature. The equilibrium pressure for palladium sponge, which contains 0.1% of hydrogen, amounts to 0.025 mm. at  $-78^{\circ}$  and 0.001 mm. at  $-190^{\circ}$ . The absorption coefficient also increases considerably with diminution of pressure, and this is especially marked at the temperature of liquid air. The determination of the true value of the equilibrium is, however, complicated by the fact that the absorptive capacity of the palladium is found to depend on its previous history.

On account of the extremely large absorptive capacity for hydrogen at  $-190^{\circ}$  and low pressures, palladium can be very conveniently employed for the removal of the last traces of hydrogen from other gases, and experiments are recorded which show that this can be done effectively.

H. M. D.

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## Mineralogical Chemistry.

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**Determination of the Crystallisation Power of Minerals.** V. SCHUMOFF-DELEANO and EMIL DITTLER (*Centr. Min.*, 1911, 753—757).—A small amount (about 0.5 mg.) of the powdered mineral was fused in a small silica dish on the heating stage of the microscope, and the temperature quickly reduced to a definite point below the melting point. After the temperature had remained constant for some time, the number of centres of crystallisation seen in the field of view were counted. These numbers are plotted against the temperatures, and different types of curves are so obtained. Spinel, gehlenite, and melilite exhibit a greater power of crystallisation than diopside, hedenbergite, and aegirite. L. J. S.

**Native Iron from Russian Island, Vladivostok.** A. A. INOSTZ-ANZEFF (*Zeitsch. Kryst. Min.*, 1911, 50, 61—62; from *Trav. Soc. Nat. St. Pétersbourg*, 1907, 35, *Sect. Géol. Min.*, 21—57).—The specimen described was obtained in a bore-hole passing through quartz-porphry and Triassic sandstone. It is brown and resembles limonite in appearance, but it has a much higher sp. gr. (7.007) than this, and it is strongly magnetic. On a fresh fracture, it shows a peculiar oolitic structure, with black grains set in a silver-white, metallic ground-mass. The structure of the metallic portion as seen under the microscope is not like that of other native irons, but is very similar to that of artificial cast iron, there being bands of ferrite, granular cementite, and a ground-mass of pearlite, whilst graphite is also present. Analysis by S. A. Jakowleff gave:

Fe.	Comb. C.	Free C.	Al.	Mn.	Si.	S.	Total.
93.87	0.33	2.87	0.16	0.66	1.55	0.04	99.48

In composition also the material is thus identical with artificial cast

iron. It is suggested that this "native cast iron" was formed by the action of the intruded igneous rock on coal and iron ore in the sedimentary rocks.  
L. J. S.

**Earth-gas in Transylvania in the Tertiary Basin.** JULIUS VON SZÁDECZKY (*Petroleum*, 1911, 6, 773).—A natural gas exists in the neighbourhood of Kissármás, which contains 99·25% methane, 0·75% nitrogen, and no trace of carbon monoxide, and is ejected in daily yield of over 912124 cubic metres and with a noise discernible at a distance of 10 kilometres. The geological aspect of the district is also described.  
F. M. G. M.

**A Hydrocarbon from the Diamond-washings of Bahia, Brazil.** JOHN CASPER BRANNER (*Amer. J. Sci.*, 1912, [iv], 33, 25—26).—The material is found as rounded masses beneath the diamond-bearing gravels at Chique-Chique in the State of Bahia. It is jet-black and opaque; and very friable, breaking with a conchoidal fracture; D 1·51, H 2½. Analysis, by L. R. Lenox, gave: water, 19·43; volatile combustible matter, 35·47; fixed carbon, 40·06; ash (mainly Al<sub>2</sub>O<sub>3</sub>), 5·07=100·03. The material is soluble in sulphuric acid, nitric acid, and potassium hydroxide, but insoluble in alcohol, ether, benzene, etc.  
L. J. S.

**Origin of Naphtha.** WLADIMIR N. IPATIEFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1437—1445 \*).—The author discusses the theories of the mineral and organic origin of naphtha and the reason for the displacement of the former by the latter during recent years. All the available geological data testify that original deposits of naphtha occur only where there has been life, and that emanation of naphtha has taken place only when it originated in presence of strata permeable to naphtha, secondary deposits being thus obtained. Support to the theory of organic origin is also given by the investigations of geologists and biologists on the destruction of life on the shores of seas and oceans, such as is occurring at the present time in the Black Sea, and by Andrusoff's observations on the formation of hydrogen sulphide in the Black Sea owing to this loss of life.

A further hypothesis of the formation of naphtha might be based on the various simple syntheses of representatives of the different classes of hydrocarbons. Reference is made to Sabatier's results, which explain the formation of naphtha from acetylene; to the formation of methane and ethylene by the action of water vapour on carbon in presence of lime (compare Vignon, *Abstr.*, 1911, ii, 391), and to the author's own experiments, which show that, under the influence of heat and pressure, ethylene condenses to higher hydrocarbons.

T. H. P.

**Application of Colloid Chemistry to Mineralogy and Geology.** Bauxite, a Natural Alumina Hydrogel. EMIL DITTLER and CORNELIO DOELTER (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 282—296).—The behaviour of the chief constituents of bauxites towards certain colouring matters has been examined, and the informa-

\* and *J. pr. Chem.*, 1911, [iii], 84, 800—808.

tion thus obtained has been applied, in combination with microscopic observations, to the examination and classification of bauxites from different sources. True bauxite is regarded as a hydrogel of alumina, which has a large capacity for taking up other substances, such as silica, water, carbon dioxide, sulphur dioxide, phosphoric oxide, and titanium dioxide.

H. M. D.

**Baddeleyite [Native Zirconia] from Montana.** AUSTIN F. ROGERS (*Amer. J. Sci.*, 1912, [iv], 33, 54—56).—This mineral, previously known only from Ceylon, Brazil, and the Island of Alnö (Sweden), has been found in a gneissoid corundum-syenite from near Bozeman, Montana. The minute crystals and grains are black with a sub-metallic lustre, and they occur embedded in the felspar and in the corundum, or more frequently on the surface of the latter. The mineral is infusible before the blowpipe (but fusible in the oxygen-gas blowpipe), and is decomposed by strong sulphuric acid. The corundum-syenite consists of felspar (microcline-micropertthite), biotite, and corundum, with subordinate amounts of muscovite, sillimanite, and zircon. The low percentage (about 44) of silica in this rock no doubt caused the zirconia to crystallise as baddeleyite rather than as zircon.

L. J. S.

**Analysis of Thorianite from Ceylon.** W. JAKÓB and STANISLAW TOLLOCZKO (*Bull. Acad. Sci. Cracow*, 1911, A, 558—563).—A specimen of Ceylon thorianite gave on analysis :

SiO <sub>2</sub> .	PbO.	Bi <sub>2</sub> O <sub>3</sub> .	CuO.	Ce <sub>2</sub> O <sub>3</sub> .	(La, Di) <sub>2</sub> O <sub>3</sub> .	Y <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	TiO <sub>2</sub> .
0.250	2.867	0.003	0.008	0.107	0.178	0.030	0.260	0.348	1.295
ZrO <sub>2</sub> .	CaO.	Rh.	ThO <sub>2</sub> .	U <sub>3</sub> O <sub>8</sub> .	H <sub>2</sub> O.	CO <sub>2</sub> .	He.	Insol.	Total.
0.920	0.17	0.008	65.370	23.470	0.605	0.275	0.225	0.150	99.67

Also As<sub>2</sub>O<sub>3</sub> (?), SnO<sub>2</sub> (?), Sb<sub>2</sub>O<sub>4</sub>, HgO, traces.

This result when compared with those of other observers (which are tabulated) shows, in most cases, a much larger amount of uranium oxide and a consequent decrease in thorium oxide. This may be explained by the fact that the mineral is really an isomorphous mixture of uranium and thorium oxides.

L. DE K.

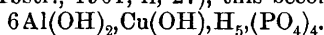
**Minerals Accompanying the Ferriferous Deposit of the Buca della Vena near Stazzema, Apuan Alps.** UGO PANICHI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 568—571).—Interposed between the calcareous rock and the iron ore at this place is a reddish-brown mineral of which the main portion is a reddish-brown, crystalline substance, D 2.88, having the following composition :

CaO.	FeO.	MnO.	CO <sub>2</sub> .	H <sub>2</sub> O.	Total.
52.58	1.21	0.98	43.10	2.46	100.33

The mineral is therefore a calcite containing iron and manganese. It bears crystals of pure calcite, and is traversed by veins of manganite with which a quantity of wad is associated. In the manganite, crystals of magnetite and of manganiferous siderite occur, whilst in the



near Lynch Station, Campbell Co., Virginia, shows thin layers of crystals cementing together irregular fragments of glassy quartz, and in part a drusy botryoidal surface. The minute crystals, not exceeding  $\frac{1}{3}$  mm. across, are triclinic with very nearly the same habit and angles as crystals of chalcosiderite ( $\text{CuO}, 3\text{Fe}_2\text{O}_3, 2\text{P}_2\text{O}_5, 8\text{H}_2\text{O}$ , or more probably  $9\text{H}_2\text{O}$ ), with which turquoise is regarded as isomorphous. The mineral is insoluble in hydrochloric acid, but soluble after ignition. No water is lost below  $200^\circ$ ; most is expelled below  $400^\circ$ , and all below  $650^\circ$ , the material being then green in colour. It is infusible before the blowpipe, but becomes brown. Analysis I, after deducting insoluble quartz, gives the figures under II, corresponding with the formula  $\text{CuO}, 3\text{Al}_2\text{O}_3, 2\text{P}_2\text{O}_5, 9\text{H}_2\text{O}$ . Written in the form of Penfield's turquoise formula (Abstr., 1901, ii, 27), this becomes



	$\text{P}_2\text{O}_5$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{CuO}$ .	$\text{H}_2\text{O}$ .	Insol.	Total.	Sp. gr.
I.	29.84	31.91	0.18	7.87	17.59	12.57	99.96	2.816
II.	34.13	36.50	0.21	9.00	20.12	—	99.96	2.84

L. J. S.

Pickeringite (= Picroallumogene) from the Island of Elba. GIOVANNI D'ACHIARDI (*Jahrb. Min.*, 1911, ii, Ref. 188; from *Proc. verb. Soc. Toscana Sci. Nat.*, 1910, 19, 23—25).—Analysis I is of a mineral labelled as "picroallumogene" recently collected from an iron mine in Elba, and II of an original specimen of the "picroallumogene" of G. Roster (1876). They prove the identity of the mineral with pickeringite, and there must be an error in the old analysis of Roster. The mineral is soluble in water. It forms fibrous crusts with a silky lustre and white colour, or when containing impurities of a yellow, rose-red, or brown colour. The fibres give bright polarisation-colours and an extinction-angle of  $30^\circ$ ; the optical sign is positive:

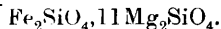
	$\text{SO}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{MgO}$ .	$\text{H}_2\text{O}$ .	Insol.	Total.
I.	37.11	10.21	5.25	[47.21]	0.22	100.00
II.	36.70	10.42	5.21	[46.89]	0.78	100.00

L. J. S.

Composition of the Platiniferous Dunite of the Urals. S. PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1911, 9, 87, 294—308).—Numerous analyses of dunite disclose the composition as follows:

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Cr}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{MgO}$ .	$\text{TiO}_2$ .	Total.
40.13	0.45	0.49	8.45	50.45	0.03	100.00

The composition corresponds with that of an olivine,



The rock is of remarkably uniform composition and free from calcium.

G. D. L.

Bertrandite from Iveland in Southern Norway. THOROLF VOGT (*Zeitsch. Kryst. Min.*, 1911, 50, 6—13).—Pseudomorphs after large hexagonal prisms of beryl, from the felspar quarries in the pegmatite-veins at Iveland in Sætersdalen, consist of a compact mixture

of muscovite, bertrandite, and quartz, together with some phenacite, secondary beryl, chlorite, and orthoclase. The bertrandite, a mineral not before recorded from Norway, forms minute scales to plates 2 cm. across. In cavities minute crystals are rarely developed; these are orthorhombic and hemimorphic; they show a new crystal-form,  $k\{023\}$ , and are often twinned on  $e(011)$ . There are cleavages parallel to  $a(100)$ ,  $b(010)$ , and  $m(110)$ , the two former showing a pearly lustre.  $D^{20}$  2.597;  $H$   $6\frac{1}{2}$ . Refractive indices (Na),  $\alpha=1.5914$ ,  $\beta=1.6053$ ,  $\gamma=1.6145$ ;  $2V=74^{\circ}32'$ . Analysis of free-h, clear material gave:

SiO <sub>2</sub> .	AlO.	CaO.	H <sub>2</sub> O.	Total.
51.03	41.45	0.25	7.18	99.91

agreeing closely with the formula  $H_2Gl_4Si_2O_9$  or  $2Gl_2SiO_4 \cdot H_2O$ . The water is expelled only at a red-heat. The suggestion of Vrba that bertrandite may be isomorphous with hemimorphite, and with the formula,  $Gl_2SiO_4 \cdot H_2O$ , is thus not confirmed. L. J. S.

**Nephrite Occurrences in the Alps and in the Frankenwald.** OTTO A. WELTER (*Jahrb. Min.*, 1911, ii, 86—106).—Masses of nephrite have been discovered in association with serpentine and gabbro rocks at the following localities. Salux in Oberhalbstein, Grisons (anal. I by F. Mathei, II by H. Ludwig); here only as a loose block. A large mass in situ between serpentine and spilite at Mühlen in the Val da Faller, Oberhalbstein (anal. III by W. Mau, IV by L. Hezner); the somewhat weathered material consists of a felted mass of actinolite fibres with chlorite, pale green garnet, picotite, and apatite, and it presents the same characters as the nephrite implements of the ancient lake-dwellings in Switzerland. In serpentine and diabase at Schwarzenbach on the Saale, in Frankenwald (anal. V by Stoepel); and in gabbro-serpentine rocks in the Harz (J. Uhlig, *Abstr.*, 1911, ii, 46).

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	CaO.	H <sub>2</sub> O (comb.)	H <sub>2</sub> O (hygrosc.)	Total.	Sp. gr.
I.	57.1	2.3	4.0	—	21.2	13.4	1.9	—	}	3.025
II.	57.1	1.1	5.0	—	23.0	12.4	—	—		
III.	56.1	6.4	2.1	—	20.2	13.7	2.4	—	}	3.02—2.98
IV.*	47.85	4.65	1.28	2.02	26.98	9.95	5.82	0.17		
V.	55.41	2.79	—	3.32	22.41	11.75	3.80	0.11	99.59	3.01—3.02

\* Also  $P_2O_5$ , 0.39;  $MnO$ , 0.15;  $NiO$ , 0.47;  $Na_2O$ , trace;  $K_2O$ , 0.12;  $TiO_2$ ,  $Cr_2O_3$ , nil.

The nephrite of these occurrences has probably been formed by the "edem-metamorphism" (G. Steinmann, 1908) of dyke rocks from the gabbro mass intrusive into the serpentine. L. J. S.

**Apophyllite from Toms, Siberia.** P. P. PILIPENKO (*Zeitsch. Kryst. Min.*, 1911, 50, 71—73; from *Annuaire Géol. Min. Russie*, 1908, 10, 189—211).—A detailed description is given of apophyllite crystals found lining geodes in melaphyre on the Lower Tersya, a tributary of the Tom. The crystals show zonal structures, optical anomalies, etched figures, contraction figures, and glide-planes. Analysis gave:

SiO <sub>2</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	K <sub>2</sub> O.	F.	N.	H <sub>2</sub> O.	Total.
52.12	0.26	24.56	5.23	1.73	0.02	16.63	100.55

The mineral loses water quickly at 250—260° with the production of "dissociation figures," etc., and it can be completely dehydrated at as low a temperature as 180—190° if the heating is prolonged and the material finely divided.

L. J. S.

**An Apophyllite-Analcite Bomb from Monte Somma, Vesuvius.** STANISLAUS J. THUGUTT (*Centr. Min.*, 1911, 761—765).—Zeolites are of rare occurrence at Vesuvius, and only phillipsite, scolecite, thomsonite, and analcite have hitherto been recorded from this locality. Analcite forms the main portion of the bomb now described, occurring as small trapezohedra, which show a milky cloudiness and usually a rose-red colour (due to enclosed hæmatite). Analysis I shows a slight excess of silica over that (54.63%) required by the analcite formula ( $\text{NaAlSi}_2\text{O}_6, \text{H}_2\text{O}$ ), and it is suggested that this is present as opal, giving rise to the milkiness of the crystals. The analcite is pseudomorphous after leucite ( $\text{KAlSi}_2\text{O}_6$ ), which contains rather more silica than analcite, and the difference appears to have separated as opal when the leucite was converted into analcite. The presence of opal in cloudy crystals of analcite can be demonstrated by staining with methylene-blue.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	F.	H <sub>2</sub> O.	O for F.	Sp. gr.
I.	56.27	22.24	—	—	0.04	13.39	—	8.45	100.39	2.25—2.265
II.	52.76	—	23.69	0.05	5.14	0.65	1.35	16.85	99.62	2.37

The apophyllite is present as clear, asparagus-green crystals (anal. II). It has been derived, together with some calcite, from wollastonite. This apophyllite-analcite bomb thus represents an altered form of the wollastonite-leucite bombs which have been found as rarities at Monte Somma.

L. J. S.

**Russian Zeolites: Leonhardite and Laumontite from the Crimea.** ALEX. FERSMANN (*Zeitsch. Kryst. Min.*, 1911, 50, 75—76; from *Trav. Mus. Géol. Pierre le Grand, Acad. Sci. St. Pétersbourg*, 1908, 2, 103—150).—Laumontite ( $\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24}, 8\text{H}_2\text{O}$ ) and leonhardite are regarded as distinct species. Of the latter, two kinds are distinguished, namely: secondary leonhardite,  $\text{Ca}_2\text{Al}_4\text{Si}_8\text{O}_{24}, 7\text{H}_2\text{O}$ , which results when laumontite loses part of its water on exposure to the air; and primary leonhardite,  $(\text{Ca}, \text{K}, \text{Na})_2\text{Al}_4\text{Si}_8\text{O}_{24}, 7\text{H}_2\text{O}$ , which results by the weathering of diorite rocks in the Crimea, and is of importance in the formation of soils. Analyses of primary leonhardite from two localities near Simferopol gave:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	H <sub>2</sub> O	110°.	>110°.	Total.	Sp. gr.
50.94	22.30	0.12	7.65	—	4.01	2.06	2.03	11.39	100.50	2.9992	—2.3094	
51.30	21.01	0.55	7.58	0.19	4.02	2.90	1.96	11.14	100.65	2.3134	—2.3214	

L. J. S.

**Composition of Nephelite.** N. L. BOWEN (*Amer. J. Sci.*, 1912, [iv], 33, 49—54).—The excess of silica over that required by the orthosilicate formula  $(\text{Na}, \text{K})\text{AlSiO}_4$ , which is invariably shown by analyses of nephelite, can be imitated in the artificial soda-

nephelite,  $\text{NaAlSiO}_4$  (hexagonal,  $\omega=1.537$ ,  $\epsilon=1.533$ ,  $D\ 2.619$ ). By fusing together sodium carbonate, alumina, and silica in the proportions required for this formula there is always a partial volatilisation of the soda, and the product contains some corundum in addition to the soda-nephelite. The corresponding excess of silica cannot, however, be detected under the microscope, and it must, therefore, be held in solid solution in the soda-nephelite. Mixtures containing an excess of silica up to that given by  $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 2.2\text{SiO}_2$  are completely crystalline and perfectly homogeneous. This lies in the diagram (mentioned below) on the line between soda-nephelite and albite ( $\text{NaAlSi}_3\text{O}_8$ ); and it seems probable that, with a still greater excess of silica, albite should separate.

When the results of nephelite analyses are plotted on a triangular diagram, with  $\text{SiO}_2$ ,  $\text{K}_2\text{O}, \text{Al}_2\text{O}_3$ , and  $\text{Na}_2\text{O}, \text{Al}_2\text{O}_3$  at the three corners, it is seen that the composition of the mineral cannot be expressed by the mixing of any two components. With three components a number of alternatives are possible. From the experimental data noted above, the three most likely components are those recently suggested by Schaller (Abstr., 1911, ii, 992), namely, the molecules  $\text{NaAlSiO}_4$  (soda-nephelite),  $\text{KAlSiO}_4$  (kaliophilite), and  $\text{NaAlSi}_3\text{O}_8$  (albite). (Compare also Foote and Bradley, Abstr., 1911, ii, 122.)

L. J. S.

**Some Rock-forming Minerals from Hungary.** BELA MAURITZ (*Jahrb. Min.*, 1911, ii, Ref. 191—194; from *Földtani Közlöny, Budapest*, 1910, 40, 581—590).—The following analyses are given: I, Microcline from the elæolite-syenite of Ditró; molecular percentages Ab 31, Or 69; optical extinction on (001) = +17°, on (010) = +6°. II, Oligoclase [?] from the miascite variety of the same rock;  $\text{Ab}_{64}\text{Or}_{31}\text{An}_5$ . III, Large feldspars from pebbles of pegmatite in the Ditró stream;  $\text{Ab}_{82.9}\text{An}_{12.0}\text{Or}_{5.1}$ ; extinction on (001) = +2°, on (010) = +13°. IV, Elæolite as crystals 4—5 cm. across from the elæolite-syenite of Ditró; the material is quite fresh, but encloses a few small needles of ægirite. V, Amphibole, in crystals several cm. in size from a pegmatitic facies of the elæolite-syenite of Ditró;  $c:t=11^\circ$ , optic axial angle very small. VI, Albite crystals on a matrix of chalybite from Sajohaza, Com. Gömör;  $\text{Ab}_{99}\text{An}_{0.5}\text{Or}_{0.5}$ ; extinction on (001) = +4°30', on (010) = +19°. VII, Garnet (almandine) from the andesite of the Garnet Hill at Szokolhyahuta, Com. Nograd. VIII, Olivine crystals several cm. across occurring as enclosures in the basalt of Medves, near Salgó-Tarján; molecular

	$\text{SiO}_2$ .	$\text{TiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{MnO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .	$\text{H}_2\text{O}$ .	Total.
I. 65.29	—	—	19.06	trace	—	—	trace	—	3.44	11.47	0.24	99.50
II. 60.28	—	—	22.40	—	—	—	1.17	0.09	8.44	6.37	1.61	100.36
III. 63.51	—	—	22.14	—	—	—	2.65	trace	10.13	1.00	0.62	100.05
IV. 43.96	—	—	33.01	0.87	—	—	—	—	15.84	5.39	0.67	99.74
V. 37.69	5.67	—	13.41	6.33	10.43	0.43	10.97	8.61	3.66	2.33	—	99.53
VI. 68.95	—	—	19.60	—	—	—	0.13	—	11.72	0.10	—	100.50
VII. 37.20	—	—	20.32	1.79	28.67	1.56	5.86	4.28	0.34	0.05	—	100.07
VIII. 39.22	—	—	—	—	16.57	—	—	44.01	—	—	—	99.80
IX. 42.59	3.54	—	10.63	6.52	5.56	0.87	21.47	7.86	1.67	—	—	100.21
X. 61.27	—	—	24.15	trace	—	—	4.99	—	8.47	1.00	0.42	100.30

percentages  $\text{Fe}_2\text{SiO}_4$  17.5,  $\text{Mg}_2\text{SiO}_4$  82.5. IX, Augite, pitchy-black crystals several cm. across, occurring as enclosures in the same rock; the dispersion is very strong, probably owing to the large amount of titanium present. X, Oligoclase, crystals 7–8 cm. across occurring as enclosures in the same rock;  $\text{Ab}_{71.1}\text{An}_{28.2}\text{Or}_{5.7}$ ; extinction on (001) =  $+1^\circ$ , on (010) =  $0^\circ$ .  
L. J. S.

**Glaucinite from the Kurische Nehrung, East Prussia.**  
ARRIEN JOHNSEN (*Zeitsch. Kryst. Min.*, 1911, 50, 90; from *Schriften phys.-ökon. Ges. Königsberg i. Pr.*, 1908, 49, 51–60).—Analysis of a green mineral occurring in this spit of sand proves it to be glaucinite. The mineral has probably been derived from the Lower Oligocene beds of the neighbourhood.

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{FeO}$	$\text{MgO}$	$\text{CaO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{H}_2\text{O}$	Total
49.67	9.29	19.88	1.28	4.03	1.95	3.00	3.68	7.88	100.66

L. J. S.

**Poechite, an Iron Manganese Ore from Vareš, in Bosnia.**  
FRIEDRICH KATZER (*Oesterr. Zeitsch. Berg. Hüttenw.*, 1911, 59, 229–232).—A specimen of the mineral poechite, obtained from Vareš, was amorphous, with D 3.65–3.75, and hardness by Mohs scale of 3.5–4; its chemical composition was:

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{MnO}$	$\text{CaO}$	$\text{MgO}$	$\text{BaSO}_4$	P.	S.	$\text{H}_2\text{O}$
15.28	3.66	49.5	14.77	1.96	0.84	0.86	0.42	0.03	12.06

with traces of Cu, Pb, Zn, and  $\text{CO}_2$ ; and corresponding with the formula:  $(\text{MnO})_2\text{SiO}_3, 2(\text{FeO})_2\text{SiO}_3, 5\text{H}_2\text{O} + 2\text{Fe}_2\text{O}_3, 3\text{H}_2\text{O}$ .

F. M. G. M.

### Physiological Chemistry.

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**Gaseous Metabolism of Animals with Plain and Striated Musculature.** OTTO COHNHEIM (*Zeitsch. physiol. Chem.*, 1912, 76, 298—313).—The investigation was undertaken with the view of ascertaining whether animals with smooth muscles differ in their gaseous metabolism from those in which the muscles are striated. The animals used were various crustacea, molluscs, and worms. No typical differences were discovered between animals in relation to their muscular structure. The numerous analyses made are given in tabular form. The gaseous metabolism in these invertebrates is always small, although perhaps not much lower than in the smooth muscles of vertebrates. W. D. H.

**The Primary and Accessory Respiration.** FR. BATTELLI and (Mile.) LINA STERN (*Biochem. Zeitsch.*, 1912, 38, 163—165).—The

authors reply to some criticisms of Harden and Maclean (Abstr., 1911, ii, 905), who failed to obtain the same results as themselves in experiments on pnein. They maintain the correctness of their own experimental results. S. B. S.

**The Specific Action of Carbon Dioxide on the Respiratory Centre.** ERNST LAQUEUR and FRITZ VERZÁR (*Pflüger's Archiv*, 1911, 143, 395—427).—The respiratory centre is excited by carbon dioxide and by other acids (hydrochloric, acetic). The cause, however, is not increase in the concentration of hydrogen ions, but to the amount of  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ , or  $\text{HCO}_3'$  liberated in the tissues by the acid. The stimulating effect of carbon dioxide on the respiratory centre is specific; in acetic acid, however, the aceto-ions form the specific factor.

W. D. H.

**The Influence of Adrenaline on Gaseous Metabolism.** PAUL HÁRI (*Biochem. Zeitsch.*, 1912, 38, 23—45).—The experimental method employed for measuring the gaseous exchanges was Tangl's modification of Zuntz-Geppert's method. It was found that adrenaline in doses of 0.0005 to 0.001 gram per kilo. of body-weight, when given intraperitoneally, and of 0.0001 to 0.0002 gram when given intravenously, cause measurable changes in the gaseous metabolism of dogs. The changes consist, in the case of curarised animals, in a considerable diminution of the oxygen consumption and a slight diminution of the carbon dioxide production, and consequently an increase in the respiratory quotient. This result indicates that the carbohydrates take a larger part in the general metabolism, a fact which is in accord with the observed glycaemia after administration of adrenaline and the so-called "sugar-mobilisation"; in other words, adrenaline causes increased combustion of the sugars. The rise of blood-pressure and the "sugar mobilisation" occur at the same time. S. B. S.

**The Influence of Acids on the Reduction of Arterial Blood.** G. C. MATHISON (*J. Physiol.*, 1911, 43, 347—363).—A simple method for bubbling gases through blood is described. In the present experiments this method was used for observations on the rate of reduction of arterial blood by the passage of a current of nitrogen. The reduction is accelerated by the presence of carbon dioxide, and also by lactic, acetic, formic, hydrochloric, and sulphuric acids. This effect is mainly due to change in concentration of hydrogen ions, but there are indications that this is not the sole factor. Since concentrations of carbon dioxide or lactic acid, such as occur in the tissues during deficient oxygenation, frequently double the rate at which arterial blood gives up its oxygen at low oxygen tensions, their presence must be an important factor in tissue respiration. W. D. H.

**The Relative Rates of Oxidation and Reduction of Blood.** SOROKU OINUMA (*J. Physiol.*, 1911, 43, 364—373).—The rate of reduction of blood is greatly increased and that of oxidation somewhat retarded by a rise of temperature. Carbon dioxide not only increases the rate of reduction, but retards the rate of oxidation. At the

temperature, and carbon dioxide tensions of the body, the curves representing the rate of reduction by a neutral gas (hydrogen) and of oxidation are symmetrical with those produced by a mixture equivalent to alveolar air. If the amount of oxygen in this mixture is halved, the rate of oxidation is halved also. W. D. H.

**The Electrometric Method for Measuring the Reaction of the Blood at Body Temperature.** KARL ALBERT HASSELBALCH and CHR. LUNDSGAARD (*Biochem. Zeitsch.*, 1912, 38, 77—91).—In the investigations, Hasselbalch's apparatus (Abstr., 1911, ii, 182) was employed. The hydrogen-ion concentration at 38.5 under a carbon dioxide tension of 40 mg. mercury was  $0.44 \times 10^{-7}$ . The variations of the hydrogen-ion concentration due to the respiratory changes of carbon dioxide tension are measurable quantities. The results indicate the presence of "buffer" substances in the blood to prevent large changes in the hydrogen-ion concentration, a fact which was ascertained by measuring the variations of this constant under different carbon dioxide tensions with different solutions, such as the Sørensen's phosphate mixtures. The importance of the slightly alkaline reaction of the blood in regulating the variations of the hydrogen ion concentration was demonstrated by measuring changes when the blood was made slightly acid. The concentration of the whole blood is greater than that of serum, and less than that of the corpuscles under the same carbon dioxide tension. It is suggested that for clinical purposes, the hydrogen-ion concentration of the blood should be measured under the mean carbon dioxide tension of the alveolar air. S. B. S.

**The Nitrogen and Sulphur Content of Human Blood.** KENJI KOJO (*Zeitsch. physiol. Chem.*, 1912, 76, 170—172).—Two specimens of blood were obtained from women suffering from uterine operations. In both the percentage of nitrogen was 3.8; that of sulphur was 0.19 in one case, and 0.21 in the second. W. D. H.

**Physiology of Blood Sugar. IV. The Carbohydrates of Red Corpuscles.** E. FRANK and A. BRETSCHNEIDER (*Zeitsch. physiol. Chem.*, 1912, 76, 226—233. Compare Abstr., 1911, ii, 301, 409).—Washed blood corpuscles yield no dextrose, because the dextrose is removed by the process of washing. The fresh red corpuscles of man, dog, cat, and rabbit all contain dextrose in considerable amount. There is also present in both plasma and corpuscles a complex carbohydrate of uncertain nature; it is not fermentable with yeast, but after boiling it with dilute acid, a fermentable sugar is obtained from it. W. D. H.

**The Distribution of Reducing Substances in Blood.** IVAR BANG (*Biochem. Zeitsch.*, 1912, 38, 166—167).—In view of the recent controversies as to the distribution of sugars in blood, the author insists on the fact that the presence of dextrose or other sugars in the corpuscles has not yet been positively demonstrated. S. B. S.

**Action of Salts on the Coagulation of the Blood.** C. GESSARD (*Compt. rend.*, 1911, 153, 1241—1243).—The fact that blood from which calcium has been removed by the addition of an oxalate is no longer coagulable has been thought to be due to an inhibitory action of the excess of soluble oxalate. On the other hand, it has been supposed that calcium is essential to the coagulation of blood. In the author's opinion, the former view is the more correct, and experiments are described which support this contention. W. O. W.

**The Individual Differences of the Blood Corpuscles.** LUDWIG DIENES (*Biochem. Zeitsch.*, 1912, 38, 159—160).—A reply to a criticism of Rusznyák (*Abstr.*, 1911, ii, 1108). S. B. S.

**Substances which Constrict and Dilate the Blood-vessels of the Frog.** S. SAMELSON (*Arch. exp. Path. Pharm.*, 1911, 66, 347—351).—The method of Laewen and Trendelenburg was employed. Choline was found to act as a vaso-constrictor, and it is thus considered not to be an antagonist of adrenaline. Substances of the digitalin group act in the same way, except strophanthin, which causes vasodilatation. Bile acts as a vaso-dilator, but a second dose causes constriction; the second effect is attributed to some intermediate substance formed from the bile salts. W. D. H.

**The Influence of Diuretics of the Purine Series on the Permeability of the Blood-vessels.** FELIX GAISBÖCK (*Arch. exp. Path. Pharm.*, 1911, 66, 387—397).—The same alteration in the water and sodium chloride concentration of the blood is produced by diuretics of the purine group as is produced by simple bleeding. This holds for normal animals, and for those from which the kidneys have been removed. It is independent of the previous state of chlorine nutrition. This gives no support to the view that purine derivatives increase the permeability of the blood-vessels. W. D. H.

**Total Energy Exchanges of Intact Cold-blooded Animals at Rest.** ARCHIBALD V. HILL (*J. Physiol.*, 1911, 43, 379—394).—The rate of heat production for frogs, snakes, and newts measured in the author's micro-calorimeter is about 0.5 calorie per hour at 20°, either in oxygen or air. A rise of 10° in frog and snake increases this rate two or three times. If the rate is calculated for 37°, it would be much the same as in man and in other large warm-blooded animals, but less than in small warm-blooded animals. In the newt, a rise of 10° only increases the rate 1.5 times; this may be due to a rudimentary form of heat-regulation. Fasting produces a decline in the rate to a constant value. W. D. H.

**Enzyme of Saliva which Decomposes Di- and Tri-peptides.** ARTHUR H. KOELKER (*Zeitsch. physiol. Chem.*, 1911, 76, 27—36).—Experiments on the hydrolysis of alanyl-glycine by saliva from nine different sources gave positive results in every case. The saliva was sometimes slightly acid or slightly alkaline, and sometimes neutral. Further experiments with *D*-alanyl-*D*-glycine, glycyl-*L*-tyrosine, racemic

leucyl-glycine, and racemic glycyl-alanine showed that all these substances, except the last, are hydrolysed.

The tripeptide, *l*-leucyl-glycyl-*d*-alanine, yields *l*-leucine and glycyl-*d*-alanine. In this case, therefore, the action of saliva is identical with that of the erepsin from dogs' intestines. N. H. J. M.

**The Distribution of Enzymes in the Stomach and Intestines of Fish.** OSW. POLIMANTI (*Biochem. Zeitsch.*, 1912, 38, 114—128).—The following fish were used as subjects of experiment: *Scyllium catulus*, *Scyllium canicula*, *Box salpa*, *Conger vulgaris*. The enzymes were extracted from various parts of the mucosa by means of Hamburger's agar-agar-gelatin cylinders. The pepsin, pepsinogen, and chymosin distribution in the stomach varied in the different varieties of fish, but the largest quantities were always found in those parts of the stomach where the food remains longest. Amyolytic ferments and invertase were never found in the stomachs. The lipase distribution varied in the different fish investigated. Erepsin increases in quantity in the passage from the duodenum towards the rectum. S. B. S.

**The Secretion of Gastric and Pancreatic Juice.** SVANTE ARRHENIUS (*Medd. K. Vetensk. Nobelinst.*, 2, No. 1, 1—20).—The author discusses the results obtained by Khigine, Lobasoff, Lönnqvist, and London on the influence of various foodstuffs on the rate of digestion, and the rates of secretion of the juices and their compositions, in experiments on dogs, most of which were carried out by the technique of Pawloff. The main conclusion drawn from the various results is that the mean amount of gastric secretion within a given time (which is less than that of the digestion time) is proportional to the square-root of the amount of foodstuff. A similar law applies to the relationship between the amount of pancreatic juice secreted and the amount of acid causing the secretion. Phosphoric, lactic, and acetic acids in this case have a more powerful effect than hydrochloric acid. Similar conclusions can be drawn as to the laws governing the secretion of bile from the limited number of experiments on record. S. B. S.

**The Biological Importance and Metabolism of Proteins.** V. **The Metabolism of Young Dogs Fed on Meat, and the Products of the Artificial Digestion of Meat.** GIUSEPPE BUGLIA (*Zeitsch. Biol.*, 1911, 57, 365—396).—The experiments recorded confirm the previous work of others that the cleavage products obtained by digesting meat are of equal metabolic value to the meat itself. The former, indeed, are more readily absorbed; the urine under these conditions contains a relatively large amount of nitrogen in the form of ammonia and amino-acids. This militates against the view held by some observers that synthesis of protein from its cleavage products occurs in the wall of the intestine. W. D. H.

**Protein Absorption.** III. OTTO COHNHEIM (*Zeitsch. physiol. Chem.*, 1912, 76, 293—297).—Experiments on fishes are described in

which the absorption of tyrosine, alanine, sodium aspartate, and glutamic acid was studied. It was found in all cases that a partial splitting off of ammonia took place, and it is considered probable that this also occurs in the absorption of customary diets. Experiments on higher animals are contemplated. W. D. H.

**The Ovarian Factor Concerned in the Recurrence of Œstrus.** F. H. A. MARSHALL (*Proc. Physiol. Soc.*, 1911, xxi—xxii; *J. Physiol.*, 43).—In the dog, the interstitial cells in the ovary appear to be the source of the internal secretion formed during "heat," and not the corpora lutea. W. D. H.

**The Reduction Ferments. The Presence of a Co-ferment of Perhydridase in Animal Tissues.** ALEXIS BACH (*Biochem. Zeitsch.*, 1912, 38, 154—158).—Animal tissues contain a co-ferment, capable of accelerating the reduction of nitrates by milk, which is stable on heating, is not precipitated by alcohol, is easily dialysable, and not destroyed when a stream of air is led through the solution. The liver is richest in the co-ferment, and then follow the other organs in the following order: kidneys, spleen, brain, and lungs. It is suggested that the co-ferment may be an alloxan-like substance, which when it acts on amino-acids produces therefrom aldehydes, with scission of ammonia (Strecker's reaction). S. B. S.

**The Chemistry of the Cell Granules. The Composition of the Eosinophile Granules of the Bone-Marrow of the Horse.** EUGEN PETRY (*Biochem. Zeitsch.*, 1912, 38, 92—112).—The granules from the bone marrow were prepared by washing it several times with water containing ether and centrifugalising, then treating the residue with trypsin, as the granules resist digestion by this enzyme. The product thus obtained was examined chemically, and found to contain sulphur, but no phosphorus, and to behave generally as a protein. In its general properties it appears to behave like elastin and horn. The ash contains relatively large quantities of iron. The iron is not, however, bound in the form of hæmatin, but appears to exist in a somewhat labile form, and can be detected by somewhat prolonged action of ordinary reagents for iron, and can also be separated from a state of organic combination by trypsin. A method is given by means of which iron-containing granules can be obtained from the blood. A description is given of the microscopic appearances of the granules, and the conclusion is drawn that it is probable that these granules play an important part in the iron transport in the body. S. B. S.

**The Duration of Contraction of Plain Muscle.** OTTO COHNHEIM and J. VON UEXKÜLL (*Zeitsch. physiol. Chem.*, 1912, 76, 314—321).—The prolonged contraction (tonus) of plain muscle was studied in various invertebrate animals; it is accompanied with an increase in oxygen consumption, and this is roughly parallel to the amount of work done. Numerical details are given. W. D. H.

**The Influence of Calcium on the Action of Muscular Excitation by their Constant Current.** EDUARD KAHN (*Pflüger's Archiv*, 1911, 143, 428—452).—If calcium is added in excess to a physiological saline solution, the irritability of muscle (frog's uncurarised sartorius) to the constant current is increased.

W. D. H.

**The Passage of Colostrum into Milk, Especially in Relation to Nitrogenous Substances (Cow, Sheep, Mare).** ST. ENGEL and A. DENNEMARK (*Zeitsch. physiol. Chem.*, 1912, 76, 148—158).—The properties of colostrum and its passage into milk are about the same in cows which are primipara or multipara. In the disease of cows known as milk fever, the milk may remain in the colostrum state for a week. The colostrum of the sheep behaves like that of the cow, but the colostrum properties are not so marked. The colostrum of the mare is richer in caseinogen than the milk. The acidity in all three animals' colostrum is high. The change in acidity occurs simultaneously with the change in the protein.

W. D. H.

**Mechanism of Milk Secretion.** KENNETH MACKENZIE (*Quart. J. exp. Physiol.*, 1911, 4, 306—330).—The secretion of milk is not under the direct influence of the nervous system; neither section nor stimulation of the nerves supplying the mammary gland has any effect on the secretion. Pilocarpine which stimulates, and atropine which inhibits, secretory nerve-endings have no effect on the secretion of milk. The agents which cause activity of the gland, or the reverse, reach it by the blood stream. The following organs produce hormones, which stimulate the gland to activity: pituitary body, corpus luteum, pineal body, involuting uterus, and the lactating gland itself; of these, the pituitary (posterior lobe) is the most powerful. Extracts of the bird's pituitary also contain the galactagogue substance. Hormones which inhibit the mammary secretion are produced by the foetus and the placenta.

W. D. H.

**The Iron Content of Cow's Milk.** F. EDELSTEIN and F. VON CSONKA (*Biochem. Zeitsch.*, 1912, 38, 14—22).—The iron was estimated by various methods, including the recently published colorimetric method of Lachs and Friedenthal (*Abstr.*, 1911, ii, 542). When the milk was collected directly into glass vessels, the iron content was found to vary between 0.4 and 0.7 mg. of iron per litre (average 0.5 mg.). The fact that this result is smaller than that recorded by earlier observers is due to the method in which the milk was collected, being kept entirely out of contact with metallic vessels. Nevertheless, the quantity of iron in cow's milk is only one-third to one-half of that in human milk.

S. B. S.

**Influence of Salts on the Action of Rennet on Milk.** A. F. STANLEY KENT (*Proc. Physiol. Soc.*, 1911, xxiv; *J. Physiol.*, 43).—Certain salts (not mentioned) increase the amount of curd obtainable from a given quantity of milk by the action of rennet.

W. D. H.

**The Passage of Drugs into the Sweat.** HERMANN TACHAU (*Arch. exp. Path. Pharm.*, 1911, 66, 334—346).—A great number of

medicaments (iodine, bromine, boric acid, phenol, salicylic acid, salol antipyrine, methylene-blue) are excreted in the sweat. The amount is, however, extremely small; they pass into other secretions, milk, bile, etc., in larger quantity. The amount, however, may be sufficient to cause skin eruptions in certain cases.

W. D. H.

**Physico-chemical Researches on Animal Liquids. VIII. Chemical Reaction of Urine.** G. QUAGLIARIELLO (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 659—666).—The author has estimated the phosphoric acid by titration, and measured the concentration of the hydrogen ions and the neutralising power in the case of a number of fresh samples of urine from healthy individuals. The concentration of hydrogen ions was determined by means of a hydrogen electrode, 0.01*N*-hydrochloric acid being the second solution, and a solution of potassium chloride being used to connect it with the urine. The quantities of alkali and of acid which must be added to the urine to make the concentrations of the hydrogen ions  $1 \times 10^{-9}$  and  $2 \times 10^{-4}$  respectively are called the potential acidity and potential alkalinity of the urine, and the sum of the two is the neutralising power. The degree of acidity found varies from  $82.6 \times 10^{-7}$  to  $2 \times 10^{-7}$  gram-equivalents of hydrogen ions per litre. The ratio of the potential acidity to the potential alkalinity bears a relation to the concentration of the hydrogen ions. The neutralising power gives an approximate idea of the concentration of the phosphates, and if the amount of phosphates present be known, the ratio between the neutralising power of the urine and that calculated for a solution of phosphoric acid of the same concentration as in the urine can be used to estimate the net concentration of the other acids and bases in the urine. The neutralising power of urine is about four times as great as that of a solution of phosphates of the same concentration as in the urine. It is pointed out that a simple titration of urine is absolutely worthless for the purpose of obtaining information as to its degree of acidity. On the other hand, if the urine is titrated as an acid against phenolphthalein and as a base against methyl-orange, results are obtained which may be taken as an approximate measure of the relative concentrations of hydrogen ions in different urines.

R. V. S.

**The Excretion of Ammonia in Human Urine by the Administration of Urea and Sodium Hydrogen Carbonate.** N. JANNEY (*Zeitsch. physiol. Chem.*, 1912, 76, 99—135).—The ammonia of human urine has only one function, namely, to neutralise acid substances. If by the administration of sodium hydrogen carbonate this is superfluous, the urinary ammonia vanishes almost completely. A conversion of urea into ammonia never occurs in the human body normally. Fifteen grams of sodium hydrogen carbonate in an adult on a mixed diet reduces urinary acidity to nil, and lessens the ammonia to one-third. Urea given by the mouth causes increased protein catabolism, or the washing out of nitrogen from the body. In acute catarrhal jaundice, true acidosis accompanied by an increase of acid substances in the urine occurs.

W. D. H.

**The Excretion of Quinine by the Dog, and a New Method for the Estimation of this Alkaloid.** G. GIEMSA (*Biochem. Zeitsch.*, 1912, 38, 161—162).—A claim for priority with regard to certain results and methods described by Katz (Abstr., 1911, ii, 1013).

S. B. S.

**Certain Concretions in a Cyst of the Mammary Gland in a Horse.** ARTHUR SCHEUNERT and WALTHER GRIMMER (*Zeitsch. physiol. Chem.*, 1912, 76, 322—329).—The concretions examined contained in percentages: water, 69; protein, 4·5; fat, 13·7; cholesterol, 10; lecithin, 0·7, and ash, 1·7. Casein was absent, and the fat present is not identical with the milk fat or the body fat of the horse, but somewhat resembles colostrum fat in being intermediate between the two.

W. D. H.

**The Chemical Nature of the Substance which Cures Polyneuritis in Birds Induced by a Diet of Polished Rice.** CASIMIR FUNK (*J. Physiol.*, 1911, 43, 395—400).—Polyneuritis in birds on a diet of polished rice is due to the lack of a substance which is present in the polishings in minute amount, probably not more than 0·1 gram per kilo. of rice. The substance in question is an organic base, which is completely precipitated by phosphotungstic acid, silver nitrate, and barium hydroxide. It is partly precipitated by mercuric chloride in alcoholic solution in the presence of choline, and is not precipitated by platinum chloride in alcoholic solution. It yields a crystalline nitrate containing C 55·63, H 5·29, N 7·68%; but these figures must be regarded as provisional until a larger yield is obtained. The curative dose for pigeons is very small.

W. D. H.

**The Influence of Intravenous Injections of Pancreatic Extract on Pancreatic Diabetes.** ERNEST LYMAN SCOTT (*Amer. J. Physiol.*, 1912, 29, 306—310).—Intravenous injection of pancreatic extract in depancreatized dogs diminishes the glycosuria temporarily. Whether this is due to the internal secretion of the gland or to a rise of body temperature which occurs is not yet definitely settled. Control experiments with extracts of other organs are in progress.

W. D. H.

**Metabolism in Experimental Salt Fever.** HERMANN FREUND and E. GRAFE (*Arch. exp. Path. Pharm.*, 1911, 67, 55—71).—After the injection of rabbits with isotonic solutions of sodium chloride, sugar, adrenaline, and Ringer's solution, fever sets in, with rise of temperature and increase of protein catabolism, and in this and in other ways the fever produced resembles that due to infection.

W. D. H.

**Infective Methæmoglobinæmia.** ARTHUR E. BOYCOTT (*J. Hygiene*, 1911, 11, 443—472).—In rats, infection with Gartner's bacillus causes methæmoglobinæmia, and sometimes anæmia. The same strains do not cause this effect in rabbits, mice, or guinea pigs.

W. D. H.

**The Excretion of Creatine and Creatinine Under Pathological Conditions.** BERNHARD VAS (*Biochem. Zeitsch.*, 1912, 38, 65—76).—In the two cases of leucæmia investigated, no direct relationships between the excretion of creatinine and the purine bases could be ascertained; there was, however, a certain parallelism between the excretion of creatinine and the total nitrogen. No rise in the creatinine value could be ascertained after treatment by light. In a case of muscular atrophy (where a limb was kept in plaster after operative treatment), creatine could be detected in the urine as a consequence of muscular atrophy. S. B. S.

**The Serum Reactions (Complement Fixation) of the Meningococcus and the Gonococcus.** J. A. ARKWRIGHT (*J. Hygiene*, 1911, 11, 515—530).—Gonococcus serum and extracts are on the whole more potent than similar preparations from meningococci as regards complement-fixation, but no satisfactory distinction between the two can be demonstrated. W. D. H.

**The Physiological Influence of Ozone.** LEONARD E. HILL and MARTIN FLACK (*Proc. Roy. Soc.*, 1911, B, 84, 404—415).—Ozone, although a deodoriser, masks rather than destroys smells. A concentration of one part in a million irritates the respiratory tract; exposure for two hours to a concentration of 15 to 20 per million is not without risk to life. In concentration even less than one per million, it reduces respiratory metabolism, and rapidly causes a fall of body temperature. Its beneficial effect, as popularly believed in, is a myth. The irritation of the olfactory nerves may relieve the monotony of close air, and in concentrations of more than 1 per million for brief periods may be of therapeutic value by acting in appropriate cases as a sort of "blister" to the respiratory tract. W. D. H.

**Persistent Radioactivity of the Organism under the Influence of Injections of Insoluble Radium Salts. Radium Serotherapy.** H. DOMINICI, G. PETIT, and A. JABOIN (*Compt. rend.*, 1912, 154, 1509—1511).—One mg. of radium sulphate was injected into the venous system of an old horse. For a short time after injection, the elimination of radium from the organism was rapid, but afterwards became very slow. After a year the blood was still radioactive. Increase in weight was produced after a second injection, and the number of red blood-corpuscles was doubled. Preliminary experiments appear to show that the blood serum of animals treated in this way is effective in alternating or arresting pathogenic processes of infectious origin in man and animals, and that it tends to raise the resistance to infection. W. O. W.

**The Influence of Sulphur and Thiocarbamide on the Excretion of Phenol.** KENJI KOJO (*Zeitsch. physiol. Chem.*, 1912, 76, 159—169).—The administration of finely divided sulphur and thiocarbamide raises, especially on the second day, the total sulphur, the ethereal sulphates, and the phenol of the urine. This is probably due, not to increased formation of phenol, but because less is oxidised in the body, as it combines with sulphuric acid and is excreted. W. D. H.

**The Action of Intravenous Injections of Concentrated Solutions of Salt and Sugar.** FRANK P. UNDERHILL (*Arch. exp. Path. Pharm.*, 1911, **66**, 407—408).—Polemical against Wilenko, who has made certain mistakes in his references to the work of the present author in relation to the glycosuria produced by salt solution.

W. D. H.

**The Degree of Acidity of Monatomic Alcohols.** HERMANN FÜHNER (*Zeitsch. Biol.*, 1912, **57**, 465—494).—In the homologous series of alcohols starting with methyl alcohol, the capillary activity of the individual members stands according to Traube in the relation  $1 : 3 : 3^2 \dots$  (Abstr., 1905, ii, 13). As their pharmacological activity on plant-cells, blood corpuscles, and sea-urchin eggs increase in the same manner, it appears that in these cases the action is not dependent on the lipoids present in the cells. Their narcotic action, however, tested on various aquatic animals, is in the relation  $1 : 4 : 4^2 \dots$ . This is parallel to the increased lipid content in the central nervous system of such animals, and these observations therefore support the Meyer-Overton theory of narcosis.

W. D. H.

**Influence of Trimethylamine Hydrochloride on Nutritive Exchanges.** ALEXANDRE DESGREZ, P. REGNIER, and R. MOOG (*Compt. rend.*, 1911, **153**, 1238—1241. Compare Abstr., 1902, ii, 574).—Injection of trimethylamine hydrochloride diminishes the excretion of nitrogen with men and guinea-pigs and lowers the respiratory quotient. In the case of men suffering from obesity who were given doses of 0.05 gram of the hydrochloride three times a day during one to four months, loss of weight to the extent of 1.5—6 kilograms was observed. The author considers that trimethylamine increases the amount and activity of internal secretions and is the cause of the physiological action of choline.

W. O. W.

**Formation of Methyl Propyl Ketone from  $\alpha$ -Ethylbutyric Acid in the Animal Organism.** LÉON BLUM and MAX KOPPEL (*Ber.*, 1911, **44**, 3576—3578).—The subcutaneous injection of aqueous sodium  $\alpha$ -ethylbutyrate into dogs causes the appearance in the urine, not of acetone substances (Blum and Baer, Abstr., 1907, ii, 285; Embden and Wirth, Abstr., 1910, ii, 789), but of methyl propyl ketone (identified as the *p*-nitrophenylhydrazone). Without doubt it is produced from the primarily-formed ethylacetoacetic acid, the formation of which is regarded as a strong support of the theory of the oxidation, in the animal organism, of fatty acids at the  $\beta$ -carbon atom.

C. S.

**The Fate of the Stereoisomerides of Lactic Acid in the Organism of the Normal Rabbit.** JAKOB PARNAS (*Biochem. Zeitsch.*, 1912, **38**, 53—64).—The optically active isomerides of lactic acid behave differently in the organism of the normal rabbit, for whereas the dextrorotatory isomeride is non-toxic and is almost entirely burnt in the organism, the *l*-isomeride is toxic, and is for the most part secreted unchanged in the urine. The racemic form is attacked

unsymmetrically, and an excess of the lævo-acid is excreted; in this case, however, considerably more of the lævo-acid is burnt up in the organism than is the case if this acid be administered by itself. The author gives full details as to the method of isolating the various acids in the form of their zinc salts. S. B. S.

**The Effect of Adrenaline on the Intestine.** R. G. HOSKINS (*Amer. J. Physiol.*, 1912, 29, 363—366).—In high dilution, adrenaline inhibits peristalsis in isolated segments of rabbit's intestine. In still higher dilutions, these movements are increased. This difference nullifies attempts to estimate adrenaline by its effect on intestinal muscle. W. D. H.

**The Action of Pilocarpine on the Heart.** FELIX GAISBÖCK (*Arch. exp. Path. Pharm.*, 1911, 66, 398—406).—From experiments on frogs and cats, the conclusion is drawn that pilocarpine slows the heart by acting on a peripheral mechanism, for slowing is produced after the preganglionic fibres of the vagus are completely thrown out of action by nicotine. With certain doses of the drug, the result of vagus stimulation (either of the nerve trunk, or of the sinus) or of action of muscarine is lessened or abolished. W. D. H.

**Effects of Certain Pituitary Extracts.** H. CLAUDE and A. BAUDOUIN (*Compt. rend.*, 1912, 154, 1513—1515).—The lipid-free pituitary glands of oxen were extracted with water, and the extract treated with alcohol. The precipitate suspended in physiological salt solution partly dissolved, giving an active extract *S*. The alcoholic filtrate gave an extract *T*. Injections were carried out on men, and the results found to vary considerably according to the condition of the patient's glandular system. In general, extract *S* lowered the arterial pressure, whilst extract *T* raised it, but in cases of glandular dystrophy the reverse took place. In normal subjects, slight glycosuria was produced, but this was more marked in Basidow's disease, ovarian insufficiency, and in acromelagic, pluriglandular inadequacy. Extract *T* produces diuresis. W. O. W.

**The Influence of Benzene, Toluene, Xylene, and Light and Heavy "Benzines" on the Organism.** KARL B. LEHMANN, RUDOLF WEISSENBERG, ADOLF VON WOJCIECHOWSKI, LUIG, and GUNDERMANN (*Arch. Hygiene*, 1911, 75, 1—119).—A short account of the various products employed under different trade designations is given, together with the modes of preparation and chemical characteristics. Detailed accounts are given also of the cases of poisoning arising from the trade use on a large scale of the different products, and the conditions under which cases of poisoning are likely to occur, together with the results of personal inspection of factories. These investigations supplement a series of detailed laboratory investigations on the toxic effects of the vapours of the various substances on cats, dogs, and human beings, and the effects of both chronic and acute intoxication were investigated. Lehmann gives in conclusion the precautions which should be taken to guard against

poisoning in the technical employment of these substances on a large scale.

The methods of experiment were those repeatedly employed by Lehmann and his collaborators on previous occasions. The subjects of experiment were submitted to the action of air containing known quantities of the vapour, and the time was noted at which the onset of various symptoms took place. The chief symptoms noted were, the falling over of the subject, light narcosis, and heavy narcosis. In nearly all experiments the results were very regular, it being possible to plot the times of onset of symptoms against the quantities of the various vapours in air, and to obtain almost regular curves. A few of the cats employed showed idiosyncracies, in that they were susceptible to relatively small doses of benzene. The same idiosyncracies apparently occur in man, but they were never met with in the case of dogs. Experiments on chronic poisoning with dogs were carried out. Two animals could inhale air containing about 9 mg. of the vapour per litre five to nine hours daily for 23·35 days without injurious effects. Cats, on the other hand, showed symptoms of poisoning after inhaling air with only 5—10 mg. benzene per litre for three hours daily, generally on the third to the sixth day. The cheaper trade varieties are only slightly more toxic than the more refined varieties. "Benzine" is decidedly less toxic than benzene. S. B. S.

**The Toxic Action of Trypsin and its Capacity to Digest Living Tissues.** LUDWIG KIRCHHEIM (*Arch. exp. Path. Pharm.*, 1911, **66**, 352—386).—On subcutaneous injection, pancreatic juice and various preparations of the pancreas, which contain active trypsin, cause local œdema and hæmorrhages, followed by necrosis and digestion of the living tissues. Intravenously injected, it kills rabbits, with acute and pronounced hæmorrhages, especially in the lungs.

W. D. H.

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### Chemistry of Vegetable Physiology and Agriculture.

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**Assimilation of Ammonia and Nitrates by the Micro-organisms of Soils.** J. VOGEL (*Centr. Bakt. Par.*, 1912, ii, 32, 169—179).—Whilst the production of proteins from ammonia and nitrates takes place in liquid cultures, it was not observed in soils, even in presence of calcium carbonate, which in liquid cultures considerably increases fixation of ammonia.

The simultaneous presence in soils of ammonium salts and calcium carbonate may result in considerable losses of nitrogen from nitrates produced from the ammonium salts.

As regards denitrification in soils kept in flasks, it is pointed out that the conditions of aeration are very abnormal. Different results

are obtained when access of air from below and from the sides of the soil is made possible. N. H. J. M.

**Variability in the Gas-forming Power of Intestinal Bacteria.** N. J. PENFOLD (*J. Hygiene*, 1911, 11, 487—502).—The gas-forming powers of organisms of the *coli* group varies; the power may be lost of forming gas from sugars, whilst the power of gas formation from alcohols remains; probably two enzymes are concerned. W. D. H.

**The Indole Reaction and Allied Phenomena.** HARALD SEIDELIN and FREDERICK C. LEWIS (*J. Hygiene*, 1911, 11, 503—514).—Curves are presented of the amount of indole (tested by Seidelin's method) formed by several strains of *Bacterium coli*. Tryptophan does not appear to be always an intermediate product. In some cases the colour reaction obtained was purple instead of red; the conditions under which the blue admixture occurs were investigated, but its cause is not yet clear. W. D. H.

**The Chief Phases of the Lactic Acid Fermentation and their Practical Significance.** MAX GRIMM (*Centr. Bakt. Par.*, 1911, ii, 32, 65—70).—The fermentation induced by *Bacterium lactis acidii* shows four sharply differentiated phases.

Experiments with pure cultures of this organism at 35° showed that during the first four and a-half hours there is no acid produced, but vigorous growth takes place. The second phase then begins, and continues for about twelve hours. It is characterised by a gradual increase in the rate of acid production, and reaches a maximum at the fourteenth hour from the time of inoculation. This is followed by a period of decreasing activity, and terminates at the thirty-second hour. Although individual organisms may grow slightly after this, the power of producing acid is lost, and the organisms degenerate.

The practical significance of these experiments lies in the fact that such organisms must be transferred to fresh media at the end of sixteen hours if the activity of the cultures is to be maintained.

H. B. H.

**The Decomposition of Asparagine by Bacteria in Presence of Free Oxygen. I. The Course of the Oxidation Processes.** TOR CARLSON (*Medd. K. Vetensk. Nobelinstit.*, 2, No. 10, 1—32).—An apparatus is described for measuring the oxygen consumption under constant pressure where various strains of bacteria are allowed to grow on a medium which contains asparagine as the source of nitrogen. The results in the various experiments are plotted with the oxygen consumption as ordinates against the times as abscissæ, and the results obtained are analysed by Arrhenius. After a certain time there is a bend in the curve, which corresponds with the disappearance of the nutrient medium through consumption by the organism. If  $y$  represents the oxygen consumption, this after a time reaches a maximum,  $y_\infty$ . It was found by Arrhenius that  $dy/dt = ke^{-qt}(y_\infty - y)^n$ , which on integration and neglecting certain terms gives:

$$\frac{\log y_\infty^{1-n} - (y_\infty - y_2)^{1-n}}{\log y_\infty^{1-n} - (y_\infty - y_1)^{1-n}} = \frac{q}{2.3026} (t_2 - t_1),$$

where  $y_2$ ,  $y_1$  represent the oxygen consumptions at intervals  $t_2$ ,  $t_1$  respectively;  $n$  was found to be  $2/3$ . This equation was found to hold good in several cases. The value  $q/2 \cdot 3026$  ( $K$ ) was calculated in the case of several strains of bacteria, and was found to vary:  $K \times 10^{-2} = 6 \cdot 0$  and  $K \times 10^{-2} = 15 \cdot 2$ . The method of determining  $y_\infty$  by interpolation is described. S. B. S.

**Protein Synthesis in the Lower Plants.** KONSTANTIN A. PURIEWITSCH (*Biochem. Zeitsch.*, 1912, 38, 1—13).—The method of experiment consisted in growing *Aspergillus niger* in media containing the necessary mineral salts, together with either dextrose, succinic, malic or tartaric acids, and various substances, such as amino-acids, urea derivatives, peptones, proteins, and amides, as sources of nitrogen. The ratio of carbon dioxide evolved to dried mass of *Aspergillus* formed was estimated when the mould was grown in the presence of the various substances, but the conditions of experiments were in other respects similar. If the carbon dioxide evolved is regarded as a measure of the energy consumption during growth, it was found that this was smallest when amino-acids were employed as the source of nitrogen; with ammonium salts, and especially with nitrates, the energy consumption during growth was marked larger. The results confirm generally the conclusions of Czapek. S. B. S.

**Influence of Calcium on the Development and Mineral Composition of *Aspergillus niger*.** (Mlle.) ROBERT (*Compt. rend.*, 1911, 153, 1175—1177).—Experiments on *Aspergillus niger* grown in nutrient solutions containing definite amounts of calcium sulphate, show that small doses of calcium (1—5 mg. per litre) are almost completely absorbed and retained by the organism. The element appears to be without appreciable influence on the development of the plant. W. O. W.

**Is Iron Indispensable to the Formation of Conidia of *Aspergillus niger*?** MAURICE JAVILLIER and BENJAMIN SAUTON (*Compt. rend.*, 1911, 153, 1177—1180. Compare Sauton, *ibid.*, 151, 241).—From experiments in which definite amounts of zinc sulphate or of ferrous sulphate were added to cultures of *Aspergillus niger*, the authors found that in absence of iron and in presence of zinc no spores were produced by the organism. Sauton was in error, therefore, in attributing non-sporulation to the absence of iron, since zinc is the active inhibiting agent. Iron is indispensable to the growth of the plant, but not to sporulation. W. O. W.

**The Formation of Fumaric Acid by Moulds.** FELIX EHRLICH (*Ber.*, 1911, 44, 3737—3742. Compare Ehrlich and Jacobsen, *Abstr.*, 1911, ii, 520).—Considerable quantities of fumaric acid are formed during the growth of *Rhizopus nigricans* in natural or artificially-prepared media, especially when a certain amount of carbohydrates and nitrogen compounds is present; the main condition to success is the presence of an excess of dextrose or lævulose, the nature of the accompanying nitrogenous food being immaterial. The fumaric acid

appears to be an intermediate product in the disruption of the dextrose or lævulose molecule, and these substances cannot be replaced by alcohol or glycerol. Unduly prolonged action of the mould causes the fumaric acid itself to be attacked.

A few characteristic experiments are described in detail.

D. F. T.

**Amylomyces Rouxii.** R. GOUPIL (*Compt. rend.*, 1911, 153, 1172—1174).—This mould brings about a formation of succinic acid when grown in a dilute sucrose solution, corresponding with about 6% of the sugar destroyed. Acetic and butyric acids are also formed in small quantity, but not oxalic or lactic acid, as has been stated by other observers. The production of succinic acid is favoured by free aeration, and becomes negligible if air is excluded. Similar results have been obtained when the organism is grown in solutions of maltose, dextrose, invert sugar, or starch hydrolysed by malt extract.

W. O. W.

**Behaviour of Yeast Enzymes Free and Attached to Protoplasm.** HANS EULER (*Arkiv. Chem. Min. Geol.*, 1911, 4, No. 13, 1—11).—Attention is called to the differences between zymase, maltase and invertase of brewers' yeast, and also to *Monilia* invertase. In the living cell, with the exception of yeast invertase, the action of the enzymes is checked by antiseptics and greatly retarded by drying; they cannot be extracted from the cell by water. Yeast invertase only loses half its activity when dried.

From dry yeast, invertase is almost completely extracted by water; zymase and maltase are only partly extracted. Invertase is not affected by antiseptics; it is regarded as already split off from the protoplasm in the living cell. The other enzymes are only broken off from the protoplasm on drying or by mechanical means. *Monilia* invertase behaves like maltase and zymase, and is bound up in the protoplasm.

*Monilia* yeast ferments dextrose more quickly than sucrose, and maltose more slowly still.

E. F. A.

**Purification of Water by Infusoria.** C. S. STOKVIS and N. H. SWELLENGREBEL (*J. Hygiene*, 1911, 11, 481—486).—Infusoria only play a part in purifying river water if the temperature is between 10° and 30°, if the aquatic vegetation is rich enough to supply the necessary amount of oxygen, and if the water is not highly polluted by adjoining factories.

W. D. H.

**Atmolysis and an Atmolyser.** RAPHAËL DUBOIS (*Compt. rend.*, 1911, 153, 1180—1183. Compare *Abstr.*, 1884, 932).—A note recalling the author's earlier observations on the action of vapours on vegetable organisms. The paper contains an illustration of the apparatus employed.

W. O. W.

**Transpiration in Oil-producing Plants; Influence of Light.** LECLERC DU SABLON (*Compt. rend.*, 1911, 153, 1236—1238).—In

general, direct sunlight has a much greater effect in increasing the transpiration of plants than diffused daylight. This is due partly to the effect of a higher temperature and partly to an increased permeability of the protoplasmic membrane. The second cause is unimportant in the case of oil-producing plants, which flourish in dry climates and which have been found to behave towards diffused light in the same way as non-oily plants, but to lose water less readily than these when exposed to direct sunlight. The experiments were conducted on *Euphorbia*, *Sempervivum*, *Crassula*, and others.

W. O. W.

**Metabolism in Ripening Seeds.** W. ZALESKI (*Bied. Zentr.*, 1911, 40, 863; from *Bot. Centr.*, 1911, 117, 57).—Unripe seeds of *Pisum* and *Zea Mays*, which were kept for several days in air saturated with moisture, showed an increase in the amounts of proteins and a decrease in amides, amino-acids, and bases.

Whilst during germination proteins are broken down with production of amino-acids, the reverse process takes place during ripening. Proteases, which are supposed to bring about the reversible action, were found in ripening pea seeds. Rennin was found in unripe seeds.

N. H. J. M.

**Formation of Hydrogen Cyanide in the Germination of Seeds.** CIRO RAVENNA and C. VECCHI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 491—495. Compare Ravenna and Zamorani, *Abstr.*, 1910, ii, 1099).—When the seeds of *Linum usitatissimum* or those of *Sorghum vulgare* germinate in the presence of ammonium chloride, the amount of hydrogen cyanide liberated is considerably greater than when they germinate in the absence of this salt. Experiments with the seeds of *Sorghum vulgare* show that ammonia is present in the seeds from the beginning of germination, but hydrogen cyanide appears only when the plants have attained to a certain development. These results support the view that the hydrogen cyanide is formed synthetically from non-nitrogenous substances and ammonia. A comparison of the amounts of hydrogen cyanide formed when germination takes place in the presence of (1) water, (2) ammonium chloride (0.1%), (3) dextrose (0.2%), (4) ammonium chloride (0.1%) and dextrose (0.2%) shows that the greatest amount is formed in the presence of both dextrose and ammonium chloride.

R. V. S.

**Origin and Function of Calcium Oxalate in Plants.** IOANNES POLITIS (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 528—534).—The author discusses the hypotheses which have been put forward on this subject, and calls attention to the connexion between the deposition of calcium oxalate raphides and the occurrence of glycogen and amyloids which has been established by his recent work (compare this vol., ii, 83). He is of opinion that the oxalic acid is formed in the cells by oxidation of these substances.

R. V. S.

**Micro- and Macro-chemical Detection of Carotene.** M. TSVETT (*Ber. Deut. bot. Ges.*, 1911, 29, 630—636).—The author

examines in some detail three micro-chemical tests commonly employed for carotene, namely, Molisch's potash test, Frank and Tschirch's acid test, and his own resorcinol test, and concludes that none of them is trustworthy. Nor could any simple macro-chemical test be devised. The only safe method is actually to isolate the carotene, and as this has not generally been done, it follows that many of the statements about the distribution of carotene need revision. E. J. R.

**The Carbon-like Substance Occurring in Compositæ.** FRANZ W. DAFERT and R. MIKLAUZ (*Denkschr. Math-Naturw. Klasse K. Akad. Wiss. Wien*, 1911, 87, 143—152).—An account of the isolation of deep brown or black substances which the author designates "phytomelanes," from the so-called "Kohleschicht" of the heads of certain plants of the natural order Compositæ. The amounts (varying from 0.7—3.8%) obtained from different members of the order are stated, whilst analysis indicates that the chemical composition of phytomelane also varies in different species (C 67—76%, H 3.3—4.7%, O 20—28%). The substances are very indifferent to chemical reagents. They are probably formed from cellulose by retrogressive metamorphosis ( $x\text{C}_6\text{H}_{10}\text{O}_5 - y\text{H}_2\text{O}$ ). F. M. G. M.

**Retrogression of the Active Substance in Medicinal Plants by the Action of Enzymes.** PIO LAMI (*Boll. Chim. Farm.*, 1911, 50, 835—842).—In order to enable medicinal plants to be kept unchanged, it is proposed that the substance should be heated at about 80° in the vapour of ethyl alcohol, or at 73° in methyl alcohol vapour, and then dried in a current of warm air. N. H. J. M.

**Vegetable Phosphatides.** VLADIMIR NJEGOVAN (*Zeitsch. physiol. Chem.*, 1911, 76, 1—26. Compare Hiestand, *ibid.*, 1907, 54, 287; Winterstein and Stegmann, *ibid.*, 1908—9, 58, 501).—The phosphatides of the seeds of *Lupinus albus* which dissolved in alcohol were separated by means of different solvents into phosphatides and non-phosphatides. The three substances, A, B, C, which may be considered to be phosphatides, all yield stearic, palmitic, and unsaturated fatty acids as cleavage products. A and C yielded glycerol-phosphoric acid, and C, free phosphoric acid. As regards bases, choline was obtained from B, and from C a base,  $\text{C}_9\text{H}_{26}\text{O}_2\text{N}_2$ , to which the name *vidine* is given. The latter compound is perhaps identical with Lucius's hexamethyltrimethylenediammonium (Abstr., 1907, i, 678). The *platinichloride*, m. p. 250—252°, and the *aurichloride*, m. p. 269—272°, were prepared. N. H. J. M.

**Chemistry of the Higher Fungi. VII. *Hypholoma fasciculare*.** JULIUS ZELLNER (*Monatsh.*, 1911, 32, 1057—1063. Compare Abstr., 1909, ii, 922).—A renewed investigation of *Hypholoma fasciculare*, which contains 9.25% of dry matter, shows the presence of the following constituents, some of which have been previously identified by others: a cerebroside, an ergosterol, solid and liquid fatty acids, glycerol, lecithin, a resin, mannitol, trehalose, dextrose, tannin, phlobaphen, choline, a gum, a carbohydrate soluble in alcohol, chitin,

protein, and enzymes which hydrolyse protein, starch, maltose, and glucosides.

E. F. A.

**Chemistry of the Higher Fungi. VIII. Wheat Rust.** (*Tilletia levis* and *T. tritici*.) JULIUS ZELLNER (*Monatsh.*, 1911, 32, 1065—1074).—The analyses are based on the investigation of considerable quantities of wheat rust spores separated mechanically from badly infected wheat. The following substances have been identified: liquid and solid fatty acids, a wax, an ergosterol-like compound, glycerol, a resin, a substance insoluble in alcohol, mannitol, trehalose, dextrose, a base, carbohydrates soluble in water and in alkali, protein, invertase, lipase, and a chitin skeletal substance. In general, these constituents are the same as those of maize rust, but the differences are so marked that they would serve for the differentiation of the spores of the two species if this had been impossible morphologically.

E. F. A.

**Application of the Biological Method to *Kalmia latifolia*, and Preparation of a Glucoside.** EMILE BOURQUELOT and (Mlle.) A. FICHTENHOLZ (*Compt. rend.*, 1912, 154, 1500—1502; *J. Pharm. Chim.*, 1912, [vii] 5, 49—58).—The fresh leaves of *Kalmia latifolia*, a plant of the rhododendron family, contain sucrose and a glucoside hydrolysable by emulsin. The latter has been isolated by extraction with boiling 90% alcohol, from which it separates in slender needles, m. p. about 150°, having a chalky taste, becoming sweet, and then bitter. A solution in 50% alcohol has  $[\alpha]_D -59.1^\circ$ . Ferric chloride produces an intense red coloration. The substance gives dextrose on hydrolysis, and in its general properties resembles asebotin from *Andromeda japonica*.

W. O. W.

**Oils from Different Varieties of Oil-Palm.** ALEXANDRE HÉBERT (*Bull. Soc. chim.*, 1911, [iv], 9, 1083—1085).—Chevalier has classified the West African oil palms recently into two sub-species, *Elaeis nigrescens* and *E. virescens*, each with a number of varieties (*Documents sur le palmier à huile*, Paris. Challamel, 1910). The author has determined the yield and character of the palm oils yielded by the fruits of these varieties. The yields may vary from 41% to 63% calculated on the pericarp alone, or from 16 to 56 calculated on the whole fruit, the highest yields being afforded by *E. nigrescens* var. *Pisifera* and *E. virescens* var. *Gracilinux*, in which the nut is reduced to a mass of interlacing fibres. The palm oils obtained from the varieties examined differ but little from commercial palm oil (compare *Bull. Imp. Inst.*, 1909, 7, 357).

T. A. H.

**Rumex obtusifolius Roots.** ALEXANDER TSCHIRCH and F. WEIL (*Arch. Pharm.*, 1912, 250, 20—33. Compare Hesse, *Abstr.*, 1900, i, 41).—A concentrated alcoholic extract of the roots on distillation yielded a small amount of volatile oil having an odour of butyric or valeric acid. The extract on dilution with water gave (1) a resinous precipitate, from which ether extracted a brown residue, which probably contained emodin and chrysophanic acid, and (2) a liquid

which did not reduce Fehling's solution, but which after boiling with dilute sulphuric acid exhibited this property and contained a precipitate from which emodin and chrysophanic acid were isolated; the chrysophanic acid was probably accompanied by emodin methyl ether, since it furnished methyl iodide when heated with hydriodic acid. It is probable that emodin methyl ether is the source of the varying quantities of methyl iodide yielded in this reaction by the crude chrysophanic acid examined by various investigators.

The liquid, after hydrolysis, contained in addition *lapathic acid*,  $C_{20}H_{18}O_4$ , m. p. 228—229°, pale yellow, prismatic crystals, tannin, and reducing sugar, probably formed by hydrolysis of glucosides of emodin and chrysophanic acid. The ash from the roots contained the equivalent of 0.379% of iron.

The dry roots of *Rumex alpinus* furnished 13% of sucrose.

T. A. H.

**The Amounts of Hydrogen Cyanide Produced by Different Varieties of Sorghum.** JOHANNES SCHRÖDER and HANS DAMMANN (*Chem. Zeit.*, 1911, 35, 1436—1437).—Cases having been observed by the authors (who are working in Monte Video) of cattle poisoning by sorghum, a number of tests were carried out during the summer season, Nov., 1908, to March, 1909, to ascertain what quantities of hydrogen cyanide are present in the different varieties of this plant. The highest amounts recorded were about 0.04% in young plants growing on manured plots; the amount fell later on to 0.004%. On unmanured plots, it was always somewhat lower. Under the conditions obtaining in the experiments, *Andropogon sorghum saccharatum* contained more than either the *vulgaris* or *halepensis* variety.

E. J. R.

**Respiration of Barley during Germination, Especially its Dependence on the Amount of Protein.** B. ABRAHAMSOHN (*Bied. Zentr.*, 1911, 40, 862—863; from *Diss.*, Berlin, 1910, and *Bot. Centr.*, 1911, 117, 53).—In the germination of sterilised barley, the production of carbon dioxide is less than in seeds which are not sterilised. Small seeds show a more intense respiration than large ones.

Comparing seeds with high and low amounts of protein, it is shown that respiration is greater in the case of seeds with high percentage of protein. The difference is at first only slight, but it increases as germination proceeds. This is explained on the assumption that the amount of enzyme is only small in ripe seeds, and that it increases during germination at a greater rate in seeds rich in proteins than when proteins are less abundant.

N. H. J. M.

**The Action of Oxygen on the Alcoholic Fermentation of Peas.** LEONID IWANOFF (*Ber. Deut. bot. Ges.*, 1911, 29, 622—629).—The author states that peas contain a zymase similar in many respects to that of yeast, but differing in its necessity for oxygen. Its activity was measured by the rate of evolution of carbon dioxide, and was found to be increased to a marked extent by addition of sodium phosphate, and also by the presence of oxygen.

E. J. R.

**Soluble Substances in the Plasma of Potato Tubers.** GUSTAVE ANDRÉ (*Compt. rend.*, 1911, 153, 1234—1236).—The amount of nitrogen, phosphoric acid, and potassium existing in the state of simple aqueous solution in potatoes has been determined by immersing the tubers in ether and analysing the aqueous liquid displaced by the ether. In the case of potatoes gathered in March, this was found to contain 17·96% of the total nitrogen, 19·98% of the phosphoric acid, and 27·86% of the potassium. The proportions were smaller in the case of potatoes collected at maturity. The amount of potassium is considerably more than sufficient to neutralise the phosphoric acid, and probably corresponds with the existence of soluble organic salts.

W. O. W.

**Displacement by Water of Soluble Substances in the Plasma of Potato Tubers.** GUSTAVE ANDRÉ (*Compt. rend.*, 1912, 154, 1497—1500. Compare preceding abstract).—An account of further experiments similar to those already described. When allowed to remain for thirty-three days in water containing formaldehyde, potatoes part with only 24·02% of their total nitrogen, whereas in the same time 49·79% of the potassium is lost. A preliminary heating for three hours at 120° considerably increases the proportion of potassium subsequently lost by exosmosis, whilst it has no effect on the loss of nitrogen. This is probably due to partial hydrolysis of the proteins, accompanied by elimination of phosphoric acid.

W. O. W.

**Changes in the So-called Physical Properties of Soil by Frost, Heat, and Addition of Salts.** WILLY CZERMAK (*Landw. Versuchs-Stat.*, 1912, 76, 74—116).—Frost, heat, and electrolytes cause a diminution of the soil surface by coagulating the colloids. The soil colloids coagulated by cold absorb to some extent the dissolved nutrients of the soil, including nitrogen. Sterilisation by heat increases the solubility of the soil nitrogen.

N. H. J. M.

**The Distinctive Action of Calcium and Magnesium Oxides in Soils on Higher Plants and Micro-organisms.** OTTO LEMMERMANN, ALBERT EINECKE, and H. FISCHER (*Landw. Jahrb.*, 1911, 40, 174—254).—The account of a comprehensive study extending over a period of several years on the result of varying the ratio of calcium and magnesium oxides in soil, with an account of its effect on plants and on the bacterial properties and fertility of soil.

F. M. G. M.

**The Results of Deficiency of Lime in Field Soils, and its Influence on Vegetation.** OTTO LEMMERMANN, OTTO FORSTER, and ALBERT EINECKE (*Landw. Jahrb.*, 1911, 40, 255—324).—An account of experiments showing the results of lack of lime (in soil) on numerous crops, with a discussion on the employment of different extracting reagents in soil analysis and their relative value as indicating the available plant food present.

F. M. G. M.

**Biological Absorption in Soils.** JULIUS STOKLASA (*Chem. Zeit.*, 1911, 35, 1425—1427).—Biological absorption differs from purely

chemical absorption in that all the elements required for growth are taken up and transformed into organic compounds. Experiments in which definite quantities of a solution of monocalcium phosphate were allowed to percolate for twenty-five days through various sterilised and non-sterilised soils showed that appreciable quantities of phosphates had been absorbed. The amount absorbed was always greater in the non-sterilised soils and varied with the fertility. This is attributed to the action of bacteria, and it is claimed that the absorption is a measure of fertility.

Similar results were obtained with potassium and ammonium salts and with nitrates.

H. B. H.

**Amount and Composition of Drainage-Water Collected during the Years 1909-10 and 1910-11.** BRYCE C. BURT (*Rep. Cawnpore Agric. Stat.* for the years ending June 30, 1910, and 1911. Compare Abstr., 1909, ii, 1049).—In 1909-10 two of the gauges (Nos. 1 and 4) were sown with juar, and in 1910-11 with maize, after which fifty gallons of water (= 2·21 inches) were added. The amounts of rain and drainage, and of nitrogen as nitrates in the drainage, from June to May were as follows :

No.	Depth of soil, inches.	1909—1910.			1910—1911.		
		Rainfall, inches.	Drainage, inches.	N per acre, lbs.	Rainfall, inches.	Drainage, inches.	N per acre, lbs.
1.	72	36·67	12·78	19·85	25·63	4·40	1·50
2.	72	36·67	16·01	47·15	25·63	7·17	23·30
3.	36	36·67	15·23	36·75	25·63	7·87	34·36
4.	36	36·67	15·75	23·71	25·63	6·05	1·00

The yields of juar in 1909 amounted to (1) 6945 and (4) 3487 lb. per acre.

N. H. J. M.

## Analytical Chemistry.

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**Quantitative Treatment of Small Quantities of Precipitate.** JULIUS DONAU (*Monatsh.*, 1911, 32, 1115—1139. Compare Abstr., 1911, ii, 225).—Improvements are described in the Nernst microbalance and in the filtering crucible, in which the asbestos fibre is now replaced by spongy platinum. The technique of preparing the filter, precipitation, and filtration is described in detail. The full experimental results are given for the determination of twenty-six inorganic metals or acids made by the usual methods, but using only a few milligrams of substance. The accuracy of the method appears to be satisfactory.  
E. F. A.

**Qualitative Analysis of Complex Mixtures by Boiling with Sodium Carbonate.** A. A. IWANOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1258—1261).—For the qualitative analysis of complex

mixtures of salts, the author recommends the preliminary separation of the acids and bases in the following manner.

The mixture is first treated with sufficient saturated sodium carbonate solution to cause complete precipitation, a certain amount of the solid carbonate being then added to keep the solution saturated. The mixture is then boiled for a greater or less time according to its amount; this is best effected by means of a current of steam, which prevents bumping and ensures thorough mixing. It is advantageous to suspend the boiling two or three times, and to filter off the precipitate, which is then again treated as above. After the final filtration, the filtrate is acidified with nitric acid, the excess of which is neutralised with ammonia solution, the excess of the latter being expelled by boiling. The precipitate thus formed is added to that previously obtained. This procedure leads to almost complete separation of the acids and bases; the precipitate contains all the metals and the silicic acid, whilst the solution contains a small proportion of the silicic acid and the whole of the other acids. The insoluble residue, containing  $\text{AgCl}$ ,  $\text{PbCl}_2$ ,  $\text{Hg}$ , and  $\text{H}_2\text{SiO}_3$ , is analysed without fusion with potassium and sodium carbonates, there being no metals of the second group present. If the mixtures contain no tin, the presence of metallic mercury in the insoluble residue indicates the occurrence of univalent mercury in the mixture, the mercurous carbonate formed readily decomposing into carbon dioxide, mercuric oxide, and mercury.

The metals being obtained in the form of carbonates, readily soluble in hydrochloric acid, the use of nitric acid and consequent oxidation of the hydrogen sulphide are avoided.

Application of the method to various mixtures gave good results.

T. H. P.

**Laboratory Apparatus for Estimating the Absolute and Full Water-holding Capacity of Soils.** FR. MARSHALL (*Landw. Versuchs-Stat.*, 1912, 76, 125—134).—The apparatus, of which sketches are given, consists of (a) a U-tube, of which the one arm terminates in a bulb, and (b) a graduated 100 c.c. cylinder, for holding the soil, the lower end of which is closed by wire gauze covered with a paper filter. When in use, the lower end of the soil cylinder is inserted in the bulb of the U-tube, which is filled with water. For soils which take up large amounts of water, both arms of the U-tube have bulbs, so that the soil can be left overnight. The processes employed for the different estimations are described.

N. H. J. M.

**Fluorescein as an Indicator of Bromine.** HENRI BAUBIGNY (*Bull. Soc. chim.*, 1912, [iv], 11, 12—17. Compare Abstr., 1898, ii, 138).—Polemical. A reply to Pribram (Abstr., 1907, ii, 111). The author also criticises Labat's modification of his method (Abstr., 1911, ii, 533), and maintains the correctness of his view as to the method of employing the test with a paper soaked in a strong solution of fluorescein.

W. G.

**Iodometric Method for the Quantitative Estimation of Small Quantities of Selenium in Sulphur and Pyrites.** PETER KLASON and HJALMAR MELLQUIST (*Arkiv. Kem. Min. Geol.*, 1911, 4, No. 18, 1—14).—The authors first show that selenium, when in the form of the dioxide, may be accurately estimated by making use of the reaction  $\text{SeO}_2 + 4\text{HI} = \text{Se} + 2\text{H}_2\text{O} + 2\text{I}_2$ . The dioxide is dissolved in water in a flask, the solution diluted to 100—300 c.c., and then 2—10 drops of hydrochloric acid ( $D=1.19$ ) added. The flask and its contents are then heated on the water-bath, the air replaced by carbon dioxide, and 2—5 grams of potassium iodide added. After well corking the flask, it is shaken to dissolve the iodide, cooled, and then kept in the dark for one hour. The liberated iodine is then titrated with standard thiosulphate. Great care must be taken that the hydrochloric acid used is free from chlorine, and that the potassium iodide contains no iodate.

In contradiction to the statements of other investigators, the authors find that selenic acid is not reduced by hydriodic acid.

The thiosulphate method (Norris and Fay, *Abstr.*, 1897, ii, 70; 1900, ii, 272) for the estimation of selenious acid is not so accurate as the iodometric method; the results are always low, and the error increases with increasing weight of selenium.

For the conversion of selenium into the dioxide, the authors find that the best method is to burn it in a current of oxygen. The selenium is contained in a porcelain boat situated between two asbestos plugs in a hard glass tube. The selenium dioxide is repeatedly sublimed backwards and forwards between the two plugs until it is quite white, after which it is dissolved out with water and estimated as above. Experiments showed that no selenium is lost in these operations. If the selenium is present as a suspension in water, it may be filtered on to one of the asbestos plugs, using a tube similar to that used in sugar analyses.

For the estimation of selenium in sulphur, the sulphur is burned in a similar manner to that described above. The selenium dioxide so produced is then dissolved from the asbestos and tube by means of a warm solution of potassium cyanide, and the selenium precipitated from this solution by means of hydrochloric acid and sulphur dioxide. The precipitated selenium is then collected on an asbestos plug, as described above, converted into the dioxide again, which is then dissolved in water and estimated iodometrically.

Various specimens of Japanese sulphur contained 1.1—20.3 grams of selenium per ton, whilst a specimen of Sicilian sulphur contained 0.9 gram of selenium per ton.

For the estimation of selenium in pyrites, 20—30 grams are dissolved in concentrated hydrochloric acid ( $D=1.19$ ) and potassium chlorate. After filtering from the gangue, the iron is reduced to the ferrous state by means of zinc, more hydrochloric acid added, the solution boiled, and the selenium precipitated with stannous chloride. Since the selenium may contain arsenic, it is collected on an asbestos filter, dissolved in potassium cyanide, and then again precipitated with hydrochloric acid and sulphur dioxide. The further treatment is similar to that described for the estimation of selenium in sulphur.

89.5—90.1 Grams of selenium per ton were found in some specimens of Falu pyrites. Simply roasting the pyrites in a current of oxygen does not convert all the selenium into oxide. T. S. P.

**Kjeldahl's Method [of Nitrogen Estimation].** MAX SIEGFRIED and O. WEIDENHAUPT (*Zeitsch. physiol. Chem.*, 1912, 76, 238—240).—According to Andersen and to Kjeldahl, when permanganate has been added to the oxidation mixture in a Kjeldahl estimation, the liquid should not be subsequently boiled, otherwise loss of ammonia may take place.

Experiments are now quoted to show that further heating causes no such loss of ammonia even when heating is prolonged for two or three hours after the last addition of permanganate; in some instances, namely, the oxidation of tryptophan, the heating is essential.

E. F. A.

**Detection of White Phosphorus in Presence of Hypophosphites and Arsenic.** ANDRÉ LECLÈRE (*J. Pharm. Chim.*, 1912, [vii], 5, 15—18).—The method depends on the fact that hydrogen liberated from aluminium and potassium hydroxide solution, in presence of phosphorus forms phosphorus hydride, which blackens paper coated with ammoniacal silver nitrate. Hypophosphites are not reduced under these conditions, and the formation of hydrogen arsenide is prevented by adding a small quantity of sodium persulphate to the solution. One part of phosphorus in 10,000 may be detected in this way. The liquid may be used for the detection of arsenic by oxidising it with nitric acid, then reducing the arsenate formed by means of sulphur dioxide, boiling off the excess of the latter, and applying the test without adding persulphate. T. A. H.

**Separation of Phosphomolybdates from Silicomolybdates.** PETR G. MÉLIKOFF (*Compt. rend.*, 1912, 154, 1478—1479).—Ammonium molybdate is liable to precipitate silicomolybdates in the estimation of phosphates in minerals. To avoid this difficulty, the use of hydrogen peroxide is recommended, since this converts the silicomolybdates into permolybdates which are insoluble in hydrogen peroxide, whilst the phosphomolybdates go into solution.

The precipitate obtained with ammonium molybdate is digested with a mixture of equal volumes of hydrogen peroxide (30%) and an 8% solution of ammonium molybdate in nitric acid. In micro-chemical analysis the precipitate may be treated with a few drops of 30% hydrogen peroxide, and allowed to remain for twenty-four hours, when solution of the silicomolybdate is complete. W. O. W.

**Gravimetric Estimation of Phosphorus in Milk.** E. HOLL MILLER (*Analyst*, 1911, 36, 579—583).—Estimations of phosphoric acid in numerous samples of milk ash were made, the following processes being used: (1) Precipitating as ammonium magnesium phosphate after removal of the lime as oxalate; (2) precipitating as ammonium magnesium phosphate in the presence of lime, the latter

being held in solution by the addition of ammonium citrate; (3) precipitating as ammonium phosphomolybdate, dissolving, and re-precipitating as ammonium magnesium phosphate. In every case the precipitate was ignited and weighed as magnesium pyrophosphate. The phosphorus in the milk was also estimated in the dry milk solids by Carius' process. Provided that the ash was heated previously with nitric acid, the results obtained by the first three methods agreed closely with those yielded by Carius' method, the difference being about 0.01%. In the case of condensed milk and milk-powder, this difference was larger, and it is evident that Carius' method should be employed for the estimation of phosphorus in these products. The results obtained show that there is no appreciable loss of phosphorus during the incineration of milk (compare Abstr., 1911, ii, 438).

W. P. S.

**The Estimation of Arsenic in Organic Substances, especially Organic Arsenic Compounds (Salvarsan, etc.).** PAUL BOHRISCH and F. KÜRSCHNER (*Pharm. Zentr.-h.*, 1911, 52, 1365—1371, 1397—1400).—The distillation of organic materials with hydrochloric acid in presence of hydrazine and potassium bromide (Jannasch and Seidel, Abstr., 1910, ii, 546), followed by titration with iodine (Ney, Abstr., 1911, ii, 932), gives the best results when slightly modified. It is inapplicable to metallic arsenic and arsenious sulphide, which are incompletely converted into the chloride by hydrochloric acid. Satisfactory results are obtained from atoxyl and salvarsan, or from milk or urine containing these compounds.

From 50 to 75 c.c. of the liquid to be examined are distilled with 100 c.c. of fuming hydrochloric acid, 4 grams of hydrazine sulphate, and 2 grams of potassium bromide, the receiver containing 75 to 100 c.c. of water. About one hour is required for the distillation, which is carried almost to dryness. The distillate is neutralised with concentrated sodium hydroxide, and titrated with *N*/10-iodine after adding 3 grams of sodium hydrogen carbonate.

C. H. D.

**Estimation of Arsenic as Ammonium Arsenomolybdate.** HENRI PELLET (*Anal. Chim. anal.*, 1911, 16, 455—456).—A reply to Maderna (Abstr., 1910, ii, 896), who states that the relation between arsenic trioxide and molybdic acid is as 1 : 24, whereas Champion and the author found the relation 1 : 21.8.

The difference, which is not very appreciable, is no doubt caused by a different method of working.

L. DE K.

**Rapid Estimation of Carbon Monoxide.** LEONARD A. LEVY (*J. Soc. Chem. Ind.*, 1911, 30, 1437—1440).—The process, which is based on Gautier's iodic anhydride method, is briefly as follows : The gaseous mixture is drawn by means of an aspirator through a solution of bromine in potassium bromide to fix unsaturated hydrocarbons, and then through aqueous potassium hydroxide (1 : 1) to remove bromine vapours, and also any carbon dioxide. After removing aqueous vapours by passing the gas over phosphoric oxide, the carbon monoxide is oxidised to carbon dioxide by passing it through a U-tube

filled with a mixture of asbestos and iodic anhydride, and heated in an air-bath at  $160-180^{\circ}$ ; to the U-tube is sealed another one filled with copper turnings, which completely absorb the iodine liberated. The carbon dioxide is now absorbed, in a specially constructed apparatus resembling a Winkler coil, in a known volume of standard solution of barium hydroxide coloured with phenolphthalein, and the operation is continued until the liquid is decolorised; a simple calculation then gives the carbon monoxide. When the amount of carbon monoxide is but very small, the excess of baryta may be titrated with oxalic acid after a certain volume of the gas has passed through without waiting for complete decolorisation.

L. DE K.

**Estimation of Hydrated Silicic Acid in Clay.** FORREST K. PENCE (*Trans. Amer. Ceram. Soc.*, 1910, 12, 49—53).—A discussion of various methods employed in estimating hydrated silica in clays, with an account of experiments for the purpose of finding a cheaper reagent than methylamine or diethylamine, and a more accurate one than the 10% sodium hydroxide employed by von Piedzicki and considered valueless by the author.

The preparation of a pure hydrated silicic acid is described, a known amount of which was evaporated to dryness at  $45^{\circ}$  with a prepared kaolin previously freed from silicic acid, and attempts then made to again separate this ingredient by means of different concentrations of sodium carbonate.

The following procedure gave results accurate to within 0.1—0.2%. Five grams of the prepared kaolin containing 0.1765 gram  $\text{SiO}_2$  are boiled in a platinum basin for ten minutes over a free flame with 120 c.c. of a 5% solution of sodium carbonate, the basin being kept in motion to prevent bumping; the solution is decanted through a filter paper, and the treatment with sodium carbonate repeated twice, the residue transferred to the filter paper, and washed with hot dilute sodium carbonate; the whole of the silica is recovered subsequently from the liquid by known methods.

The author suggests the advisability of determining the solubility of quartz, mica, and felspar in sodium carbonate when in a finely divided condition, but from experiments with a flint fire clay, a stratified kaolin, and a red-burning clay, he considers that the solubility is not sufficient to introduce a serious error.

F. M. G. M.

**Variation of the Cathode Potential during Electrolysis.** P. ERCULISSE (*Bull. Soc. chim. Belg.*, 1911, 25, 427—436).—A theoretical paper in which the author criticises the theory put forward by Fischer (*Electroanalytische Schnellmethoden*, Stuttgart) as to the variation of the cathode potential, and its application to quantitative analysis by electrolytic methods.

W. G.

**Estimation of Small Amounts of Potassium.** EILHARD A. MITSCHERLICH, K. CELICHOWSKI, and HERMANN FISCHER (*Landw. Versuchs-Stat.*, 1912, 76, 139—155).—In estimating potassium in soils, 250 c.c. of soil extract with about 5 c.c. of strong nitric acid and

5 drops of sulphuric acid (1 : 3) are evaporated until about 20 c.c. remains, transferred to a platinum or quartz glass dish, evaporated to dryness, and ignited. The residue is treated with a drop of a concentrated solution of sodium carbonate and a few c.c. of warm water, and again evaporated to dryness and heated until the carbonate melts. It is then approximately neutralised with dilute nitric acid, evaporated to dryness, dissolved in about 5 c.c. of hot water, treated with 3 c.c. of 10% cobalt chloride solution and 5 c.c. of 10% sodium nitrite solution, and slowly evaporated to dryness at 80–90°, care being taken to avoid the formation of crusts. The cold residue is then rubbed with 3 c.c. of 10% acetic acid to dissolve the excess of sodium cobaltinitrite, diluted with 10 c.c. of water, and filtered through hardened filter paper in a Gooch crucible. The dish and crucible are washed with the smallest possible amount of 2·5% sodium sulphate solution. The crucible and precipitate are next added to a nearly boiling mixture of water (100 c.c.) and *N*/50-potassium permanganate (about 20 c.c.). After separation of the manganese dioxide, about 2·5 c.c. of dilute sulphuric acid are added drop by drop. The beaker is then removed from the water-bath, the contents treated with an excess of *N*/50-oxalic acid, and titrated back with *N*/50-potassium permanganate, 1 c.c. of which corresponds with 0·1571 mg.  $K_2O$ .

N. H. J. M.

**The Estimation of Calcium and Potassium in the Ash of Cereals.** FIRMAN THOMPSON and H. H. MORGAN (*J. Ind. Eng. Chem.*, 1911, 3, 398–400).—The high percentage of potassium phosphate in the ash of wheat grains and other cereals renders the estimation of calcium and potassium somewhat difficult, and the authors, after numerous experiments, suggest the following method.

*Calcium.*—Fifty c.c. of the hydrochloric acid solution of the ash (corresponding to 0·5 gram ash) are boiled, rendered slightly ammoniacal, acidified with acetic acid, using an excess of about 10 c.c. of 50% acid, and bringing the total volume to not more than 75 c.c. The precipitate is boiled, allowed to settle, and the combined phosphates of iron and aluminium collected and thoroughly washed with hot water; the filtrate, while hot, is treated with 10 c.c. of a saturated ammonium oxalate solution, and the calcium thus precipitated determined by any known method.

*Potassium.*—A modification of the method of Adie and Wood (*Trans.*, 1900, 77, 1076) was found to be rapid and accurate, and is carried out as follows. After separating the iron and aluminium phosphates as previously described, the filtrate is concentrated to 75 c.c., cooled, and treated with 25 c.c. cobaltinitrite solution (prepared by Adie and Wood's method), left overnight, the precipitate collected on asbestos felt in a Gooch crucible, and washed with cooled 10% acetic acid and, finally, once with water. The asbestos and precipitate are transferred to a beaker, treated with 40 c.c. of a saturated barium hydroxide solution, boiled, and the precipitated cobaltic hydroxide collected, whilst the filtrate and washings pass into a 200 c.c. graduated flask, are cooled, and made up to volume. A solution of 25 c.c. standard potassium permanganate is treated in a basin with 25 c.c.

of 50% sulphuric acid and 150 c.c. of hot water, into which the alkaline nitrite is slowly run from a burette until the colour disappears. The use of barium hydroxide is found to ensure the complete precipitation of cobalt, the presence of which would interfere with the titration, whilst the titrating for disappearance of colour is compensated for by the elimination of the danger of losing nitrous acid. A 0.1274*N*-solution of potassium permanganate, in which 1 c.c. is equivalent to 1 mg.  $K_2O$ , is found to be a convenient concentration to employ in this estimation.

F. M. G. M.

**Estimation of Mercury in Hydroxyphenylenedimercury Acetate and Mercurisalicyclic Acid.** RICHARD BRIEGER (*Arch. Pharm.*, 1912, 250, 62—71).—Trials of the iodometric method of estimation prescribed for mercurisalicyclic acid in the German Pharmacopeia, and for hydroxyphenylenedimercury acetate gave variable results. The variation was found to be due to the use of too much acetic acid in dissolving the compound. The solution in acetic acid should be almost neutralised with potassium hydroxide solution, the iodine solution added, and the titration with sodium thiosulphate completed after one hour.

Variable results are also obtained when the method is applied to mercurisalicyclic acid, due to the fact that commercial preparations of this compound contain mercurysalicylatesalicyclic acid. The following method of estimation is recommended: Half a gram of the substance is dissolved in 30 c.c. *N*/10 potassium hydroxide solution, then diluted with 100 c.c. of water, and a few drops of *o*-nitrophenol solution added. Thirty c.c. of *N*/10-hydrochloric acid are then added, the mixture shaken, and then titrated back with *N*/10-potassium hydroxide solution. The difference between 30 and the number of c.c. of alkali used, multiplied by 0.0138, gives the amount of salicylic acid present in the impurity, and the difference between 100 and the percentage of salicylic acid so present, multiplied by 0.5952, gives the percentage of mercury, which should correspond with that found by the following method: 0.3 gram of the compound dissolved in 10 c.c. *N*-potassium hydroxide solution is diluted with 25 c.c. of water containing 5 c.c. of 30% acetic acid, shaken, mixed with 25 c.c. *N*/10-iodine solution, and, after fifteen hours, titrated with *N*/10-thiosulphate solution. Each c.c. of iodine solution used corresponds with 0.0100 gram of mercury. T. A. H.

**Micro-chemical Reaction for Manganese.** M. WAGENAAR (*Pharm. Weekblad*, 1911, 49, 14—15).—Potassium chromate is recommended, as this forms an insoluble crystalline double chromate with manganese. Viewed under the microscope the dark brown crystals are found to be grouped into beautiful rosettes, and in the case of great dilution they are united to bundles. The solution should be neutral or but faintly acid. At the commencement, the rosettes appear like black dots, which grow to very characteristic bundles. The crystals show double refraction. 0.005 mg. of manganese may be recognised. The presence of zinc does not interfere, as zinc chromate is not crystalline. If, however, the zinc preponderates to the extent of 10 : 1 or more, a preliminary separation of the manganese should be

effected by hydrogen peroxide in ammoniacal solution. Quantities below 0.1 mg., however, can then no longer be detected. L. DE K.

**Estimation of Manganese by the Sodium Bismuthate Method.** WILLIAM F. HILLEBRAND and WILLIAM BLUM (*J. Ind. Eng. Chem.*, 1911, 3, 374—376).—The author points out an error by Brinton (this vol., ii, 93), who used an incorrect factor for the ratio of  $5\text{Na}_2\text{C}_2\text{O}_4 : 2\text{Mn}$ ; after recalculating Brinton's results, and from experiments conducted at the Bureau of Standards, the author considers that more evidence is required to justify the adoption of the suggested empirical instead of the theoretical factor, and exhibits tabulated analytical data in support of his contention. F. M. G. M.

**Estimation of Manganese by the Sodium Bismuthate Method.** PAUL H. M. P. BRINTON (*J. Ind. Eng. Chem.*, 1911, 3, 376).—The correction of an error (this vol., ii, 93) when the factor 0.16024 instead of 0.16397 was taken to represent the ratio  $5\text{Na}_2\text{C}_2\text{O}_4 : 2\text{Mn}$ ; it is pointed out that this mistake does not influence the correctness of the empirical factor 0.1656 suggested by the author, although it diminishes the necessity for its employment, neither does it affect the analytical results described in the previous communication. F. M. G. M.

**Analysis of Technical Ferro-Boron.** GASTON RAULIN (*Mon. Sci.*, 1911, [v], 1, ii, 434—438).—The volumetric estimation of boric acid in the presence of a polyhydroxy-alcohol (such as glycerol) was first employed by Thomson (Abstr., 1894, ii, 28) and by Barthe (*J. Pharm. Chim.*, 1894, 29, 163), and is now adapted for technical analysis.

The mineral (0.5—1 gram) is decomposed by boiling with 3—4 c.c. of concentrated sulphuric acid, cooled, 20 c.c. of methyl alcohol added, and the boric acid distilled into 20—25 c.c. of a 2% sodium carbonate solution; the distillation is repeated four or five times with addition of 15 c.c. of methyl alcohol each time. The distillate is freed from methyl alcohol by evaporation, just acidified with dilute hydrochloric acid, boiled, neutralised with sodium carbonate, treated with glycerol (2 parts) and alcohol (1 part), and finally titrated with standard sodium carbonate, using phenolphthalein as indicator. F. M. G. M.

**The Analysis of Ferro-Uranium. II.** WOLDEMAR TRAUTMANN (*Zeitsch. angew. Chem.*, 1912, 25, 19).—By an error in the former paper (Abstr., 1911, ii, 157), aluminium was directed to be extracted from the alloy by fusion with sodium peroxide, instead of from the residue from the treatment with ammonium carbonate. As traces may remain in solution even after twenty-four hours, it is now recommended that the fully oxidised solution should be saturated with solid ammonium carbonate, and mixed with a slight excess of ammonium sulphide. After shaking, an aliquot part is filtered, and the uranium separated from the filtrate by boiling.

Particles of silicon carbide may remain insoluble when the alloy is dissolved in aqua regia. C. H. D.

**Assay of High Grade Alloys of Tungsten.** T. KUCZYŃSKI (*Bull. Acad. Sci. Cracow*, 1911, A, 542--544).—*Chlorine Method.*—The coarsely powdered sample is placed in a porcelain boat, and introduced into a combustion tube connected with a Peligot tube filled with dilute hydrochloric acid (1 : 5). A rapid current of chlorine is passed, and when the air is completely expelled the combustion is started as usual until only a little carbon remains in the boat. When cold, the tubes are disconnected, and, after emptying the Peligot tube, both are washed, first with warm dilute hydrochloric acid and then with dilute ammonia. The mixed liquids, measuring about 500 c.c., are mixed with 5 c.c. of hydrochloric and nitric acids in excess, and boiled until 60 c.c. are left. The tungstic acid is then collected and washed, but as some remains in solution it is necessary to recover this by evaporating to dryness and heating the residue at 120°; the mass is then boiled with dilute hydrochloric acid, and the undissolved tungstic acid is collected. Should the tungstic acid contain iron, it may be freed from this by dissolving in dilute ammonia and reprecipitating by boiling with excess of dilute hydrochloric acid (1 : 10); the traces remaining in solution are then again recovered by evaporation as directed. The precipitate is finally dissolved in ammonia, evaporated to a small volume in a quartz crucible, acidified with nitric acid, evaporated to dryness, and then ignited to the trioxide.

*Hydrofluoric acid method.*—The sample, in small lumps, is treated in a platinum crucible with 5 c.c. of nitric acid (D 1·4) and 2 c.c. of water for every 0·2 gram taken from the assay. 0·5 Gram (or more) of ammonium fluoride is added, and the whole is heated on the water-bath until dissolved; sometimes it is necessary to add a few drops of sulphuric acid. Finally, 2 to 3 c.c. of sulphuric acid are added, and the fluorine is expelled by heating on the water-bath.

When cold, the contents are rinsed with water into a beaker; traces of tungstic acid adhering to the dish are dissolved in dilute ammonia. The solution, measuring about 60 c.c., is then boiled with 20 c.c. of hydrochloric acid, etc., as in the chlorine method. L. DE K.

[Separation of Columbium and Tantalum.] OTTO RUFF and EMIL SCHILLER (*Zeitsch. anorg. Chem.*, 1911, 72, 329—357).—See this vol., ii, 168.

**Estimation of Small Quantities of Methyl Alcohol [in Presence of Ethyl Alcohol].** CHARLES SIMMONDS (*Analyst*, 1912, 37, 16—18).—The liquid (a medicinal tincture, for instance) is submitted to distillation, and if necessary purified by the method of Thorpe and Holmes (*Trans.*, 1903, 83, 314) or by other suitable means. It is then diluted with water or ethyl alcohol until it contains 10% of alcohol by volume.

To 5 c.c. of this liquid placed in a wide test-tube are added 2·5 c.c. of permanganate solution (21 grams per 100 c.c.) and then 0·2 c.c. of sulphuric acid. After three minutes, 0·5 c.c. of oxalic acid (9·6 grams per 100 c.c.) is added, followed by 1 c.c. of sulphuric acid; 5 c.c. of Schiff's reagent are now added, and a violet colour, which takes

some time to develop, according to the amount of methyl alcohol originally present, will then be noticed (formaldehyde reaction).

The colour may be matched by means of solutions treated as above, and containing the formaldehyde produced from 0.001 to 0.004 gram of methyl alcohol.

L. DE K.

**Systematic Analysis of Phenols.** JEAN A. SANCHEZ (*Bull. Soc. chim.*, 1911, [iv], 9, 1056—1059).—A system of detecting phenols by means of colour reactions and precipitates is given.

To 1 c.c. of the liquid to be examined, 1 c.c. of mercuric nitrate solution is added; a slate-black precipitate indicates catechol. Two c.c. of the original liquid are mixed with 4 c.c. of lead acetate solution. The precipitate (*a*) is separately examined, and the filtrate is divided into two parts (*b*) and (*c*). Formaldehyde and hydrochloric acid give on boiling a gooseberry-red, flocculent precipitate with (*b*) if resorcinol is present, and ammonium sulphomolybdate solution produces an indigo-blue coloration with (*c*) if quinol is present. The precipitate (*a*) gives a red coloration changing to violet-red with formaldehyde and hydrochloric acid if pyrogallol is present.

The original liquid with formaldehyde and hydrochloric acid gives a green coloration if it contains phloroglucol; (2) a ruby-red tint with potassium cyanide if it contains gallic acid; (3) a white precipitate with solution of nicotine hydrochloride if tannic acid is present; and (4) a ruby-red tint with phloroglucinol and hydrochloric acid if it contains vanillin. For the detection of salicylic acid the original liquid is treated with lead nitrate solution and 2 drops of ammonia, and to the filtrate, acidified with 2 drops of hydrochloric acid, ferric chloride is added. A bluish-violet coloration is produced if salicylic acid is present.

Directions are given for the preparation of the various reagents.

T. A. H.

**New Method for the Estimation of Sugar.** FRANZ VON FILLINGER (*Zeitsch. Nahr. Genussm.*, 1911, 22, 605—607).—Two solutions are required in the process described, one containing 250 grams of potassium thiocyanate, 250 grams of potassium carbonate, and 25 grams of potassium hydrogen carbonate per litre, and the other containing 4.278 grams of crystallised copper sulphate per litre. Twenty c.c. of each of these solutions are placed in a flask, the latter being then closed with a rubber stopper, through which passes the lower end of the burette containing the sugar solution under examination. A side-tube on the neck of the flask is connected, by means of a T-piece, with two wash-bottles containing alkaline pyrogallol solution, the tubes in which are so arranged that all air entering or leaving the flask passes through one or the other wash-bottle, respectively. The solution in the flask is now boiled to expel the dissolved and free oxygen, and the sugar solution is then added gradually to the boiling contents of the flask until the colour is discharged. The percentage quantity of sugar in the solution is found by dividing 1 by the number of c.c. of the solution required for the titration. The sugar solution should contain approximately 0.1% of sugar.

W. P. S.

**Sugar Analysis.** CARL NEUBERG and MIGAKU ISHIDA (*Zeitsch. ver. deut. Zuckerind.*, 1911, 1113—1139).—Carbohydrate solutions are precipitated first with mercuric acetate in 50% solution and then with phosphotungstic acid in 25% solution. The precipitates settle quickly, and are easily filtered. These reagents do not affect carbohydrates at all, but completely precipitate all purines, alkaloids, nucleic acids, phosphatides, and dyes, as well as all protein decomposition products; the clear, almost colourless sugar solutions remaining are polarised directly. Excess of the reagents is avoided, and the mercuric acetate precipitate is filtered off before the addition of the phosphotungstic acid. The reagents have no influence on the rotatory power of the sugars. Glucosamine solutions can be purified in the same manner, and the method is particularly suited for the analysis of molasses, of which several examples are quoted. E. F. A.

**The Estimation of Sugar in Urine.** IVAR BANG (*Biochem. Zeitsch.*, 1912, 38, 168).—In view of the recent publication of Andersen (this vol., ii, 101) that the pigment can be removed from urine by charcoal in the presence of acetic acid, the author states that he has successfully employed alcohol instead of the acid, using 2 c.c. of alcohol to 18 c.c. of urine. The urine should be diluted if it contains more than 0.5% of sugar. S. B. S.

**Stability of Different Types of Smokeless Powder Towards Ultra-violet Light.** DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1911, 153, 1220—1223).—Exposure to ultra-violet light considerably accelerates the spontaneous decomposition of smokeless explosives, and this can be made the basis of a useful stability test. The explosives examined were cut into cylinders weighing 0.25—0.45 gram, placed over mercury in a quartz tube, containing nitrogen or carbon dioxide, and exposed to the radiation from a quartz mercury lamp at a distance of 78—80 mm. for six hours. In all cases rapid decomposition occurred with production of carbon monoxide or dioxide, nitrogen, and frequently nitrous and nitric oxides. Powders consisting only of nitrated cellulose were found to be more stable than those containing nitroglycerol. An English cordite containing 30% of the latter and 5% of vaseline, exposed in 1 c.c. of carbon dioxide, gave a mixture composed of the following volumes of gases:  $\text{CO}_2$ , 1 c.c.;  $\text{CO}$ , 0.17 c.c.;  $\text{NO}$ , 0.10 c.c.;  $\text{N}_2\text{O}$ , 0.02 c.c.;  $\text{N}_2$ , 0.10 c.c. Numerical results are also given for the French A and B powders, and for balistite of different ages and with different stabilisers. W. O. W.

**Estimation of Citral in Lemon Oil.** J. R. RIPPETOE and LOUIS E. WISE (*Amer. J. Pharm.*, 1911, 83, 558—562).—A method proposed originally by Hiltner is recommended as being trustworthy; it depends on the coloration produced when citral is treated with *m*-phenylenediamine hydrochloride. The reagent solution is prepared by dissolving 1 gram of the salt in 100 c.c. of alcohol and filtering the solution through bone-charcoal. From 2 to 4 c.c. of a 3% alcoholic solution of the lemon oil are placed in a graduated cylinder, 10 c.c. of

the reagent are added, and the mixture is diluted with alcohol to a volume of 25 c.c. The coloration is then compared with that obtained with mixtures containing known amounts of citral. W. P. S.

**Estimation of Acids in Wine with a View to Discover Adulteration.** FERDINAND REPITON (*Mon. Sci.*, 1911, [v], 1, i, 379—382).—The acidity of wine can be represented by the formula :

$$A_t = A_f + A_v + A_g,$$

where  $A_t$  is the total acidity,  $A_f$  the fixed acidity,  $A_v$  volatile acidity, and  $A_g$  gaseous acidity; the author discusses their relationship and transformations by the action of disease and organisms, and describes methods of estimating and distinguishing between them.

F. M. G. M.

**The Estimation of Volatile Acids in Wines.** FRITZ KOCZIRZ (*Zeitsch. landw. Wesen. Oesterr.*, 1911, 14, 866—871).—A discussion of numerous methods employed in the estimation of volatile acids in wine, with a sketch and description of a distilling apparatus which the author considers to give satisfactory results. F. M. G. M.

**Estimation of Acids in Oils and Fats.** HEINRICH LOEBELL (*Seifensied. Zeit.*, 1911, 38, 501—502, 530—532).—A method for the estimation of the acidity of fats and machine oils in which the presence of any acid is undesirable. The titration is carried out in a flask fitted with a tap at the base, and three openings at the top into which are fitted respectively a tube packed with soda-lime, a burette from which the standard alcoholic sodium hydroxide (or barium hydroxide) is delivered, and a dropping funnel containing about 100 c.c. benzyl alcohol and 2 c.c. of a 2% solution of alkali-blue.

F. M. G. M.

**Analysis of Lactic Acid.** W. KLAPPROTH (*Chem. Zeit.*, 1911, 35, 1409).—In replying to criticisms by Besson (compare Abstr., 1911, ii, 1140), the author points out that the method described by himself (Abstr., 1911, ii, 1038) is not a new method, but one which has been in general use for some time. Whilst heating the neutralised lactic acid solution after the addition of an excess of standard alkali accelerates the hydration of the anhydride, it is better to avoid boiling at any stage of the estimation. The methods described by Besson and the author are similar in principle, and, after further investigation, will probably be equally trustworthy. W. P. S.

**New Reaction for Uric Acid.** DIOSCORIDE VITALI (*Boll. Chim. Farm.*, 1911, 50, 799—803. Compare Ganassini, Abstr., 1909, ii, 100).—The author substituted a number of other oxidisers for the potassium persulphate employed by Ganassini in his reaction for the detection of uric acid, but sodium peroxide was the only one with which the reaction could be effected. No other metallic salt was found capable of replacing the zinc salts used by Ganassini, but the behaviour of some of them towards the solution containing alkali, urate, and sodium peroxide was characteristic. Copper sulphate gave a green precipitate (blue with larger quantities), cobaltous chloride a bluish-violet precipitate, and nickel salts a green precipitate having a

yellow tinge. Neutral lead acetate in the same conditions gave a red precipitate.

R. V. S.

**A New Ureometer.** ESPINOZA TAMAYO (*Ann. Chim. anal.*, 1911, 16, 453—454).—The apparatus figured in the original is a modification of that constructed by Esbach, and consists of a gas burette connected at the upper end with a generating bulb arrangement, at the bottom of which are placed 2 c.c. of urine. A kind of separatory funnel containing hypobromite solution is ground into the neck of the bulb, and the ground joint is also arranged to act as a tap to admit or cut off air from the bulb. After placing the whole in a water trough, the funnel is turned so as to stop the communication with the air, and by opening the stopcock the bulk of the hypobromite is allowed to flow into the urine. The nitrogen collecting in the burette is then measured with the usual precautions.

L. DE K.

**A Modification of Riegler's Method of Estimating Urea in Urine.** THOR EKECRANTZ and K. A. SÖDERMAN (*Zeitsch. physiol. Chem.*, 1912, 76, 173—176).—Riegler's method consists in warming the urine with nitric and nitrous acids, which decomposes the urea, so that it yields equal volumes of carbon dioxide and nitrogen. If this is combined with Dumas' method for estimating nitrogen, the method is simple and accurate. The details of the suggested modification are described, and the apparatus employed is figured.

W. D. H.

**Estimation of Cinnamein in Balsam of Peru.** FRANZ LEHMANN and A. MÜLLER (*Arch. Pharm.*, 1912, 250, 1—5).—The following method is recommended: Five grams of water are mixed with 2.5 grams of balsam of Peru in a 75 c.c. bottle, and to this 30 c.c. of ether are added, and the whole shaken during one minute. Five grams of sodium hydroxide solution are then added, and the mixture again shaken during one minute. The bottle is securely corked, and set aside bottom upwards during ten minutes. The cork is then carefully loosened, and about 3 c.c. of the aqueous layer run off. Half a gram of tragacanth gum is then added to the contents of the bottle, and the whole shaken. After five minutes, the clear ethereal solution is run into a tared, wide-mouthed flask and its weight ( $w$ ) noted. The solvent is then distilled off, the residue dried at 100° during thirty to forty-five minutes, and its weight ( $w'$ ) determined. The percentage,  $x$ , of cinnamein in the balsam is given by the following equation:  $x = (30w'/w - w')40$ .

T. A. H.

**Coagulation of Albumin by Heat. Consequences in Connexion with the Estimation of Urinary Albumin.** LUCIEN VALLERY (*Compt. rend.*, 1911, 153, 1243—1244).—The filtrate from albuminous urine which has been acidified and coagulated by heat in presence of ammonium chloride still gives a precipitate with Tanret's reagent. The use of Tanret's or Esbach's reagent is therefore recommended for the accurate estimation of urinary albumin.

W. O. W.

## General and Physical Chemistry.

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**Proposed System of Notation for Physico-chemical Quantities.** ARTHUR A. NOYES (*J. Amer. Chem. Soc.*, 1912, 34, 1—6).—An outline is given of a system of notation for physico-chemical quantities which is intended to serve as a basis for further discussion. An endeavour has been made to formulate a rational and consistent scheme, and at the same time to retain as far as possible the specific symbols at present in general use. E. G.

**Determinations of Refractive Indices of Gases Under High Pressures. I. The Dispersion of Hydrogen.** L. H. SIERTSEMA and M. DE HAAS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 592—603).—The refractive index of hydrogen has been measured at pressures from 40 to 80 atmospheres and for different wave-lengths by the interferometer method. From these data it is found that the dispersion constant of hydrogen is independent of the pressure within the above limits. The constants for the different wave-lengths are compared with the values obtained by calculation or graphical interpolation from the results of previous observers.

The natural vibration of hydrogen is found to correspond with the wave-length  $\lambda = 0.08703\mu$ , which agrees with the values calculated by Koch and by Natanson. H. M. D.

**Spectrochemical Investigations.** KARL AUWERS (*Annalen*, 1912, 387, 165—166. Compare following abstracts).—The investigations of the author and Eisenlohr (*Abstr.*, 1910, ii, 365, 367; 1911, ii, 781, 782) have materially increased the dependence which can be placed on the constitution of an organic substance determined by refractometric measurements. These investigations are being continued, of aromatic and of nitrogenous compounds by Eisenlohr, of acyclic and of hydroaromatic substances by the author. C. S.

**Refraction and Dispersion of Organic Substances containing Several Isolated Double Linkings.** KARL AUWERS and W. MOOSBRUGGER (*Annalen*, 1912, 387, 167—199).—The generally accepted view that acyclic dienes containing isolated double linkings are optically normal rests on a very narrow experimental foundation. The authors, therefore, have determined the molecular refractions and dispersions of a number of hydrocarbons, alcohols, ketones, acids, and esters containing two or more isolated (not conjugated) double linkings, and have established with practical certainty the fact that such substances exhibit normal optical behaviour. The substances which have been examined are  $\beta$ -methyl- $\Delta^{\beta\epsilon}$ -hexadiene,  $\beta\zeta$ -dimethyl- $\Delta^{\beta\epsilon}$ -heptadiene,  $\beta\zeta$ -dimethyl- $\Delta^{ac}$ -heptadiene,  $\beta\zeta$ -dimethyl- $\Delta^{\beta\epsilon}$ -octadiene,  $\beta\zeta$ -dimethyl- $\Delta^{\beta\theta}$ -nonatriene,  $\epsilon$ -ethyl- $\Delta^{a\theta}$ -nonatriene, *as*-diallylacetone, *s*-diallylacetone, diallylacetic acid and its ethyl ester, ethyl diallylmalonate, triallyl tricarballoylate, and triallyl citrate.

The positions of the double linkings in the preceding dienes and trienes (which have been obtained by dehydrating the corresponding alcohols) have not been determined with certainty. Their absolute position, however, is immaterial for the authors' purpose, because the optical (and also the thermal) behaviour of the hydrocarbons is independent of the relative positions of the double linkings, provided they are not conjugated. C. S.

**Spectrochemical Differentiation between Hydroaromatic Compounds with Endocyclic and with Semicyclic Double Linkings.** KARL AUWERS and PHILIPP ELLINGER (*Annalen*, 1912, 387, 200—239).—See this vol., i, 187.

**Constitution of Camphene.** KARL AUWERS (*Annalen*, 1912, 387, 240—253).—The author calls attention to the necessity of expressing densities as  $D'_t$ , not as  $D_t$ , in the calculation of specific and molecular refractions; in the latter case, the error exceeds 4% at 100°.

The exaltations of the specific refractions,  $\Sigma_D$ , of terpenes containing a semicyclic double linking (sabinene, *dl*-fenchene, terpinolene,  $\beta$ -terpinene,  $\beta$ -pinene) vary from 0.3 to 0.5, and, therefore, are just what is to be expected from a comparison with the exaltations of  $\Sigma_D$  of the alkylidenecycloparaffins (this vol., i, 187). The vexed question of the constitution of camphene appears to be settled definitely in favour of Wagner's methylene formula by the fact that the exaltation of  $\Sigma_D$  is 0.37, thus indicating that camphene also contains a semicyclic double linking. C. S.

**Spectroscopic Investigations in Connexion with the Active Modification of Nitrogen. II. Spectra of Elements and Compounds Excited by the Nitrogen.** (Hon.) ROBERT J. STRUTT and ALFRED FOWLER (*Proc. Roy. Soc.*, 1912, A, 86, 105—117. Compare Abstr., 1911, ii, 482, 678).—As a result of the examination of the spectra obtained when various elements and compounds are subjected to the action of the active modification of nitrogen, it is found that these spectra do not differ fundamentally from those obtained by other methods of excitation. In many cases, however, the band spectra are better displayed in the nitrogen after-glow, and the more refrangible parts of the spectrum are more completely developed.

In the case of metallic substances, the spectra resemble closely those obtained in the arc, or are intermediate between the arc and flame spectra. The *D* lines of sodium are nearly extinguished, and the maximum intensity in the principal series is found at  $\lambda = 3303$ . The spectra exhibited by iodine, stannic chloride, and mercuric chloride are more completely developed in the more refrangible region than the corresponding vacuum tube spectra. Cuprous chloride shows a similar behaviour when the after-glow and flame spectra are compared, the former giving an additional series of bands in the ultra-violet. Sulphur, hydrogen sulphide, and carbon disulphide exhibit band spectra, which are quite different from those

afforded by sulphur in a discharge tube, but resemble the bands of the carbon disulphide flame in air.

The cyanogen spectrum which appears when various organic compounds are subjected to the after-glow is appreciably different from that of the cyanogen flame or carbon arc. The after-glow spectrum shows a new set of bands near the more refrangible edges of the violet groups.

The after-glow is not only generated by discharge with spark-gap and condenser, but can be obtained from the electrodeless ring discharge if the presence of the nitrogen is suitably adjusted.

The destruction of the after-glow by small amounts of oxygen has been found to be due to the formation of a small quantity of nitric oxide, the effect of which is to suppress the  $\alpha$ -group of bands, leaving the rest of the after-glow spectrum unaltered.

H. M. D.

**The Less Refrangible Spectrum of Cyanogen and its Occurrence in the Carbon Arc.** ALFRED FOWLER and HERBERT SHAW (*Proc. Roy. Soc.*, 1912, *A*, 86, 118—130).—Wave-length measurements have been made in the less refrangible region of the cyanogen spectra afforded by (1) the flame of cyanogen burning in air; (2) the discharge through exhausted tubes containing cyanogen, and (3) the interaction of certain carbon compounds with active nitrogen. The data show that the heads of the bands can be arranged in regular series similar to those forming the first positive band spectrum of nitrogen. According to the method of producing the spectrum, considerable variations are found in the relative intensities of the various bands. A comparison of the spectra of cyanogen and of the carbon arc shows that the bands in the red and yellow regions of the arc spectrum are almost entirely due to cyanogen.

H. M. D.

**Comparison of Spectra in the Oxy-Hydrogen and Chlorine-Hydrogen Flames.** ALFRED HARNACK (*Zeitsch. wiss. Photochem.*, 1911—12, 10, 281—312, 313—346).—Photographs have been obtained of the spectra of calcium, strontium, barium, magnesium, copper, manganese, lead, nickel and cobalt in the oxy-hydrogen and chlorine-hydrogen flames. By means of these it has been possible to compare the emission spectra in the two flames over the visible and ultra-violet regions. In general, the chlorine-hydrogen flame spectra are characterised by the presence of relatively few lines. Bands are present in both series of spectra, but apart from those which are attributable to the chlorides of the metals, it is found that the spectral bands in the two flames are quite different. Bands characteristic of the nitrates of the metal were not found in any single case. In addition to the bands which are attributed to the metals and their oxides, calcium and strontium exhibit certain bands which are considered to be the result of oxidation in the oxy-hydrogen flame. In appearance these oxidation bands are quite different from the oxide bands, and disappear completely when the oxy-hydrogen flame is replaced by the chlorine-hydrogen flame. In the same circumstances, the oxide bands are replaced by a new series of bands.

The presence of comparatively few lines in the hydrogen-chlorine

flame spectrum is supposed to be due to the effect of the strongly electro-negative chlorine, the action of which is compared with the influence of electro-negative gases on the fluorescence of iodine vapour.

Wave-length measurements of bands which have not been previously described are recorded in detail in the paper. H. M. D.

**Emission Spectra of Aromatic Compounds Exposed to Ultra-violet Light, Cathode Rays, Radium Rays, and Canal Rays.** EUGEN GOLDSTEIN (*Ber. Deut. physikal. Ges.*, 1912, 14, 33—42).—It has been shown previously (compare Abstr., 1911, ii, 560) that solid aromatic substances emit the principal spectrum on exposure to ultra-violet light, if previously subjected to the action of cathode rays. In some cases, for example, cuminic acid, *o*-toluic acid, acenaphthene, and aceto-*p*-toluidide, this property is retained for months after the cathode ray treatment, whilst in others, such as phenylacetic acid, the principal spectrum is no longer observable after an interval of a few days.

The question as to whether the change produced by cathode rays is chemical or physical in nature has been examined. If the substances after treatment with cathode rays are melted, sublimed or dissolved and recrystallised, the principal spectrum is no longer emitted, and these observations seem to be in favour of the view that the change is a physical one.

In addition to cathode rays, the  $\beta$ -rays from radium, mesothorium, and actinium, as well as canal rays, are able to bring about the transformation which is characterised by the emission of the principal spectrum. During exposure to canal rays, it has been observed that the initial luminosity fades away gradually, and none of the substances examined recover their original properties on keeping, either in the dark or exposed to light. The same behaviour is exhibited by diamond powder, and since a chemical change is improbable in this case, the observations point to a physical change as the cause of the alteration in the optical properties. H. M. D.

**Absorption Spectra of Comparatively Rare Salts. XXXV. Spectrophotography of Certain Chemical Reactions, and the Effect of High Temperature on the Absorption Spectra of Non-aqueous Solutions.** HARRY C. JONES and W. W. STRONG (*Amer. Chem. J.*, 1912, 47, 27—85, 126—179).—A continuation of work described in earlier papers (Abstr., 1907, ii, 147; 1909, ii, 359; 1910, ii, 87; 1911, ii, 166, 168). A detailed account is given of the absorption spectra of salts of gadolinium, dysprosium, and samarium, and additional observations are recorded of the spectra of neodymium and uranium salts in various solvents. It has been found that the spectra of dysprosium and samarium salts have sharp, characteristic bands.

The effect of oxidising agents on uranous chloride, bromide, and sulphate has been further investigated by the spectrophotographic method.

The absorption spectra of solutions of salts in methyl and ethyl alcohols have been studied at various temperatures up to 195°. The absorption bands become wider as the temperature increases, and coloured solutions therefore gradually become more nearly opaque. The effect of a rise of temperature on the spectra of neodymium salts in mixtures of alcohol and water in which both the "alcohol bands" and "water bands" appear simultaneously has been investigated. The "water bands" are more affected than the "alcohol bands," and the "hydrates" are, therefore, less stable at high temperatures than the "alcoholates."

A discussion is given of a theory of absorption spectra, based on the conception of the existence of aggregates composed of one or more molecules or ions of the dissolved salt and one or more molecules of the solvent.

E. G.

**Spectrophotographic Investigation of Urobilin.** LOUIS LEWIN and E. STENGER (*Pflüger's Archiv*, 1912, 144, 279—286).—All the substances described as urobilin show an absorption band in the green-blue region, the centre of which is  $\lambda 494$ ; this is the case for alcoholic and aqueous acid solutions; on the addition of alkali, the band shifts towards the red end of the spectrum. The same shifting takes place when the fluorescent reaction is obtained by adding zinc chloride and ammonia to the alcoholic solution, and is due to the alkali. Hydrobilirubin and the material prepared from hæmatoporphyrin by Nencki and Sieber give a band between  $\lambda 580$  and  $\lambda 628$ .

W. D. H.

**Phosphorescence of Organic Compounds at Low Temperatures.** JOSEPH DE KOWALSKI (*Arch. Sci. phys. nat.*, 1912, [iv], 33, 5—27).—A résumé of the author's work on this subject (Abstr., 1907, ii, 727; 1908, ii, 79; 1909, ii, 282, 845; 1910, ii, 371, 1016).

The introduction of one or more groups into the benzene nucleus produces the following effects on the absorption spectra: the number of doublets and triplets diminishes, the bands become less distinct, those in the extreme ultra-violet are displaced towards the red, and the extent of the phosphorescence spectrum is reduced.

Those substituents which displace the limit of the phosphorescence spectrum towards the violet are termed *hypso-phosphic*, whilst those which displace the limit towards the red are *batho-phosphic*. Batho-phosphic mono-substituents are particularly cyano, CN, also amino,  $\text{NH}_2$ , and carboxyl,  $\text{CO}_2\text{H}$ . All other mono-substituents are hypso-phosphic. In the case of di-substituents, the difference between the extent of the phosphorescence spectrum when these are in the ortho- and para-positions respectively is a constant.

The influence of a second substituting group on the mono-substituted compound is specific. CN and  $\text{CO}_2\text{H}$  are always batho-phosphic, methyl is batho-phosphic in the para-position, and may be hypso-phosphic in the ortho-position. Hydroxyl is strongly hypso-phosphic. The more negative the radicle the greater its batho-phosphic action. Cyano and  $(\text{CH}_3)_2$  also influence the nature of the phosphorescence spectrum, converting doublets into triplets.

Each absorption band corresponds with a group of bands in the

phosphorescence spectrum, and this group only differs from the absorption band by a practically constant number of oscillations.

E. F. A.

**Rotatory Dispersion and Mutarotation of the Carbohydrates in Water, Pyridine, and Formic Acid.** HERMANN GROSSMANN and F. L. BLOCH (*Zeitsch. ver. deut. Zuckerind.*, 1912, 19—74).—The dispersion coefficient violet/red for solutions of the simple carbohydrates in water, pyridine, or formic acid is usually between 2.2 and 2.4. Abnormal values were found for rhamnose in water, 2.03, and for lactose in pyridine.

The change of rotation of the carbohydrates, usually for red light, has been studied in water, pyridine, and formic acid; in the last solvent the change is probably due to the formation of formyl compounds; it is usually in the opposite sense to the mutarotation changes.

The following values refer to  $[\alpha]_D^{20}$ . Xylose in water changes from  $+80^\circ$  to  $18.2^\circ$ . In pyridine the rotation increases from  $+117^\circ$  to  $+122^\circ$  during the first ten minutes, and then falls steadily to  $+40.6^\circ$ . In formic acid it changes from  $+40^\circ$  to  $+66.6^\circ$ .

Rhamnose changes in water from  $-4.43^\circ$  to  $+8.6^\circ$ ; in pyridine from  $-41.39^\circ$  to  $-45.12^\circ$  during the first half-hour, and finally to  $-33^\circ$ .

The rotation of galactose in water falls from  $+141^\circ$  to  $+80.2^\circ$ ; the initial rotation in pyridine is probably  $200^\circ$ , falling to  $59.8^\circ$ . In formic acid the change is from  $89.1^\circ$  to  $127.3^\circ$ .

Dextrose in water changes from  $111^\circ$  to  $52.6^\circ$ ; in pyridine from  $149.6^\circ$  to  $74.8^\circ$ , and in formic acid from  $73.8^\circ$  to  $123.1^\circ$ .

Lævulose changes very rapidly in water from  $-101.9^\circ$  to  $-90.46^\circ$ ; in pyridine from  $-160^\circ$  to  $-35^\circ$ , and in formic acid from  $-86.5^\circ$  to  $-46.7^\circ$ .

N/8-Sucrose has a rotation  $+66.5^\circ$  in water;  $+84.37^\circ$  in pyridine, and changes from  $+2.64^\circ$  to  $+39.95^\circ$  in formic acid.

Lactose alters from  $83.1^\circ$  to  $52.5^\circ$  in water; the final value in pyridine is  $41.33^\circ$ . For this carbohydrate a change in the concentration has almost no influence. In formic acid the rotation changes from  $+68.2^\circ$  to  $+96.6^\circ$ .

Maltose in water varies from  $121.6^\circ$  to  $130.5^\circ$  (hydrate); in pyridine from  $103.5^\circ$  to  $123.5^\circ$ , and in formic acid from  $129.1^\circ$  to  $172.1^\circ$ .

Raffinose has the rotation  $105.2^\circ$  in water and  $117.2^\circ$  in pyridine for N/16-solutions; in formic acid the value changes from  $72.3^\circ$  to  $109.4^\circ$ ; during the first few minutes, the rotation diminishes. All the values cited are affected considerably by alterations of the concentration of the carbohydrate.

E. F. A.

**Photochemical Studies. IV. Photochemical Temperature-coefficients of Bromine.** JOH. PLOTNIKOFF (*Zeitsch. physikal. Chem.*, 1912, 78, 573—581. Compare Abstr., 1911, ii, 452).—The temperature-coefficients for  $10^\circ$  for three light reactions in which bromine is concerned are as follows: the addition of bromine

to cinnamic acid in benzene as solvent, 1.37; the same reagents in carbon tetrachloride as solvent, 1.41; the action of bromine on benzene, 1.40. It is shown that the temperature-coefficients for  $10^\circ$  for the light reactions hitherto examined can be referred to one of three groups of values:  $1.04 \pm 0.03$ ,  $1.20 \pm 0.03$ , and  $1.39 \pm 0.03$ .

G. S.

**Influence of Gas Pressure on the Bleaching of Dyes in the Visible Spectrum.** P. LASAREFF (*Zeitsch. physikal. Chem.*, 1912, 78, 657—660. Compare *Ann. Physik*, 1907, [4], 24, 661).—A colloidal film, stained with a particular dye, was arranged in such a way that it was in contact with air under different pressures up to atmospheric, and the rate of bleaching was measured with a spectrophotometer. As dyes, cyanine, pinachrome, and lepidinecyanine were used. The bleaching is the more rapid the greater the oxygen pressure. When the rates of bleaching at constant absorption are plotted against the corresponding pressures, a straight line is obtained which does not pass through the origin, so that the velocity of bleaching must have a definite value in a vacuum.

G. S.

**Bleaching of Methylene-blue in the Visible Spectrum.** P. LASAREFF (*Zeitsch. physikal. Chem.*, 1912, 78, 661—666).—Methylene-blue is bleached on exposure to a fairly intense light, most rapidly in absence of oxygen, but the colour returns when the bleached material is kept for a long period in the dark, provided that oxygen is present. In the experiments films of gelatin coloured with methylene-blue were exposed to light from a Nernst lamp, and examined with a spectrophotometer. After exposure to light of wave-length  $620\mu$ , the film regains its original properties in the dark; with light of wave-length greater than  $688\mu$  the absorption does not regain its original value in the dark. These results can be explained on the assumption that the bleached substance becomes oxidised in the dark to products which for short waves have an absorption identical with, for long waves and absorption different from, that of methylene-blue.

G. S.

**Some Relations Existing between the Radio-elements.** RICHARD SWINNE (*Physikal. Zeitsch.*, 1912, 13, 14—21).—The relation between the logarithm of the period and the velocity of the  $\alpha$ -particle expelled (compare Geiger and Nuttall, *Abstr.*, 1911, ii, 953) is discussed in detail, and slightly different relations are proposed. The period of ionium calculated from the range of its  $\alpha$ -particle is  $3.3 \times 10^5$  years. Taking in each of the three series the range of the last  $\alpha$ -ray producing member and subtracting this from the range of the  $\alpha$ -rays of corresponding members in the three series, it is found that the differences are the same for several pairs. In the single series a relation between the period of the member and the velocity of the  $\beta$ -particle expelled is found to exist similar to that obtaining for the  $\alpha$ -particle.

F. S.

**The  $\beta$ -Rays of the Radium Family.** J. DANYSZ (*Le Radium*, 1912, 9, 1—5).—This paper contains a description in full of the methods employed, together with remarkable reproductions of the photographs obtained in the work already published (this vol., ii,

113). Twenty-three beams of  $\beta$ -rays have been observed, making with two more each from radium, radium-*B*, and radium-*D* observed by others, 29 in all for the radium family, and rendering the hypothesis that each beam corresponds with a particular radio-element very improbable. F. S.

**The  $\beta$ -Rays of the Slow-changing Active Deposit of Radium.** J. DANYSZ and J. GÖTZ (*Le Radium*, 1912, 9, 6).—An old tube containing radium-*D* and products was examined two months after it had been filled with emanation, precautions being taken to remove any still adhering emanation. The photographs obtained were entirely different from those previously obtained with the emanation. Two wide beams, of which the neighbouring sides alone are sharp and correspond with velocities of 0.963 and 0.944 (light = 1), are easily distinguished. The fast side of the faster beam is difficult to determine, and corresponds with a velocity of 0.995. The slow side of the slower beam is not sharp, but two maxima of intensity at 0.67 and 0.48 are distinguishable. The slow beam gives a very intense image, but the rapid beam is very feeble. The very feeble beams obtained previously with the emanation were not observed with radium-*D*. F. S.

**The Growth of Radium-*C* from Radium-*B*.** KASIMIR FAJANS and WALTER MAKOWER (*Phil. Mag.*, 1912, [vi], 23, 292—301).—The object of the experiments was to find out whether radium-*C*<sub>1</sub> as well as radium-*C*<sub>2</sub> emits  $\beta$ -rays, by observing the rise and fall of the  $\beta$ -radiation, through 1 mm. of aluminium, from a plate covered with pure radium-*B*, obtained by recoil from radium-*A*. It was found, as Schmidt had stated, that radium-*B* emits some  $\beta$ -rays capable of traversing 1 mm. of aluminium, which observation Hahn and Meitner have called in question. Allowing for these, the curves agreed with the theoretical ones drawn on the assumption that the whole of the  $\beta$ -rays are due to radium-*C*<sub>1</sub>. The proportion contributed by radium-*C*<sub>2</sub> was too small to be detected in these experiments, hence the ratio of the number of atoms of radium-*C*<sub>2</sub> to that of radium-*C*<sub>1</sub>, in equilibrium, must be very small, which supports the view that radium-*C*<sub>2</sub> is in a branch series.

With regard to the  $\beta$ -rays of radium-*B*, similar experiments through a variety of thicknesses of aluminium gave data for calculating the absorption of the  $\beta$ -rays of radium-*B* in that metal. The absorption coefficient for the main soft  $\beta$ -radiation was found to be  $91(\text{cm.})^{-1}$ , but  $1\frac{1}{2}\%$  of the ionisation was due to  $\beta$ -rays of absorption coefficient  $13(\text{cm.})^{-1}$ , identical with the rays of radium-*C*. No evidence of any rays of absorption coefficient  $890(\text{cm.})^{-1}$ , as found by Schmidt, was obtained. F. S.

**$\gamma$ -Radiation from Radium-*B*.** H. G. J. MOSELEY and WALTER MAKOWER (*Phil. Mag.*, 1912, [vi], 23, 302—310).—It was to be expected, since radium-*B* emits some  $\beta$ -rays as penetrating as those of radium-*C*, that radium-*B* should emit some  $\gamma$ -rays as penetrating as

the  $\gamma$ -rays of radium-*C*. Investigation showed that radium-*B* does emit  $\gamma$ -rays, which have hitherto escaped detection, of much greater absorption coefficient than those of radium-*C*. The method was the same as that used for the  $\beta$ -rays of radium-*B* (preceding abstract), except that sufficient lead to absorb all the  $\beta$ -rays, instead of aluminium, was employed as absorbing material; 12.7% of the ionisation produced by the  $\gamma$ -rays of radium-*B* and -*C* in equilibrium was found to be due to radium-*B*. The absorption coefficient for these rays was  $4(\text{cm.})^{-1}$  between 3 and 6 mm., and  $6(\text{cm.})^{-1}$  between 0.97 and 1.72 mm. of lead. The rise of  $\gamma$ -radiation from a tube containing initially pure radium emanation when taken through various thicknesses of lead agreed with the above conclusions. Through 2.3 cm. of lead the amount of ionisation, if any, contributed by the  $\gamma$ -rays of radium-*B* is less than 1% of that contributed by radium-*C*. F. S.

**Nature of  $\gamma$ -Rays.** T. H. LABY and P. W. BURBIDGE (*Ls Radium*, 1911, 8, 464—465).—The ionisation currents in two similar ionisation chambers, placed symmetrically with regard to a source of  $\gamma$ -rays of radium, were arranged to balance one another over long periods, so that the electrometer showed no appreciable deflexion. Variations in the balance, first in one direction and then in the other, were observed, which are due either to variations in the number of ions produced by a constant source of  $\gamma$ -rays from instant to instant, or to a von Schweidler variation in the radiation itself, such as would be produced if the  $\gamma$ -rays were corpuscular rather than of wave-form.

F. S.

**$\delta$ -Rays.** II. NORMAN CAMPBELL (*Phil. Mag.*, 1912, [vi], 23, 46—64. Compare Abstr., 1911, ii, 841).—The previous experiments have been repeated with soot-covered electrodes, for Baeyer has shown that the reflexion of the rays from a soot-covered surface is very small. The theory used previously has been shown to be quite incapable of explaining the results. The differences obtained when electrodes of various metals are employed are probably due to surface difference rather than to differences of speed of the electrons generated from the metal. A minimum estimate of the speed of the  $\delta$ -rays generated is that corresponding with a *P.D.* of 3 volts. But neither the method employed nor other methods of various investigators gives information as to what the maximum limit of speed may be. So far as is known the speed may be independent both of the velocity of the exciting  $\alpha$ -rays and of the nature of the material generating the  $\delta$ -rays. There is no such difference between the  $\delta$ -rays emitted, for example, by gold and by aluminium as there is between the secondary *X*-rays from these metals. With regard to the quantities of incident and emergent  $\delta$ -radiation, there is no evidence that these may not be equal, nor is there evidence that polonium emits a  $\delta$ -radiation other than that generated by the  $\alpha$ -rays it expels. F. S.

**Mobility of the Positive and Negative Ions in Gases at High Pressures.** ALOIS F. KOVARIK (*Proc. Roy. Soc.*, 1912, A, 86, 154—162).—The mobilities of the positive and negative ions in dry

air, dry hydrogen, and moist carbon dioxide have been determined from observations of the current flowing between two plates, at the surface of one of which an intense ionisation was maintained by means of an ionium preparation. In dry air and hydrogen the mobility varies inversely as the pressure up to 75 atmospheres, which was the highest pressure used. In moist carbon dioxide the same relationship holds up to 40 atmospheres, but at higher pressures the product of pressure and mobility decreases as the gas approaches the liquid state.

The mean values of this product, over the range for which it is constant, are for the positive and negative ions respectively 1.346 and 1.89 in air, 6.20 and 8.19 in hydrogen, and 0.705 and 0.67 in moist carbon dioxide. Mobilities are here referred to cms. per second, and a potential gradient of 1 volt per cm.

H. M. D.

### Ionisation in Gaseous Mixtures by Röntgen Radiation.

CHARLES G. BARKLA and L. SIMONS (*Phil. Mag.*, 1912, [vi], 23, 317—333).—Experiments under a great variety of conditions showed that the relative ionisation in hydrogen sulphide is about 1.24 times that in sulphur dioxide, although the absorption of the rays in the latter gas is greater than that in the former. Characteristic  $X$ -radiations varying enormously in penetrating power, from that characteristic of chromium to that characteristic of antimony, were employed. The ionisation in a mixture of hydrogen sulphide and oxygen was 1.17 times as great as in a mixture of the same composition of sulphur dioxide and hydrogen. The conclusion is drawn that ionisation by  $X$ -rays is not fundamentally atomic, but depends to some extent on chemical combinations, equal absorptions of the  $X$ -rays and their secondary radiation being accompanied by unequal ionisations. The results so far attained point to the relative ionisation in different gases by  $X$ -rays being the same as for the corpuscular rays generated by  $X$ -rays. Preliminary experiments indicate that much of the ionisation by  $X$ -rays is not produced by the secondary corpuscular radiation.

F. S.

**Ionisation by Radioactive Recoil Products.** LOUIS WERTENSTEIN (*Le Radium*, 1912, 9, 6—19).—The active deposits from the radium emanation twenty minutes after preparation (radium- $B$  and - $C$ ) emits, in addition to the known radiations, a relatively intense ionisation very easily absorbed due to radium- $C$ . The radiation consists of a small proportion easily deviable in a magnetic field ( $\delta$ -rays excited by the  $\alpha$ -rays of radium- $C$ ) and of a more important part of the same penetrating power not so deviable. The product of the pressure (mm.) and the range (mm.) is about 110, which is nearly the value found (90) for radium- $B$  recoiled from radium- $A$ . The value of this part is much affected by the nature and state of the surface made active, and is greatest with platinum, when it gives in favourable circumstances over the initial part of its range five times as much ionisation as is produced by the  $\alpha$ -rays. The range is about 1/500th of that of the  $\alpha$ -rays of radium- $C$ , or 1/7th mm. of air at atmospheric pressure, so that in all ordinary experiments the total ionisation it

gives is less than 1% of that due to the  $\alpha$ -rays. The effect of change of pressure on the ionisation, and of change of distance between the source, the rays of which were canalised by means of a bundle of short, narrow tubes, and a shallow ionisation chamber were studied in a special apparatus analogous to that employed by Bragg for the range of the  $\alpha$ -rays. The radiation of low penetrating power, which is uninfluenced by a magnetic field, is attributed to the particles of radium-*D* recoiling from radium-*C*. The ionisation per mm. of path decreases as the distance traversed from the source increases, which is the opposite of that found for the  $\alpha$ -rays. It was proved that the ionisation due to these new rays decayed with the period of radium-*C*, and was given also by pure radium-*C*, as well as by radium-*B* and -*C*.  
F. S.

The Emanation Content in the Sea-Water and the Active Deposit from the Air between the Chilian Coast and the East Indies. I. and II. WALTER KNOCHÉ (*Physikal. Zeitsch.* 1912, 13, 112—115, 152—157).—I. The mean, in Mache units, of thirty estimations of the emanation content of sea-water taken during a round voyage in March to May, 1911, between Valparaiso and the East Indies gave a mean content of 0.05, the extremes varying from 0.00 to 0.20, as compared with a mean of 0.12 (0.00 to 0.29) found in September and October, 1908, by Engler and Sieveking for the Atlantic Ocean. Twenty-one results were below 0.05, two were between 0.05 and 0.10, and five were between 0.15 and 0.20. The activity of the water changes extraordinarily with the locality. The source of the emanation cannot be the atmosphere, for no relation exists between emanation content and the atmospheric active deposit. The emanation content increases with the sp. gr. of the water and with its temperature.

II. The active deposit on a wire five metres long elevated seventeen metres above the sea-level and charged to  $-2000V$  after two hours' exposure was measured at various intervals after being placed in the electroscope. After fifteen to twenty-five minutes the curves showed that only the radium active deposit was present. A résumé is given of the results in connexion with the numerous data published by other investigators, and are discussed with the view to showing that the active deposit in the air over the ocean is derived from the land. A chart is given showing the proportion of such active matter remaining after having been transported various distances by various winds, and it is shown that there is no difficulty in ascribing the results observed to active matter carried from the land.  
F. S.

The Dependence of the Penetrating Power of Röntgen Rays on the Pressure and Nature of the Contained Gas. CHARLES L. LINDEMANN and F. A. LINDEMANN (*Physikal. Zeitsch.*, 1912, 13, 104—106).—Tables of measurements are given of the penetrating power of *X*-rays, on the Wehnelt scale and by the Bauer qualimeter, when a constant current of 1.5 milliamperes was passed through a properly prepared *X*-ray bulb filled with air, hydrogen,

oxygen, chlorine, carbon dioxide, argon, and helium at known various pressures. It is considered to be possible, with a suitably calibrated bulb, to determine the gas pressure by means of a Wehnelt scale.

F. S.

**Explosion of Radium Bromide through the Action of Water.** B. JOST (*Chem. Zeit.*, 1912, 36, 138).—In order to transfer some radium bromide from the capsule containing it to a spinthariscopescope, a needle, the point of which had been slightly moistened, was used for picking up the small particles of the salt. In two cases the particles exploded during the act of transference. Such explosions seem to be connected with the purity and age of the salt, and with the amount of moisture present.

T. S. P.

**Radioactivity of the Rocks of the St. Gothard Tunnel.** JOHN JOLY (*Phil. Mag.*, 1912, [vi], 23, 201—211).—A new series of measurements has been carried out by means of the electric furnace fusion method of the radium in thirty-six rock samples from the St. Gothard tunnel, together with measurements of the thorium content also. The following table gives the mean results for four sections of the tunnel :

	Ra per gram ( $\times 10^{12}$ ).	Th per gram ( $\times 10^5$ ).
Granite and gneiss of the Finsteraarhorn massif	7.2	1.85
	<i>6.0</i>	<i>2.64</i>
Altered sediments of the Usernmulde .....	4.9	0.97
	<i>2.6</i>	<i>1.70</i>
Schists, etc., of the St. Gothard massif.....	3.9	1.18
	<i>2.8</i>	<i>1.10</i>
Altered sediments of the Tessinmulde .....	3.4	0.51
	<i>2.0</i>	<i>0.44</i>

The figures in italics refer to the new determinations, the others being those previously obtained for the fifty-one original specimens examined. There is about double as much of the radioactive substances in the granite as in the schists, and the heat derived from these substances agrees with Stapff's measurements of the temperature gradients, 20.9 metres per  $1^\circ$  in the granite, and 46.6 metres in the schists. The radioactive hypothesis of the origin of the abnormal heat in the St. Gothard tunnel is the most probable.

F. S.

**Radium Content of Secondary Rocks.** ARNOLD L. FLETCHER (*Phil. Mag.*, 1912, [vi], 23, 279—291).—The radium in eighty-two specimens of secondary rocks has been determined by the fusion method. With the exception of the small and relatively unimportant class of calcareous rocks, all the secondary rocks were found to contain very nearly the same quantity of radium, namely,  $1.4 (\times 10^{-12}$  gram per gram). The mean found for the calcareous sediments was 0.8. The coarse detrital sediments contained somewhat higher amounts of radium on the average than the fine, classed as Argillaceous and Schistose.

F. S.

**Dielectric Constants of Binary Mixtures and their Refractivity for Long Waves.** ALFRED SCHULZE (*Zeitsch. Elektrochem.*, 1912, 18, 77—93. Compare Dolezalek, *Abstr.*, 1909, ii, 22).—The dielectric constants of the four binary mixtures ether-chloroform, benzene-carbon tetrachloride, benzene-chloroform, and benzene-ether have been determined at a series of temperatures by the bridge method, and from the results the molecular refractivities for long waves have been calculated by the known formula. If two liquids mix without alteration of properties, the molecular refractivity of the mixture expressed according to the method of Lorentz must be represented by a straight line. If the liquids enter into chemical combination, it is plausible to assume that the refractivity will increase with the size of the molecule, and therefore that the experimental curve will be above the straight line for an ideal mixture. If, on the other hand, the molecular complexity of one of the components diminishes on mixing with the other component, the refractivity of the mixture should be less than the mean refractivity of the components. On this basis the equilibrium constants or association constants are calculated, as already described in connexion with the vapour pressures of binary mixtures (*loc. cit.*), and it is shown that ether and chloroform form a compound containing one molecule of each, that carbon tetrachloride is associated, that benzene and chloroform mix with very slight alteration of properties, and that benzene and ether enter into chemical combination. The results confirm in all respects those deduced from the vapour-pressure measurements.

G. S.

**Some Electrical Properties of Sodium and Potassium and their Alloy.** EDWIN F. NORTHRUP (*Trans. Amer. Electrochem. Soc.*, 1911, 20, 185—204).—The electrical resistance of metallic sodium increases proportionally with the temperature. There is a sudden and large increase at the melting point, and the resistance of the liquid sodium then increases in linear proportion. At 20° the specific resistance is  $4873 \times 10^{-9}$ , and at 100°,  $9724 \times 10^{-9}$ . Potassium behaves in a similar manner, the specific resistance being  $7116 \times 10^{-9}$  at 20° and  $15306 \times 10^{-9}$  at 100°. The liquid alloy, containing equal volumes of sodium and potassium, has a much higher specific resistance,  $33792 \times 10^{-9}$  at 20° and  $37872 \times 10^{-9}$  at 100°.

C. H. D.

**The Conductivity of Mixtures of Copper Sulphate and Sulphuric Acid.** HENRY K. RICHARDSON and FLOYD D. TAYLOR (*Trans. Amer. Electrochem. Soc.*, 1911, 20, 179—184).—Addition of copper sulphate increases the conductivity of a solution of sulphuric acid containing less than 3 grams per 100 c.c., and diminishes the conductivity of the mixture if more sulphuric acid is present.

C. H. D.

**Potential of the Potassium Electrode.** GILBERT N. LEWIS and FREDERICK G. KAYES (*J. Amer. Chem. Soc.*, 1912, 34, 119—122).—The potential of the potassium electrode has been determined by the method employed by Lewis and Kraus (*Abstr.*, 1910, ii, 127) in the case of the sodium electrode.

The results show that the potential of potassium in a *N*-solution of potassium ions at 25° is 3.2084 volts against the normal calomel electrode taken as zero. This value is the sum of (1) 2.1603 volts, the potential of potassium amalgam (containing 0.2216% K) against an aqueous solution containing potassium ions in *N*-concentration, and (2) 1.0481 volts, the difference of potential between potassium and 0.2216% potassium amalgam in a solution of potassium iodide in ethylamine.

The temperature-coefficient of the latter *E.M.F.* is 0.000272 volt per degree, and hence the heat of solution of 1 gram-atom of potassium in 0.2216% potassium amalgam is 26,050 cal.

Preliminary experiments have been made to ascertain the extent to which this method is applicable in the case of lithium, rubidium, caesium, and the alkaline-earth metals.

E. G.

**Galvanic Cells with Carbon Anodes.** P. BECHTEREFF (*Chem. Zentr.*, 1912, i, 106—108; from *Iwiestja Petersburg Polytech.*, 1911, 15, 443—526).—Measurements have been made of the *E.M.F.*, electrode potentials, and polarisability of cells with a carbon anode, a metal cathode, and fused sodium hydroxide as electrolyte, at temperatures between 300° and 1400°. The influence of the addition to the fused electrolyte of selenium, selenium dioxide, sodium selenate, and sodium nitrate was also examined for the temperature interval 320—650°. At 400°, the carbon anode becomes less electro-positive to the extent of 0.3 volt on the addition of 6% sodium nitrate. In contact with a fused mixture of the carbonates of lithium, sodium, and potassium, the anode potential differs from that for carbon in contact with fused sodium hydroxide by 0.8 volt. These changes indicate that the carbon electrode behaves as a gas electrode.

The behaviour of different passive metals, such as iron, cobalt, nickel, platinum, gold, silver, and copper, as well as that of constantan and the oxide  $\text{Fe}_3\text{O}_4$ , is exactly the same according to electrode potential measurements. It follows from this observation that the measured cathode potential is that of air in contact with fused sodium hydroxide.

Sodium nitrate, chlorate and perchlorate, potassium permanganate, selenium, and tellurium were found to act as depolarisers for the carbon anode. Platinum and silver are less readily polarised than iron and nickel, and the tendency towards cathodic polarisation is diminished by the addition of sodium peroxide. The *E.M.F.* of the cell  $\text{C} \mid \text{fused NaOH} \mid \text{Fe}$  increases with rising temperature to a maximum of 0.9 volt, and then diminishes when the electrolyte begins to boil.

Cells of the type  $\text{C} \mid \text{fused B}_2\text{O}_3 \mid \text{Pt}$  were also examined at high temperatures, oxygen compounds of iron, cobalt, nickel, copper, and silver being added to the fused electrolyte. Such cells at high temperatures have an *E.M.F.* which in some cases exceeds 1 volt.

H. M. D.

**A Generalisation of van't Hoff's Formula.** EDOUARD HERZEN (*Bull. Soc. chim. Belg.*, 1912, 26, 15—18).—From a consideration of the equilibrium between two electrolytes having an ion in common, and the solution saturated with respect to both, the author deduces an

expression from which the ionisation of each electrolyte in the common solution may be calculated. The data required are the concentration and degree of ionisation of each electrolyte in its own saturated solution, and the concentration of both in the common solution.

H. M. D.

**Conductivity and Photoelectric Hysteresis of Isomorphous Mixtures of Sulphur and Selenium and of Selenium and Tellurium.** LAVORO AMADUZZI and MAURIZIO PADOA (*Nuovo Cim.*, 1912, [vi], 3, i, 66—70).—Isomorphous mixtures of sulphur and selenium containing respectively 88.99 and 95.884 atomic % Se show photoelectric sensibilities, expressed as the ratio of the conductivities in darkness and under illumination, of 1.20 and 3.6. The second mixture shows considerable sensitiveness to variations of strong light, whilst the first hardly responds to such variations. Hysteresis is observed of different character in the two mixtures.

Isomorphous mixtures of selenium and tellurium, from 0.887 to 10.081 atomic % Te, give a curve of sensibility which falls, rapidly at first and then slowly, with increasing tellurium content.

Mixtures of sulphur and tellurium are devoid of photoelectric properties.

C. H. D.

**The Hallwachs Effect and Phototropy.** LAVORO AMADUZZI and MAURIZIO PADOA (*Nuovo Cim.*, 1912, [vi], 3, i, 41—50).—The substance to be examined is connected with a negatively charged electroscope, ultra-violet light is allowed to fall on it from a mercury lamp, and the time taken to discharge the electroscope is observed. In order to examine the effect at different temperatures, the substance is attached to the surface of a copper cube, which may be filled with warm oil. The experiment is repeated with the same substance after it has undergone phototropic change of colour under the influence of sunlight.

The examination of a number of arylhydrazones of various aldehydes shows that the change of colour corresponds with a change of photoelectric power, the latter being usually increased, but occasionally diminished. Exposure to ultra-violet rays changes the photoelectric power, even when a change of colour is not produced. Fatigue is observed. The photoelectric power of benzaldehydephenylhydrazone varies greatly with the temperature, whilst piperonaldehyde-*o*-tolyllosazone and anisaldehyde- $\beta$ -naphthyllosazone vary very little.

C. H. D.

**Thermomagnetic Properties of Elements.** MORRIS OWEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 637—644. Compare Honda, Abstr., 1910, ii, 686).—Further measurements have been made of the magnetic susceptibility of the elements at temperatures between that of the room and  $-170^{\circ}$ . The new data indicate that the connexion between the magnetic susceptibility and the atomic weight is more intricate than was formerly supposed, although a general periodic relationship is still observable. The influence of polymorphism is very pronounced, and this introduces difficulties into

the comparison of the susceptibilities of certain elements. According to the variation of the susceptibility with the temperature, the elements fall into six different groups. H. M. D.

**Researches on Magnetism. IV. Para-magnetism at Very Low Temperatures.** H. KAMERLINGH ONNES and ALBERT PERRIER (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 674—678. Compare Abstr., 1911, ii, 694).—It has been found previously that the magnetic susceptibility of solid oxygen does not follow Curie's law at liquid hydrogen temperatures. Data are now recorded which show that the susceptibility decreases slightly as the temperature is lowered from 20·3° (absolute) to 13·9°. The change in the magnetic susceptibility when oxygen passes from the solid to the liquid condition is found to be about four times as large as the change indicated in previous experiments with a different form of apparatus. The discrepancy between the two results is attributed to the magneto-crystalline properties of solid oxygen, and if this is the correct explanation, it is probable that the new method of determination affords a more exact value of the change in susceptibility at the melting point.

Some experiments with ferrous sulphate (anhydrous) show that the susceptibility increases as the temperature falls from 293° to 20·3° (abs.), and then diminishes as the temperature falls from 20·3 to 13·9°. The susceptibility has a maximum value at a certain temperature, and the behaviour is quite similar to that of solid oxygen. H. M. D.

**The Magnetic Susceptibility and the Magnetron Number of the Oxides and Sulphides of Vanadium.** EDGAR WEDEKIND and C. HORST (*Ber.*, 1912, 45, 262—270).—The specific magnetic susceptibility ( $\chi$ ) and the magneton number ( $n = \sigma m / 1123\cdot5$ , where  $\sigma m$  is the molecular saturation: compare Abstr., 1911, ii, 250, 367, 694) of the various compounds are as follows:

	VO.	V <sub>2</sub> O <sub>3</sub> .	VO <sub>2</sub> .	V <sub>2</sub> O <sub>5</sub> .	VS.	V <sub>2</sub> S <sub>3</sub> .	V <sub>2</sub> S <sub>5</sub> .	VOCl.	VN.
$\chi \times 10^{-6}$ ...	50·06	13·88	3·73	0·86	7·22	8·95	12·55	27·16	4·13
$n$ .....	13·90	10·92	4·19	2·99	5·86	10·00	11·90	13·18	3·92

It is noteworthy that whilst the magnetic susceptibility decreases from the monoxide to the pentoxide, it increases from the monosulphide to the pentasulphide. The second component may thus exert a decisive influence on the susceptibility of simple compounds of paramagnetic metals. The curve showing the relation between the magnetic susceptibility and (a) the sulphur content, is a straight line on which the point for vanadium itself lies; (b) the oxygen content, has a break corresponding with the position of each oxide.

The magneton numbers differ very little from whole numbers, and increase or decrease with the susceptibility, without proportionality existing; they are smaller than those which have been found for chromium, manganese, or iron salts.

The following special methods of preparation of vanadium monoxide and monosulphide are given. The monoxide is best prepared by heating the solid oxychloride, VOCl, to a red heat in a current of pure hydrogen until the brown mass has become quite black in colour, and

no longer gives the test for chlorine; the reaction takes twelve to sixteen hours. Vanadium monoxide forms a black, amorphous powder,  $D^{14} 5.758$ , which dissolves in dilute acids to a blue solution, without gas being evolved. In the compressed condition, it conducts electricity.

The pure monosulphide could not be prepared by heating the trisulphide,  $V_2S_3$ , in a current of hydrogen, even at  $1100\text{--}1200^\circ$  (compare Kay, Trans., 1880, 37, 728). Better results were obtained by heating the monoxide to a red heat in a current of hydrogen sulphide, although even then the monosulphide was not quite pure. It forms a dark brown powder, which is insoluble in alkalis and in hydrochloric acid, but soluble in cold concentrated or in warm dilute nitric acid. T. S. P.

**Magnetic Properties of Manganese and Nickel Steels.** SIEGFRIED HILPERT and WALTER MATHESIUS (*Zeitsch. Elektrochem.*, 1912, 18, 54—64. Compare Abstr., 1911, ii, 1057).—The effect of heating to different temperatures followed by more or less rapid cooling on the magnetic properties of the following alloys has been determined: nickel steel containing 12% nickel; manganese steel containing 5, 10, and 20% of manganese, and manganese-carbon steel containing 10% of manganese and 1 or 2% of carbon.

All steels show a maximum of magnetic power when quenched from about  $450^\circ$ . Steels quenched from  $1200^\circ$  are more magnetic than those quenched from  $900^\circ$ , or slowly cooled from  $750^\circ$ . The manganese-carbon steels are practically non-magnetic when quenched from  $900^\circ$ . From the behaviour of the steel quenched from  $1200^\circ$  when cooled in liquid air, the conclusion is drawn that it contains several magnetic constituents.

With steels containing 5% of manganese, or 12% of nickel, the coercive power diminishes as the magnetic power increases, whereas with 10% of manganese the coercive power and magnetic power increase concurrently. A steel containing 20% of manganese cannot be made magnetic by thermal treatment. From the magnetic behaviour of iron alloys, conclusions can be drawn as to their previous thermal treatment.

Photomicrographs of some of the quenched steels are given.

G. S.

**Use of the Magnetic Field in Determining Constitution.** XII. PAUL PASCAL (*Bull. Soc. chim.*, 1912, [iv], 11, 111—121).—A further selection of compounds showing anomalous magnetic susceptibility is dealt with (compare Abstr., 1911, ii, 850, 1058).

Whilst the  $-\text{CO}-$  group in ketones and aldehydes is associated with reducing power in these substances, this property is less marked in acids, amides, etc., probably because the residual affinities of the group are saturated in these cases. In harmony with this view, it is found that whilst in the aldehydes and ketones the influence of the  $-\text{CO}-$  group on the magnetic susceptibility is  $+66 \times 10^{-7}$ , it falls to  $+13 \times 10^{-7}$  for acids and esters, to  $+32 \times 10^{-7}$  for monoamides, and to  $+26 \times 10^{-7}$  for diamides and imides. In carbamide the influence disappears entirely. In the acid chlorides, on the con-

trary, the effect of the  $\text{-CO-}$  group is normal, probably because the supplementary valencies of chlorine do not affect oxygen, since these two elements do not easily combine.

Among halogen compounds the magnetic susceptibility is not abnormal so long as the group containing the halogen is not so situated that the halogen can easily be eliminated as hydracid, but where this latter condition enters, the magnetic susceptibility shows a decrease; thus for methyl chloride  $S_M$  is 333 in place of 363.5 calc. For alkyl chlorides the depreciation is about  $31.5 \times 10^{-7}$ , and for alkyl bromides or iodides about  $42.5 \times 10^{-7}$ , the difference corresponding with the greater ease with which the bromides and iodides lose their halogen atoms as hydracids, as compared with the chlorides. These depreciations in value, it is assumed, are due to deformation of the molecule in the direction of an ethylene linking, and it is argued that the amount of the depreciation may be taken as a measure of the tendency of the alkyl haloid to become an ethylene derivative, and by taking account of all possible linkings in the substance in this way, it is shown that the depreciation can be calculated fairly approximately, and a number of examples are given.

T. A. H.

**New Thermodynamic Theories (Nernst's Heat Theorem and Quanta-Hypothesis).** MAX PLANCK (*Ber.*, 1912, 45, 5—23).—A lecture delivered before the German Chemical Society.

T. S. P.

**A Simple Relation between the Expansion Coefficient of Liquids and Temperature.** MARCEL OSWALD (*Compt. rend.*, 1912, 154, 61—63).—The author develops the expression  $\alpha = 1/(2T_c - T)$ , where  $\alpha$  is the coefficient of expansion of a liquid at absolute temperature,  $T$ , the absolute critical temperature being  $T_c$ . This is similar to an equation given by Thorpe and Rücker (*Trans.*, 1884, 45, 135). On applying it in the generalised form,  $\alpha = 1/(\lambda T_c - T)$ , to 15 simple organic and inorganic liquids, satisfactorily constant values for  $\lambda$  were obtained, the mean being 1.967. Liquids containing polymerised molecules show some departure from the rule. The anomalous case of water is discussed; at  $100^\circ$  the calculated value for  $T_c$  is  $322.5^\circ$ . The formula may be useful in calculating approximate values for critical temperatures.

W. O. W.

**The Measurement of Very Small Gas Pressures.** CLARENCE F. HALE (*Trans. Amer. Electrochem. Soc.*, 1911, 20, 243—258).—The low pressure manometer devised by Pirani (*Ber. deut. physikal. Ges.*, 1906, 8, 686) depends on the fact that at low pressures the thermal conductivity of a gas is a function of its pressure. The sensitiveness has been greatly increased by the following improved construction. A platinum wire, 0.028 mm. in diameter and 450 mm. long, is looped and attached to glass supports sealed into a glass bulb, provided with a side-arm for connexion with the system of which the pressure is to be examined. The compensator is identical in form, but without the side-arm. Both bulbs are immersed in a bath at constant temperature. The manometer and compensator form two arms of a Wheatstone bridge, and the current from five cells is regulated so as to be 0.00925

ampere, which keeps the platinum wires at about  $125^{\circ}$  at the lowest pressures. The manometer is calibrated against a McLeod gauge, with the same gas as that for which it is to be used. Trustworthy measurements are given down to 0.00001 mm. of mercury.

C. H. D.

**Elastic Force of Saturated Vapours.** F. OLLIVE (*Compt. rend.*, 1912, 154, 188—190).—When the temperature of a vapour is raised by increments in arithmetic progression, the elastic force of the vapour should rise in geometrical progression. The correctness of this conclusion is shown by applying it to the case of water vapour at temperatures between  $0^{\circ}$  and  $100^{\circ}$ , employing the formula  $\Delta = aq^{n-1}$ , where  $a$  and  $q$  are constants, and  $\Delta$  represents the successive increments in pressure. Between  $0$  and  $40^{\circ}$ ,  $a = 0.32$  mm.,  $q = 0.36/0.34$ ; between  $40$  and  $50^{\circ}$ ,  $a = 3.2$  mm.,  $q = 3.3/3.2$ ; at  $50$ — $70^{\circ}$ ,  $a = 4.6$  mm.,  $q = 4.8/4.6$ ; at  $70$ — $100^{\circ}$ ,  $a = 10.5$  mm.,  $q = 1.033$ . For other liquids,  $a$  and  $q$  vary to a less extent with temperature.

W. O. W.

**Thermal Conduction and Convection in Gases at Extremely High Temperatures.** IRVING LANGMUIR (*Trans. Amer. Electrochem. Soc.*, 1911, 20, 225—242).—Former experiments with a Nernst filament (Abstr., 1906, ii, 848) led to some unexpected conclusions as to conduction and convection in the neighbourhood of the filament, these properties increasing very rapidly at high temperatures. The range of temperature over which the Nernst filament can be used is very limited, and experiments have now been made with ductile tungsten wires in hydrogen. The energy required to heat the wire to any given temperature is nearly independent of the size of the vessel containing the hydrogen. The fraction of the current carried by the hot gas near the wire is inappreciable, even at the highest temperatures, when the wire is straight, but becomes considerable at  $2900^{\circ}$  (abs.) when loops are used. The loss of energy at first increases proportionally to a power of the temperature between 1 and 2, but then much more rapidly, and at  $3400^{\circ}$  (abs.) is increasing with the tenth power of the temperature. In a vacuum, the loss is proportional to the 4.8 power of the temperature, and this exponent is constant over a wide range.

The melting point of tungsten is at least  $3450^{\circ}$  (abs.). C. H. D.

**Thermal Conductivity of Graphite and Diamond.** JOHANNES KOENIGSBERGER (*Ber. deut. physikal. Ges.*, 1912, 14, 9).—The marked contrast between the thermal and electrical conductivities of graphite is also found in the case of diamond. The high thermal conductivity of carbon (and silicon) is supposed to be connected with the rapid diminution of the specific heat which is exhibited by these substances when the temperature is lowered.

H. M. D.

**The Thermal Conductivity of Graphite and Copper Sulphide at Various Temperatures.** ICOLE (*Ann. Chim. Phys.*, 1912, [viii], 25, 137—144).—The thermal conductivity of graphite

has been measured by placing a cylinder, 18 mm. in diameter and 7.9 mm. long, between the ends of two copper rods, each of the same diameter and 50 cm. long, the temperature of the copper being read by means of thermo-couples in transverse holes. The conductivity is expressed by the formula  $K = 0.0384 - 9 \times 10^{-5}t + 9.3 \times 10^{-7}t^2$ . The conductivity of synthetic copper sulphide, determined in the same manner, is very nearly proportional to the temperature, and may be expressed by the formula  $K = 0.00106 + 4.3 \times 10^{-6}t$ . C. H. D.

**Specific Heat of Gases.** II. NIELS BJERRUM (*Zeitsch. Elektrochem.*, 1912, 18, 101—104. Compare *ibid.*, 1911, 17, 731).—In the previous paper (*loc. cit.*), formulæ for the specific heats of a number of gases were deduced on the basis of the quanten theory, the constants being calculated from the results of Pier's determinations of specific heats by the explosion method (compare Abstr., 1909, ii, 789; 1910, ii, 1031). A slight correction rendered necessary by loss of heat during the explosion is now applied. Some of the recalculated molecular heats at constant volume are as follows: hydrogen, 5.23 at 1461°, 5.57 at 1916°, 5.79 at 2368°; nitrogen, 5.43 at 1519°, 5.93 at 2367°; argon, theoretical 2.978, found 2.93; water vapour, 8.13 at 1734°, 8.52 at 2134°; 9.39 at 2375°. The corrected results are compared with those calculated from the formulæ; the agreement is good throughout. G. S.

**Specific Heat Measurements at Low Temperatures.** ALEXANDER S. RUSSELL (*Physikal. Zeitsch.*, 1912, 13, 59—64).—The results of measurements of mean specific heats over the temperature ranges +45° to 0°, 0° to -78°, and -78° to -190° are recorded. The calorimeter described by Nernst and Lindemann (Abstr., 1910, ii, 263) was used, and observations made with the oxides of copper, lead, magnesium, mercury, iron, chromium, aluminium, arsenic, scandium, cerium, manganese, thorium, tungsten and uranium, the sulphides of mercury, copper, cadmium and antimony, the chlorides of sodium, potassium and thallium, and also with metallic thallium, amorphous and crystalline quartz, and silicon carbide.

In general, the data show that the molecular heats at low temperatures diverge considerably from the values calculated by adding together the atomic heats of the component elements. By reference to the Nernst-Lindemann formula for the molecular heat, this means that the characteristic vibration frequencies of the elements in their compounds are different from the frequencies of the free elements. In the case of metals, such as lead, tungsten, and mercury, which have low vibration frequencies, the differences are comparatively small, and for these metals the observed molecular heats of the oxides and sulphides are in fairly close agreement with the requirements of the additive law. The behaviour of oxygen at low temperatures does not depend to any appreciable extent on the metal with which it is combined. H. M. D.

**Molecular Heat of Hydrogen at Low Temperatures.** ARNOLD EUCKEN (*Sitzungsber. K. Akad. Wiss. Berlin*, 1912, 141—151).—A form of apparatus is described for the determination

of the specific heat of compressed gases at constant volume and at any desired temperature. With this, measurements have been made of the specific heat of hydrogen at temperatures between  $35^{\circ}$  and  $273^{\circ}$  (absolute). The data thus obtained, when reduced to the ideal gas condition, show that the molecular heat falls from 4.84 at  $273^{\circ}$  to about 3.0 at  $60^{\circ}$  (abs.). Below  $60^{\circ}$ , the molecular heat remains constant. The observed temperature variation of the molecular heat at constant volume can only be accounted for qualitatively on the basis of existing theories, and the additional hypotheses necessary for its interpretation are discussed.

H. M. D.

**A General Law of Dissolution.** ÉMILE BAUD (*Compt. rend.*, 1912, 154, 198—201. Compare Abstr., 1910, ii, 268—689).—The equation  $\Delta_t = K \log x T_2$ , deduced to express the depression of the freezing point of binary mixtures, where  $x$  is the concentration of a component  $A$  in a mixture depositing pure  $A$ , at an absolute temperature,  $T_2$ , does not hold for incompletely miscible liquids. In such cases the more general equation  $T_2 = T_1 (1 - q/Q) / (1 + k \log x)$ , deduced from Clapeyron's equation, is applicable.  $T_1$  represents the freezing point of the solvent, and  $k$  the ratio  $RT_1/EQ$ ,  $q$  being the heat of dilution, that is, the heat developed by the addition of one molecule of  $A$  to a large quantity of solvent. This expression has been tested experimentally in the case of mixtures of acetic acid with benzene or ethylene dibromide with satisfactory results.

W. O. W.

**Fused Salts as Solvents. I. Cryoscopic Investigations. II. Solubility Determinations.** OTTO SACKUR (*Zeitsch. physikal. Chem.*, 1912, 78, 550—563, 564—572).—I. As solvents, the chlorides of sodium, potassium, calcium, strontium and barium, and sodium sulphate were used, and as solutes a number of alkali and alkaline-earth salts. The investigation shows that, as a rule, the laws of dilute solutions are approximately valid up to concentrations of 1 mol. per litre. Dissolved salts, which have an ion in common with the solvent, have either the normal molecular weight or show a slight dissociation, independent of the concentration. This result is probably to be explained by considerable ionisation of the solvent itself. Salts which have no ion in common with the solvent produce nearly double or nearly three times the normal depression, according as they are binary or ternary electrolytes.

A number of binary mixtures of salts form solid solutions, and therefore the laws of dilute solutions do not apply to cryoscopic measurements with such mixtures. When, for example, strontium carbonate is added to fused potassium or sodium carbonate, the melting point rises at first with increasing concentration of the strontium salt, and then gradually diminishes, so that a flat maximum is obtained. Flat maxima are also obtained with strontium carbonate and barium sulphate in sodium sulphate as solvent.

II. In the solubility determinations, the same fused salts were used as solvents, and as criterion of solubility the effect of the substance added on the melting point of the solvent was used. It was found that all those substances which can readily dissociate into two or more

stable ions are readily soluble, whereas those substances which do not readily ionise (for example, the aluminates and ferrites of the alkalis, the oxides of the alkaline earths and heavy metals, and the sulphides of the heavy metals) are practically insoluble. The only exception to these rules are the oxides of the alkaline earths, which are readily soluble in fused chlorides with a common ion; for example, calcium oxide is readily soluble in fused calcium chloride. G. S.

**Cryoscopy in the Fused Pentahydrate of Sodium Thio-sulphate.** CH. LEENHARDT and A. BOUTARIC (*Compt. rend.*, 1912, 154, 113—114. Compare Abstr., 1911, ii, 1061).—The latent heat of fusion of the salt  $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$  at the melting point  $48.5^\circ$  is found to be  $47.9^\circ$  as the mean of three concordant determinations. Employing van't Hoff's formula this gives  $K$  42.8 as the molecular lowering of the freezing point, a number which agrees well with that found by dissolving carbamide in the fused salt.

Trentinaglia's values (*Wien Ber.*, 1876, 72, 669) are considered to be untrustworthy owing to the possibility of his salt containing water. To avoid this, it is necessary to dry the pentahydrate in presence of the dihydrate. W. O. W.

**Improvements in the Ebullioscopic Method.** ERNST BECKMANN [with WALTER WEBER] (*Zeitsch. physikal. Chem.*, 1912, 78, 725—740. Compare Abstr., 1908, ii, 663).—The irregularities in ebullioscopic measurements, which are especially pronounced when the solution froths, are not got rid of by using wire of other metals instead of platinum for internal electric heating; of the different metals used only gold gave rather better results than platinum. The introduction of a stream of a permanent gas, such as hydrogen, air, or carbon dioxide, is also not satisfactory, as among other drawbacks the end of the tube through which the gas enters tends to get choked up by the entry of solution and evaporation of part of the solvent. The usual device of introducing filling material gives the best results.

A considerable improvement is obtained by so modifying the apparatus that part of the solvent (containing traces of volatile substances, especially moisture) can be distilled off, a current of dry air being introduced at the same time to prevent the condensation of moisture in the upper part of the apparatus. The fraction passes off through the side-tube used for introducing the solid; for this purpose the usual stopper is replaced for the time by another connected with a long bent tube as condenser.

The use of an aneroid barometer has been recommended to correct for variations in atmospheric pressure during an observation, but it is shown that a control boiling-point apparatus gives much better results G. S.

**Fractional Distillation with Steam.** A. GOLODETZ (*Zeitsch. physikal. Chem.*, 1912, 78, 641—656).—It is shown that a mixture of low-boiling liquids insoluble in water can be more effectively separated by distilling with steam than by ordinary fractional distillation under

the same conditions. The advantages of steam distillation are much less for the separation of high-boiling liquids. Young's law, according to which the amount of the mixture which distils up to the middle of of the temperature-interval between the boiling points of the two components is approximately equal to the amount of the more volatile component, is confirmed. In the course of the experiments, binary mixtures of benzene and toluene, of amyl formate and acetate, of mono- and di-ethylaniline were fractionated, and several types of fractionating column were used.

G. S.

**Heats of Formation of Certain Silicates.** D. TSCHERNOBÉEFF and L. WOŁOGDINE (*Compt. rend.*, 1912, 154, 206—208. Compare Abstr., 1905, ii, 678).—Mixtures of calcium carbonate with silica or kaolin, or with silica and alumina were heated with a definite amount of carbon in the Mahler bomb calorimeter. From the heats of reaction thus determined, the following values for the heats of combination were calculated, the numbers being in Calories:  $\text{CaO} + \text{SiO}_2$ , 17.4;  $2\text{CaO} + \text{SiO}_2$ , 28.7;  $3\text{CaO} + 2\text{SiO}_2, \text{Al}_2\text{O}_3$ , +50.2;  $3\text{CaO} + 2\text{SiO}_2 + \text{Al}_2\text{O}_3$ , 38.2;  $\text{SiO}_2 + \text{Al}_2\text{O}_3$ , -12.0. The heat of formation of anhydrous kaolin,  $\text{Al}_2\text{O}_3, 2\text{SiO}_2$ , is therefore negative. These results are not in harmony with those previously published.

W. O. W.

**Heat of Combustion and Heat of Transformation of the Cinnamic Acids.** W. A. ROTH (*Zeitsch. Elektrochem.*, 1912, 18, 99—100).—The heat of transformation of *allocinnamic* acid to *cinnamic* slightly exceeds 6000 cal. per mol.; the heat development accompanying the change of the *allocinnamic* acid melting at 42° to that melting at 58° is about 100 cal. The heat of combustion of *cinnamic* acid at constant volume is 7025 cal. per gram.

G. S.

**Method of Measuring Absolute Viscosity.** HAROLD P. GURNEY (*J. Amer. Chem. Soc.*, 1912, 34, 24—28).—Apparatus is described for the determination of absolute viscosity. The method is simple, rapid, and extremely accurate, requires only a very small quantity of the liquid, and enables opaque liquids to be tested.

Into the neck of a small flask are fitted three glass tubes, one connected by a stopcock to the vacuum pump, the second by rubber tubing to a vertical glass tube of capillary bore, whilst the third carries a stopcock opening to the air. The capillary tube has three rings etched round it at different heights, and its lower end dips into a small cup with vertical walls which contains the liquid. If determinations are to be made at other temperatures than that of the air, the tube must be jacketed.

In carrying out an experiment, the liquid is poured into the cup until it rises just within the capillary tube up to the lowest ring. It is then sucked up the tube by means of the pump until it is above the level of the highest ring. The stopcock connecting the apparatus with the pump is then closed, and that opened which is in communication

with the atmosphere, so that the air above the liquid in the tube is under atmospheric pressure. The liquid in the capillary descends with but slightly diminishing velocity, and the time taken by it to pass from the highest ring to that next below it is observed with a stop-watch.

A mathematical discussion is given leading to the development of a formula for calculating the results. E. G.

**Viscosity of Solutions of the Metal Ammonia Salts.** ARTHUR A. BLANCHARD and HAROLD B. PUSHEE (*J. Amer. Chem. Soc.*, 1912, 34, 28—32).—Blanchard (Abstr., 1904, ii, 805) has shown that when ammonia is added to solutions of salts of copper, silver, and zinc, a phenomenon similar to negative viscosity is produced. This was explained on the assumption that the ions combine with a certain number of molecules of the solvent.

Determinations have now been made of the viscosities of solutions obtained by adding successive quantities of ammonia to solutions of ammonium chloride, calcium chloride, and lithium sulphate at 25°, and to solutions of lithium chloride at 1°. The results show that, in these cases, instead of a negative viscosity, a slight increase in the viscosity occurs. It is evident, therefore, that such unstable complexes as are formed between ammonia and salts of lithium, ammonium, and calcium are somewhat more viscous, and hence either larger or less symmetrical, than the ordinary complexes of the same salts with water in simple aqueous solutions. E. G.

**Adsorption. III.** GERHARD C. SCHMIDT (*Zeitsch. physikal. Chem.*, 1912, 78, 667—681).—The adsorption formula  $[(a-x)S]/v = Kxe^{A(S-x)/S}$  ( $x$  representing amount adsorbed,  $a$  the amount of solute originally present,  $v$  the volume,  $S$  the maximum amount adsorbed, and  $A$  and  $K$  constants) already deduced by the author (compare Abstr., 1911, ii, 969) is shown to represent with great accuracy the results of Titoff (Abstr., 1910, ii, 1041) on the adsorption of gases by charcoal, and with fair accuracy the corresponding measurements of Homfray, (Abstr., 1910, ii, 771, 1041). Neither of these observers determined the maximum adsorption, and the author has estimated it by extrapolation.

The simpler adsorption formula recently suggested by Arrhenius (this vol., ii, 139) does not represent satisfactory the author's results on the adsorption of acetic acid from aqueous solution by charcoal, whereas they are represented with great accuracy by the above formula (*loc. cit.*). G. S.

**Adsorption in Solutions. III. Relations between the Adsorbability and other Properties.** GEORG VON GEORGIEVICS (*Monatsh.*, 1912, 33, 45—62. Compare Abstr., 1911, i, 537; ii, 1070).—The distribution of nitric, hydrobromic, propionic, and butyric acids between water and wool has been examined, and it is shown that the data are in agreement with the exponential adsorption formula. The adsorbability of different acids appears to have no connexion with the degree of ionisation, although in general the strong acids are more

readily adsorbed than the weak acids. Experiments with hydrochloric and sulphuric acids indicate that the adsorption of these is not influenced to an appreciable extent by the addition of small quantities of the corresponding sodium salts, although larger quantities give rise to increased adsorption.

The influence of other factors on the adsorption is discussed, and it is shown that in certain groups of acids the adsorbability appears to be connected with the surface tension, the compressibility, and the viscosity of the solutions.

H. M. D.

**Adsorption. IV. Thermodynamics of Irreversible Processes and Chemical Hysteresis.** ADAM W. RAKOWSKI (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1762—1784. Compare Abstr., 1911, ii, 470, 471).—This is a mathematical paper, the principal conclusions drawn by the author being as follows:

If, in Duhem's theory of chemical hysteresis (Abstr., 1900, ii, 338), the variable  $x$  is rejected and the hysteresis attributed to the specific volume and degree of hydration of the colloid, a fundamental equation is deduced completely analogous to Duhem's equation, the difference lying merely in the physical significance of the constants. The formula derived by Duhem to express the influence of variation of the pressure on the velocity of hydration and dehydration of colloids corresponds with all the phenomena observed experimentally. Duhem's theory explains satisfactorily the various phenomena of chemical hysteresis.

The isothermal equation of the natural state of an aqueous colloid represents a sine curve. Gels possess a complex isotherm, representing the sum of the sine curves characterising the two "solutions" which constitute the gel; physical explanations can be given of all the constants in the equation of such a complex sine curve.

T. H. P.

**A Method of Investigating the Transpiration of Gases Through Tubes.** JOSEPH H. T. ROBERTS (*Phil. Mag.*, 1912, [vi], 23, 250—255).—A method is described of obtaining the viscosity coefficients of gases from comparative measurements of the rates of transpiration. The transpired gases are allowed to escape into the atmosphere through short capillary tubes, the pressure in the apparatus being only slightly greater than atmospheric. This pressure is automatically kept constant, and the times required for the transpiration of the same volume of different gases are measured. With this apparatus the following viscosity coefficients were determined: air, 0.000180 at 11.75°; hydrogen, 0.0000864 at 12.25°; carbon dioxide, 0.000145 at 12.6°; coal-gas, 0.000133 at 12.9°. H. M. D.

**Mechanism of the Semi-permeable Membrane and a New Method of Determining Osmotic Pressure.** FREDERICK T. TROUTON (*Proc. Roy. Soc.*, 1912, A, 86, 149—154).—A method of measuring the osmotic pressure of an aqueous solution is described, which consists in determining the pressure to which a suitable liquid must be subjected when in contact with the solution, in order that the liquid may take up as much water from the solution as it takes up from pure water at atmospheric pressure.

From experiments in which the amount of water taken up by 100 grams of ethyl ether from a solution containing 600 grams of sucrose per litre was determined, it has been found that this increases in a continuous manner from 0.939 gram at atmospheric pressure to 1.143 gram at a pressure of 110.5 atmospheres. From the curve representing the variation of the amount of water taken up by the ether with the pressure, it is found that the water taken up from the solution at a pressure of 79 atmospheres is equal to that taken up from pure water at a pressure of 1 atmosphere (1.0545 gram per 100 grams of ether). This value of the osmotic pressure is in good agreement with that interpolated from the results of measurements with a copper ferrocyanide membrane by Lord Berkeley and Hartley (81 atmospheres).

H. M. D.

**Theory of Dissolutions Compared with Experience (Case of Nitrogen Peroxide).** ALBERT COLSON (*Compt. rend.*, 1912, 154, 276—279. Compare Abstr., 1911, ii, 710, 1066—1071).—Polemical against Urbain and others (Abstr., 1911, ii, 861). If the dissolved particle is in the same condition as the gaseous particle, the gas equation  $\sum m \log C = K$  should hold for the same substance whether in solution or in the gaseous state. Cundall has shown for the equilibrium  $N_2O_4 \rightleftharpoons 2NO_2$  in chloroform solution that the expression does not give a constant value for  $K$ . By measuring the partial pressures of the two gases in equilibrium it has now been found that the equation does not hold for the gaseous phase.

W. O. W.

**Theory of Solubility.** DAN TYRER (*J. Physical Chem.*, 1912, 98, 69—85. Compare Trans., 1911, 98, 871).—The formation of a solution is due to (1), molecular attraction of the solvent for solute, and (2) mechanical diffusion of the solute molecules away from the parent solute by reason of their kinetic motion. Except with gases and easily volatile liquids, the factor (2) is negligible. The intensity of the molecular attraction (1) depends on the nature of the solvent and the temperature. That is to say, the solubility  $S = \phi(C, T)$ . In the case of liquids above their critical temperature, when  $T$  is maintained constant and  $C$  is altered by altering the external pressure, the solubility is proportional to the concentration ( $C$ ) of the solvent. Below the critical point,  $C$  depends on the pressure, the temperature, and the presence or absence of neutral molecules and of solute molecules.

The ordinary solubility curve is without theoretical value, since it refers to an arbitrary pressure (1 atmosphere), and a continuously varying solvent concentration. When both solvent and solute are normal, that is, free from the disturbing influences of dissociation, association, and solvate formation, the conditions at saturation can be deduced.

If the attraction between two solute molecules varies inversely as some power of the distance between them, the total force holding a molecule of solute to its parent crystal is  $K/v^n$ , where  $K$  is a constant and  $v$  the specific volume of the solute. The forces tending to draw a solute molecule into solution are (1) the attraction of the solvent

( $= K_1/V^n$ ), and (2) the attraction of the solute molecules already dissolved ( $= K_2 N^n/V^n$ ), where  $K_1, K_2$  are constants, and  $V$  the total volume of a solution containing a constant weight of solvent plus  $N$  molecules of solute. At saturation  $K/v^n = K_1/V^n + K_2 N^n/V^n$ . Now  $N = S/M$ , where  $S$  is the solubility and  $M$  the molecular weight of the solvent. It follows that  $S^n = a(V/v)^n - b$ , where  $a, b$ , and  $n$  are constants. This equation cannot be tested experimentally, since  $n$  is unknown, but it is evidently in qualitative agreement with the general phenomena attending the dissolution of normal substances, whether gaseous, liquid or solid, in normal solvents.

The author works out the conditions for complete miscibility of pairs of normal liquids. In practice all normal liquids are miscible in all proportions, that is, the solubility is infinite. It follows that normal solids become infinitely soluble at their melting points. The "molecular solvent power" of a solvent is the amount of solute dissolved at a given temperature when unit volume contains 1 gram-molecule of solvent. The molecular solvent powers of chloroform, toluene, benzene, and hexane for naphthalene are deduced.

R. J. C.

**Miscibility of Liquids.** J. P. KUENEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 644—649).—The influence of temperature on the miscibility of *n*-butane with methyl alcohol has been found to vary in a marked manner with the method of preparation of the hydrocarbon. For butane obtained by the action of magnesium on butyl halides, the critical temperature and pressure were found to be  $150.8^\circ$  and  $37.5^\circ$  atmospheres, and this becomes completely miscible with methyl alcohol at  $17.0^\circ$ . When the butane is prepared by the action of sodium, dissolved in liquid ammonia, on butyl halides, its critical temperature was found to be  $148.7^\circ$ , and the critical pressure about 39 atmospheres. In spite of the close agreement in the critical data, the second sample of butane behaved quite differently from the first in regard to its miscibility with methyl alcohol. The surface of separation appears to vanish at about  $22^\circ$ , but it reappears as the temperature rises, and the definite critical end-point is not reached until  $38^\circ$ . It is supposed that the phenomenon is due to the equality of the refractive indices of the two liquids in the neighbourhood of  $22^\circ$ , and that the difference in behaviour of the two samples of butane is due to the presence of a very small quantity of some impurity in the butane prepared by the action of sodium.

The following critical end-points are also recorded: methyl alcohol and *isopentane*,  $10.5^\circ$ ; methyl alcohol and *n*-pentane,  $19.4^\circ$ ; ethyl alcohol and *isopentane*,  $-30^\circ$ .

H. M. D.

**Neutralisation Curve of Sulphuric Acid.** JOHANNES E. ENKLAAR (*Chem. Weekblad*, 1912, 9, 28—31. Compare *Abstr.*, 1911, ii, 1071).—The author has studied the step-by-step neutralisation of sulphuric acid, effected by addition of successive quantities of *N*/10-sodium hydroxide to 10 c.c. of *N*-sulphuric acid and dilution of the mixture to 100 c.c. at  $18^\circ$ . For each addition the values of the total *E.M.F.*, the *E.M.F.* of the gas-electrode, the concentration of the

hydrogen ions, and the values of  $P_H^+$  are summarised in a table. A curve is plotted with the number of c.c. of sodium hydroxide as abscissæ, and the values of  $P_H^+$  as ordinates. This curve indicates that the dissociation is in great measure ternary, and in accordance with the scheme  $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{--}$ . The value found for the concentration of the hydrogen ions in  $N/10$ -sulphuric acid is 0.058. The value for  $K_2$  is 0.013, and not 0.018 as given in the previous paper.

A. J. W.

**A Colour Effect of Isomorphous Mixture.** HORACE L. WELLS (*Amer. J. Sci.*, 1912, [iv], 33, 103—104).—Mixed crystals as a rule take a colour intermediate between those of their component salts; for example, the yellow salt,  $Cs_2PbCl_6$ , and the deep blue salt,  $Cs_2SbCl_6$ ,

give mixed crystals of a green colour. An exception to this rule is afforded by the salts  $Cs_2PbCl_6$  and  $Cs_2TeCl_6$ , both of which crystallise in regular octahedra with a yellow colour. These salts are isomorphous and mix in all proportions, but their mixed crystals possess the peculiarity of showing a bright orange-red colour.

L. J. S.

**Crystalloids and Colloids. Basic Ferric Chloride.** GIOVANNI MALFITANO (*Ann. Chim. Phys.*, 1911, [viii], 24, 502—553).—To a large extent this is a summary of work published previously (compare Abstr., 1905, ii, 459; 1906, ii, 450, 526, 647; 1907, ii, 94; 1909, ii, 473). From the general behaviour of the colloidal ferric hydroxy-chlorides, the author draws the conclusion that the properties of the micelles are closely similar to those of molecules, and that there is no essential difference between the micellar and molecular states.

H. M. D.

**Colour and Degree of Dispersity of Colloidal Solutions.** WILLIAM HARRISON (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 45—49).—The colour changes which are observed when colloidal acid and basic dyes are acted on by acids and bases in aqueous solution are examined in reference to Ostwald's view (Abstr., 1911, ii, 868), that increase in the degree of dispersity of a colloidal solution is accompanied by a shift of the maximum absorption towards the ultra-violet end of the spectrum. The colour changes are not generally in agreement with this theory, and a modification is suggested. According to this, it is necessary that the reduction in the degree of dispersity must be accompanied by an increase in the molecular weight of the disperse substance if the maximum absorption alters its position in accordance with the above rule.

H. M. D.

**Fractional Coagulation. Relationship between the Size of Particles and the Stability of Disperse Systems.** SVEN ODÉN (*Zeitsch. physikal. Chem.*, 1912, 78, 682—707).—The results described in the early part of the paper as to the preparation of sulphur hydrosols containing particles of uniform size by the method of fractional coagulation have already been published (compare Abstr.,

1911, ii, 971). The same method has now been applied to the separation of silver hydrosols into fractions of different degrees of dispersion, and the properties of these solutions are described. The yellow and red hydrosols contain only amicroscopic particles; the purple and lilac sols contain submicrons.

The polychromatic appearance of some silver hydrosols under the ultramicroscope described by previous investigators is not observed in fresh or carefully kept solutions, but is observed when the hydrosols are kept in beakers of inferior glass or when ordinary tap water is present. The phenomenon is probably due to chemical changes on the surface of the particles.

In the case of reversible coagulation, the results show that under conditions otherwise equivalent, the electrolyte concentration required to produce coagulation is the greater the smaller the colloidal particles.

Experiments designed to find whether this rule also applies to irreversible coagulation did not lead to definite results. G. S.

**Theory of Dyeing.** W. G. SAPOSHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1565—1587).—The author has investigated the effect of varying the concentration of the bath, and the proportion of material taken, on the dyeing of cotton, mercerised cotton, and artificial silk by a number of substantive dyes.

The relation between  $p$ , the number of mgs. of the colouring matter, and  $P$ , the number of grams of the dry fibre taken, is given by the expression:  $p = 10k.P$ , where  $k$  is a coefficient termed the "modulus of the dye." In the author's experiments, the proportions between the weights of colouring matter and fibre varied from 0.5% to 10%. The quantity of colouring matter in the bath per gram of fibre is represented by  $10k$ , which is termed the "limiting dyeing." If the initial concentration of the dye in the bath is represented by  $10k/K_w$ , the magnitudes  $P$ ,  $k$ , and  $K_w$  must be regarded as the principal factors or the numerical characteristics of every substantive dyeing, independently of the nature of the fibre or colouring matter, and these magnitudes determine both the course of the dyeing and its final results. If  $x$  is the quantity of dye fixed by the fibre,  $C_f = x/P$ , the final concentration of the dye on the fibre, may be termed the "effective dyeing." The final concentration of the bath is given by  $C_b = (p - x)/K_w P$ .

It is found that, under similar conditions, the final concentration of the bath is proportional directly to the difference between the limiting and effective dyeing, and inversely to the water-modulus of the bath ( $K_w$ ), independently of the nature of the colouring matter.

In two substantive dyeings with identical moduli of bath and dye, the ratio of the difference between the effective dyeings to the difference between the final concentrations of the baths is equal to the water-modulus of the baths.

The substantive dyeing of cotton (cellulose) always follows one and the same law, no matter whether the natural structure of the fibre is unaltered (pure cotton), or ruptured (mercerised cotton), or completely destroyed (artificial silk).

Structureless celluloses, such as artificial fibres prepared from solutions of cellulose, and mercerised cellulose obtained from cotton, are allied more closely to one another than to the original cellulose. The influence of mercerisation on the structure of cellulose fibres is hence as profound as that caused by their complete solution.

Under the conditions employed in the author's experiments, mercerised cotton takes up, on an average, 10% more dye than pure cotton, this increase being due to the loosening of the fibres on mercerisation. The degree of mercerisation should hence be indicated by the extent of the increase in the effective dyeing. The ratio between the effective dyeings of cotton produced by two different substantive dyes is very nearly equal to the ratio between the molecular weights of the dyes.

T. H. P.

**Relation between the Photosensitiveness and Constitution of Dyes.** KURT GEBHARD (*J. pr. Chem.*, 1911, [ii], 84, 561—625).—A theoretical paper in which the author gives an explanation of (1) the phenomena of substitution in the benzene nucleus, (2) the differences in the reactivity of groups and atoms, (3) the colour of organic compounds, (4) the photosensitiveness of nitro-compounds and dyes, based on the theory of ionisable and partial valency. F. B.

**Theory of Vat Dyeing.** KURT GEBHARD (*J. pr. Chem.*, 1911, [ii], 84, 625—633).—An application of the author's views on ionisable and partial valency (preceding abstract) to the theory of vat dyeing. From the difference in the behaviour of indigotin in the free condition and on the fibre, Binz and Mandowsky (*Abstr.*, 1911, i, 497) have drawn the conclusion that the dye is not mechanically attached to the fibre, but exists in some kind of union with it.

The author has arrived at the same conclusion from a study of the behaviour of helindone-yellow-3GN (2:2'-dianthraquinonyl-carbamide). Fibre dyed with this substance becomes brown or violet when treated with alkalis—a change not shown by the original dye. This difference is supposed to be due to an alteration in the distribution of the ionisable and partial valencies in the molecule. Formulæ illustrating the nature of the combination of the dye with the fibre are given.

F. B.

**Three-phase Lines.** I. ANDREAS SMITS (*Zeitsch. physikal. Chem.*, 1912, 78, 708—724).—A theoretical paper. Van der Waals' theory of the three-phase equilibrium solid-liquid-gas is extended in some respects, and a mathematical and graphical discussion is given of the case where the triple point pressure of the compound is smaller than those of the components (compare *Abstr.*, 1905, ii, 683; Leopold, *Abstr.*, 1910, ii, 190).

G. S.

**Cæsium Nitrate and the Law of Mass Action.** WILHELM BILTZ (*Zeitsch. Elektrochem.*, 1912, 18, 49—51. Compare Washburn and McInnes, *Abstr.*, 1911, ii, 794).—The previous results of the author (*Abstr.*, 1902, ii, 310) and the recent measurements of Washburn and McInnes both show that in concentrations exceeding 0.1*N*-

caesium nitrate follows Ostwald's dilution law. The few results of the latter observers are not sufficient to show whether or not the law is obeyed in more dilute solutions. G. S.

**Hydrolysis. I. Hydrolysis of Carbonates.** FERNANDO AGENO and E. VALLA (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 706—712).—The authors have calculated the degree of hydrolysis of the carbonates of manganese, nickel, zinc, and lithium by Bodländer's method (*Abstr.*, 1900, ii, 715) from measurements of the solubilities of these compounds in water in an atmosphere of carbon dioxide. The percentage hydrolysis of these salts at 25° is found to be as follows: manganese carbonate 99.99, nickel carbonate 98.92, zinc carbonate 96.75, lithium carbonate 42.53. The value for lithium carbonate is apparently too high, in view of the known percentage hydrolysis of the carbonates of magnesium and sodium. R. V. S.

**The Velocity of Hydration of Some Cyclic Acid Anhydrides.** JACOB BÖESEKEN, A. SCHWEIZER, and G. F. VAN DER WANT (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 622—624. Compare *Abstr.*, 1911, ii, 197).—A theoretical paper in which a parallelism is traced between the hydration constant of the acid anhydride and the dissociation constant of the acid formed by union of the anhydride with water. H. W.

**Kinetics of Chemical Reactions of Combination, Deoxidation, and Oxidation.** E. I. ORLOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1524—1554).—The author brings forward an explanation of the time-relations of the apparently irregular process of slow oxidation by permanganate referred to in N. A. Schiloff's book on "Conjugated oxidation reactions." In spite of their external differences, all the examples of oxidation and deoxidation there given are processes of the second order, their velocities being determined from the differential equations:  $dx/dt = k(A - fx)$  and  $dx/dt = k(Bf + x)(A - fx)$ , where the magnitude  $x$ , determined by titration of the iodine liberated from potassium iodide solution, is multiplied by the coefficient  $f$  corresponding with the particular oxide of manganese formed on deoxidation of the  $Mn_2O_7$  up to the moment of observation. Some thirty-four different examples (there may be more) of the deoxidation of  $Mn_2O_7$  to various lower oxides of manganese are given, together with the corresponding values of  $f$  calculated from the amounts of iodine liberated. For instance,  $Mn_2O_7 = 2MnO + 5O$ ,  $f = 1$ ;  $3Mn_2O_7 = 6MnO_3 + 3O$ ,  $f = 0.2$ , and so on.

All the cases of slow oxidation of formic, oxalic, and tartaric acids considered are reactions of combination, the first product being formed by addition of hydroxyl or oxygen to the acid; the compounds thus formed undergo subsequent decomposition. Thus, for oxalic acid,  $Mn_2O_7 + 5H_2O = 2MnO + 5H_2O_2$  and  $CO_2H \cdot CO_2H + H_2O_2 = 2OH \cdot CO \cdot OH = 2CO_2 + 2H_2O$ ; for formic acid,  $2H \cdot CO_2H + O_2 = 2OH \cdot CO \cdot OH = 2CO_2 + 2H_2O$ , and for tartaric acid,  $CO_2H \cdot CH(OH) \cdot CH(OH) \cdot CO_2H + O_2 = CO_2H \cdot C(OH)_2 \cdot C(OH)_2 \cdot CO_2H = CO_2H \cdot CO \cdot CO \cdot CO_2H + 2H_2O$ .

The reaction may proceed with or without formation of an intermediate oxide of manganese, and in the former case this oxide may be  $\text{Mn}_2\text{O}_3$  or  $\text{MnO}_2$ , for example, (1)  $\text{Mn}_2\text{O}_7 + 8\text{MnO} = 5\text{Mn}_2\text{O}_3$  and  $5\text{Mn}_2\text{O}_3 + 5\text{C}_2\text{H}_2\text{O}_4 = 10\text{MnO} + 10\text{CO}_2 + 5\text{H}_2\text{O}$ ; (2)  $\text{Mn}_2\text{O}_7 + 3\text{MnO} = 5\text{MnO}_2$  and  $5\text{MnO}_2 + 5\text{C}_2\text{H}_2\text{O}_4 = 5\text{MnO} + 10\text{CO}_2 + 5\text{H}_2\text{O}$ . Those reactions proceeding by way of an intermediate oxide are characterised by an incubation period. That is, for some time only part of the oxidising agent ( $\text{Mn}_2\text{O}_7$ ) takes part in the oxidation, the other part being held in reserve in combination with the oxalic or tartaric acid, and set free only gradually. Hence the value of  $A_1$  in the differential equation is not constant, but increases to the final value  $A$  representing the initial concentration of the potassium permanganate.

In cases where the two stages of the reaction, for example, (1)  $\text{Mn}_2\text{O}_7 + 8\text{MnO} = 5\text{Mn}_2\text{O}_3$  and (2)  $5\text{Mn}_2\text{O}_3 = 10\text{MnO} + 5\text{O}$ , do not synchronise, intermediate oxides, such as  $2\text{MnO}$ ,  $\text{Mn}_2\text{O}_3$  and  $4\text{MnO}$ ,  $\text{Mn}_2\text{O}_3$ , are formed.

T. H. P.

**The Reaction Velocity of Reducing Sugars with Fehling's Solution, and its Application to the Study of Urinary Chemistry.** J. N. LAIRD (*J. Path. Bact.*, 1912, 16, 398—401).—At constant temperature using in all cases the same amount of diluted Fehling's solution, the reduction (first appearance of a red precipitate) begins more rapidly the more concentrated the solution of sugar. The times are plotted out in curves for solutions of dextrose and lævulose of known strengths at temperatures of  $60^\circ$ ,  $65^\circ$ , and  $70^\circ$  respectively. By comparing the times found for solutions of the sugar of unknown strength with these, their concentration is ascertained. Solutions of sugar in urine do not, however, behave like aqueous solutions, the presence of variable amounts of creatinine having a retarding effect.

W. D. H.

**Influence of Temperature on Malt Diastase.** HENRI VAN LAER (*Bull. Soc. chim. Belg.*, 1912, 26, 18—28. Compare Abstr., 1910, ii, 839; 1911, ii, 28, 478; this vol., ii, 148).—In previous papers it has been shown that, depending on the conditions of the experiment, and using a normal extract of malt in a solution of starch, the coefficient expressing the velocity of reaction either remains constant or increases. It is known, however, that in the case of an extract of malt, which has been heated to a temperature at which its activity begins to be markedly lowered, its action is slowed down, and the ratio between maltose and non-maltose materials decreases in value. The author now finds that with such attenuated extract of malt, the coefficient of velocity varies in a special manner. Thus, for the same extract of malt, acting on the same starch solution,  $K$  increased from 4000 to 5036 for unheated extract, from 4230 to 5692 for extract heated to  $30^\circ$ , remained almost constant for extract heated to  $40^\circ$  or  $50^\circ$ , diminished from 2483 to 1681 for extract heated to  $60^\circ$ , and from 1443 to 463 for extract heated to  $70^\circ$ . The time of heating was thirty minutes, and the coefficient was determined over a range of one hundred and eighty minutes in each case. The change is therefore continuous. The change is retarded by the addition of maltose, which seems, there-

fore, to protect the diastase to some extent, whence it seems likely that not only is an adsorption compound formed between diastase and starch, but also between diastase and maltose.

It appears likely that the so-called "optimum temperature" for enzymes is the resultant of two actions, namely, (1) the normal increase in velocity of reaction due to rise in temperature, and (2) the destruction of enzyme due to rise in temperature, so that in reality the coefficient of velocity in enzyme reactions tends to diminish with rise of temperature. For diastase, the coefficient of temperature,  $K_t + 10/K_t$ , of the reaction remains constant, and is about equal to 2 between 25 and 35° (at which temperatures the destruction of enzyme by heating is negligible) so long as the other conditions are such that the reaction obeys the logarithmic law.

T. A. H.

**Automatic Pressure Pipette.** WLADIMIR SKINDER (*Chem. Zeit.*, 1912, 36, 166).—The pipette, which is used for mixing two liquids at the same temperature, as in calorimetric experiments, consists of a hollow glass piston, sliding in an outer mantle of one-third its length, the upper and lower joints being ground. There is a small hole in the piston in the upper part of the pipette, and a groove in the lower ground joint, which can be brought into coincidence with a hole in the mantle. The pipette is filled by lowering into the liquid and forcing the piston downwards. When filled, it is withdrawn, and the excess of liquid allowed to escape by bringing the openings into coincidence. After rinsing, the pipette is brought to the required temperature, and the liquid can then be expelled by applying air-pressure, which lifts the mantle.

C. H. D.

**Substitute for Separating Funnels.** HEINRICH KILIANI (*Zeitsch. anal. Chem.*, 1912, 51, 102).—A doubly-perforated cork is fitted with a siphon tube and also with a small tube bent at a right angle. The siphon tube should not fit too tight. The cork is then placed on the bottle containing the two-layer liquid, and, after placing the siphon in the proper position, gentle blowing through the small tube starts the action.

L. DE K.

**Filtration with Alundum Plates.** RAYMOND C. BENNER and WILLIAM H. ROSS (*J. Amer. Chem. Soc.*, 1912, 34, 51).—Disks or plates of "alundum" (fused aluminium oxide) are recommended as substitutes for filter-plates and asbestos. An ordinary rubber band, stretched round the disk, enables it to fit closely to the funnel when suction is applied by the pump. Alundum disks are obtainable with pores of various degrees of fineness; those with the smallest pores are capable of retaining the finest precipitates. By their use, the preparation of asbestos is obviated, and the precipitates can be stirred without risk.

E. G.

**Substitute for Kipp's Apparatus.** BERTHOLD OPPLER (*Chem. Zeit.*, 1912, 36, 96).—A wide glass cylinder, open at both ends, is passed through the cork of a wide-necked bottle, the lower end of the cylinder reaching to the bottom of the bottle. The upper end of the cylinder, which should be just above the cork, is closed by means of a

second cork, through which pass a tapped delivery tube and the stem of a large bulb tube. The material from which the gas is to be evolved is placed on a perforated plate supported on rubber stoppers at the bottom of the cylinder, the lower end of the funnel stem reaching below this plate. Perforations are provided in the walls of the cylinder in order that the acid from the bulb tube may circulate in the cylinder and bottle.

W. P. S.

**Universal Apparatus.** FRANZ MICHEL (*Chem. Zeit.*, 1912, 36, 138).—In appearance the apparatus resembles a large vacuum desiccator provided with screw-clamps, so that the upper and lower portions can be firmly fixed to each other. The upper portion is of Jena resistance glass, the lower being of copper, nickel, cast iron, or porcelain; the joint is made tight by means of an asbestos ring which has been soaked with rubber solution.

The apparatus can be used for treating volatile and easily decomposable substances in a protecting atmosphere.

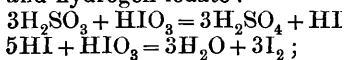
T. S. P.

**An Early Physical Chemist:** M. W. Lomonosoff. ALEXANDER SMITH (*J. Amer. Chem. Soc.*, 1912, 34, 109—119).—A biographical sketch of the Russian chemist, Lomonosoff (1711–1765), and an appreciation of his work.

E. G.

**Some Lecture Experiments.** CONSTANTIN ZENGELIS (*Zeitsch. phys. Chem. Unterr.*, 1911, 24, 137—142).—An account of the methods by which the author demonstrates (1) *Faraday's law*.—A pair of tubes, *A* and *B*, with taps at the base are joined to each other by another tube containing a tap which can be opened or shut as required, wires are connected for the passage of an electrical current, and they are filled with an *N*/10-solution of an alkali sulphate in the presence of an indicator (such as litmus or phenolphthalein). Another similar pair of tubes, *A'* and *B'*, containing the exact equivalent of another alkali sulphate are placed in series, an electric current passed, and the change of colour shown by the indicators noted; the connecting taps are then closed, and the contents of *A* and *B'* and of *A'* and *B* respectively mixed, when the original colour of the solutions will be regenerated.

(2) *Positive and negative catalysis* as shown by the interaction of sulphurous acid and hydrous iodate:



the duration of the reaction is noted in the case of varying concentrations and in the presence of different acids, the end point being sharply marked by the sudden separation of iodine; with 6.4 grams of sulphurous acid and 17.8 grams of iodic acid, each in a litre of water, the reaction was completed in 38.28 seconds (compare Landolt, *Abstr.*, 1886, 658).

(3) *The ignition of a mixture of nitric oxide and carbon disulphide*.—A wide-necked flask is filled with nitric oxide, a few c.c. of carbon disulphide added, closed with a glass plate, and heated until ignition takes place.

(4) *The burning of carbon disulphide in oxygen*.—A strong bottle

closed with a two-holed stopper: the larger opening is fitted with a silver or porcelain tube, the other one with a narrower brass tube connected outside with a source of oxygen, which after entering the bottle bends round into the other tube; carbon disulphide is placed in the bottle, heated, and the vapour ignited in the stream of oxygen at the mouth of the bottle.

(5) *The high temperature produced by burning aluminium in oxygen.*—The aluminium is heated in a Hessian crucible into which a stream of oxygen is introduced (compare Zengelis, *Abstr.*, 1904, ii, 232, and *Elektrochem. Zeitsch.*, 1903, 10, 109; see also *Abstr.*, 1905, ii, 65; 1910, ii, 1106).  
F. M. G. M.

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## Inorganic Chemistry.

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**Synthesis of Hydrogen Peroxide.** ALEXANDRE DE HEMPTINNE (*Ber.*, 1912, 45, 230).—The author points out that he has previously obtained results similar to those recorded by Fischer and Wolf (*Abstr.*, 1911, ii, 1082) in their experiments on the synthesis of hydrogen peroxide (compare *Ann. soc. sci. Bruxelles*, 1908, 1911).

He has also found that *X*-rays and ultra-violet light have no effect on the reaction. T. S. P.

**The Catalytic Decomposition of Hydrogen Peroxide by Dichromates.** ERNST H. RIESENFELD (*Zeitsch. anorg. Chem.*, 1912, 74, 48—51. Compare *Abstr.*, 1908, ii, 951; 1911, ii, 107; Spitalsky, *ibid.*, 36, 37).—Mixtures of chromates and dichromates decompose hydrogen peroxide catalytically, the velocity being the sum of the velocities due to the chromate and dichromate separately. The calculated values of  $K = k_1 + k_2 = 460c_1 + 137000c_2$ , where  $c_1$  and  $c_2$  are the concentrations of chromate and dichromate respectively, agree closely with those found by Spitalsky. When free chromic acid is present, perchromic acid is formed, which loses oxygen to form chromic salts. The quantity of chromic salt found agrees with that calculated. C. H. D.

**Solubility of Bromine in Aqueous Solutions of Sodium Bromide.** JAMES M. BELL and MELVILLE L. BUCKLEY (*J. Amer. Chem. Soc.*, 1912, 34, 14—15).—Determinations of the solubility of bromine in solutions of potassium bromide have been made by Worley (*Trans.*, 1905, 87, 1107). Joseph and Jinendradasa (*Trans.*, 1911, 99, 274) have studied the colour changes in bromine solutions on addition of bromides. Solubility determinations have now been made of bromine in solutions of sodium bromide at 25°. The solubility curve resembles that obtained by Worley. In dilute solutions the ratio of bromine to bromide is about  $\text{Br}_2 : \text{NaBr}$ , but is greater for more concentrated solutions. In the case of nearly saturated sodium bromide solutions, the ratio is about  $2.5\text{Br}_2 : \text{NaBr}$ . E. G.

**Solubility of Iodine in Aqueous Solutions of Bromides of Potassium and Sodium.** JAMES M. BELL and MELVILLE L. BUCKLEY (*J. Amer. Chem. Soc.*, 1912, 34, 10—14).—Dawson and Goodson (*Trans.*, 1904, 85, 806) studied the solubility of iodine in solutions of potassium bromide in nitrobenzene, and came to the conclusion that complex perhalogen compounds were formed of the same type as those produced in solutions of the alkali iodides.

An investigation has now been made to ascertain whether double compounds of iodine with sodium bromide or potassium bromide are formed in aqueous solutions at 25°. The method adopted was similar to that used by Worley (*Trans.*, 1905, 87, 1107) in his determination of the quantity of bromine dissolved by potassium bromide solutions. It has been found that the increase in the solubility of iodine is about  $10^{-2}$  mol. for each mol. of salt. In concentrated solutions of potassium bromide, the ratio is somewhat less, and in concentrated solutions of sodium bromide, considerably less than  $10^{-2}$ .

These results show that if double compounds are formed at all, they are present in only very minute quantities. E. G.

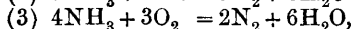
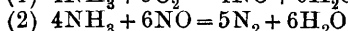
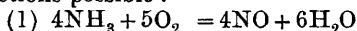
**Atomic Weight of Nitrogen.** EUGÈNE WOURTZEL (*Compt. rend.*, 1912, 154, 115—116).—Five experiments have given for the atomic weight of nitrogen the figures 14·005, 14·008, 14·006, 14·007, 14·008; mean 14·007.

The method involved determination of the weight of oxygen necessary to convert a known weight of nitric oxide into nitric peroxide. A U-tube containing cooled liquid nitric peroxide as a solvent was weighed, and a definite weight of nitric oxide passed in. Pure dry oxygen was then introduced, and the increase in weight determined, after removing excess of oxygen by evacuating the apparatus at the temperature of liquid air.

The experimental details will be published in a subsequent communication. W. O. W.

**Oxidation of Nitrogen to Nitrogen Oxides.** WILLEM REINDERS and A. CATS (*Chem. Weekblad*, 1912, 9, 47—58).—An investigation of the influence of temperature, the composition and velocity of the gas-mixture, and the nature of the catalyst on the oxidation of ammonia by air. The catalysts employed were platinised asbestos or glass or copper wire, thorium oxide and pumice, ferric oxide on glass or asbestos, oxidised iron-gauze in glass or porcelain tubes, or a porcelain tube without a catalyst. With platinum or iron oxide, 80—90% of the ammonia is oxidised to nitric acid and nitrous acid. The form of the catalyst and the velocity of the gaseous mixture have little influence. For platinised asbestos or glass, the best temperature is 600°; for ferric oxide, 650—700°.

Of the three reactions possible :



the first is much accelerated by platinum or ferric oxide, so that the gas-mixture should be in close contact with the catalyst. Reactions

(2) and (3) do not require a catalyst, but are much facilitated by glass or porcelain. The possibility of the formation of nitrous oxide is not overlooked, but the experimental difficulties precluded its detection.

A. J. W.

**Oxidation of Ammonia in Aqueous Solution.** WILLEM P. JORISSEN (*Chem. Weekblad*, 1912, 9, 58—60. Compare foregoing abstract).—A summary of methods for the oxidation of aqueous ammonia published during the period 1843—1911.

A. J. W.

**Synthetic Formation of Nitrous Oxide.** CAMILLE MATIGNON (*Compt. rend.*, 1912, 154, 203—206).—The author shows from thermodynamical considerations that the direct union of nitrogen and oxygen with production of nitrous oxide should be realisable at 3000° and 3000 atmospheres. Unless the gas was rapidly cooled, however, and removed from the sphere of action, the yield would be only 0.1%.

W. O. W.

**Electrochemical Oxidation of Some Hydrazine Salts.** J. W. TURRENTINE and WILLIS A. GIBBONS (*J. Amer. Chem. Soc.*, 1912, 34, 36—49).—Szarvasy (*Trans.*, 1905, 77, 605) studied the electrolysis of hydrazine hydrate, sulphate, and chloride, and found that in each case nitrogen and hydrogen were produced in quantities corresponding with the quantitative decomposition of the base.

It was considered probable that by varying the conditions of electrolysis so that the conditions at the anode would simulate oxidising agents of varying activity, other oxidation products than nitrogen and water would be obtained. Turrentine (*Proc. Amer. Chem. Soc.*, July, 1908) therefore electrolysed hydrazine sulphate in solutions of varying acidity, with different current densities and at different temperatures. In experiments in which high current density, low temperature, and strongly acid, saturated solutions of the salt were employed, azoimide was produced, and its formation was attributed to the action of the persulphate ion.

An investigation has now been made with hydrazine carbonate, hydrochloride, and hydrobromide. In the case of the carbonate, under conditions which would favour the formation of percarbonates, the hydrazine suffered quantitative oxidation into nitrogen and water. In the electrochemical oxidation of hydrazine hydrochloride and hydrobromide, azoimide was not obtained under any conditions. At low temperatures and with low current densities only nitrogen and water were produced, whilst at high temperatures and with high current densities considerable quantities of ammonia were formed. In certain experiments with the hydrochloride, the conditions were such as should have led to the formation of chlorate ions. The production of chlorate seemed, however, to be rendered impossible owing to the reduction of the hypochlorite by the hydrazine present.

E. G.

**Iodides of the Elements of the Nitrogen Group.** H. R. DOORNBOSCH (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 625—637).—By means of observations of the changes which occur on

solidification of molten binary mixtures and of the melting-point phenomena, the authors have investigated the nature of the iodides formed by antimony and arsenic.

Antimonous iodide melting at  $170.8^{\circ}$  is the only compound formed by antimony. The iodide is not perceptibly miscible with antimony, and on addition of excess of the latter, the liquid melt separates into two layers, one of which is almost identical in composition with the iodide, whilst the other contains 71.6 atom % of antimony. The transition temperature at which the two liquid layers are formed is  $169^{\circ}$ . The eutectic temperature is  $80^{\circ}$ , and the eutectic mixture contains 88.2 atom % of iodine. On the assumption that the iodine dissolved in antimonous iodide consists of diatomic molecules, it is calculated that the molecular heat of fusion of the iodide is 11 cal. This corresponds with a molecular lowering of the freezing point equal to  $357^{\circ}$ .

The thermal diagram for mixtures of arsenic and iodine is similar to that for antimony and iodine. In this case two compounds are formed, however,  $\text{AsI}_3$ , melting at  $140.7^{\circ}$ , and  $\text{As}_2\text{I}_4$ , which at  $135\text{--}136^{\circ}$  is transformed into a pair of immiscible liquids, one of which has a composition differing only slightly from  $\text{As}_2\text{I}_4$ , whilst the other contains 30.5 atom % of arsenic. Various observations are recorded in support of the view that the substance  $\text{As}_2\text{I}_4$  is a definite compound, and that it is formed by dissociation of  $\text{AsI}_3$  in accordance with  $2\text{AsI}_3 \rightleftharpoons \text{As}_2\text{I}_4 + \text{I}_2$ . It may also be formed by the interaction of  $\text{AsI}_3$  and metallic arsenic in consequence of the occurrence of the reversible change represented by  $8\text{AsI}_3 + 4\text{As} \rightleftharpoons 6\text{As}_2\text{I}_4$ .

From the thermal data obtained in freezing- and melting-point determinations it has also been found that antimonous iodide and arsenious iodide form a continuous series of mixed crystals, the solidus and liquidus curves meeting at a minimum temperature of about  $135^{\circ}$ .

Arsenious iodide and phosphorus tri-iodide form an isodimorphous series of crystals with a transition point at  $73.5^{\circ}$ , whereas antimonous iodide and phosphorus tri-iodide yield two distinct series, the corresponding curves meeting in a eutectic at  $56^{\circ}$ . H. M. D.

#### Transformation of Other Forms of Carbon into Graphite.

WILLIAM C. ARSEM (*Trans. Amer. Electrochem. Soc.*, 1911, 20, 105—119).

—Conflicting statements exist as to the conversion of amorphous carbon into graphite by heat, it being uncertain whether pure carbon is thus convertible, or whether the intermediate formation of carbides is necessary. Graphite must be defined by its specific gravity, 2.25 to 2.26, as many varieties of carbon, of entirely different density, yield products more or less resembling graphitic acid on oxidation.

The specimens of carbon to be tested are very finely ground, and heated in closed graphite crucibles to  $3000\text{--}3300^{\circ}$  for fifteen minutes. Petroleum coke, with only 0.10% ash, yields silvery-grey graphite, D 2.26. Bituminous coke, containing 10% ash, is less perfectly graphitised, but gives better graphite after extraction with fused sodium hydroxide and hydrochloric acid. Anthracite is very imperfectly converted. Lamp black, either alone or mixed intimately

with ferric oxide, is converted into a black, non-crystalline powder, D 2.10, which yields a yellow graphitic acid with Brodie's test, but has none of the characteristic properties of graphite. White diamond yields coke, D 1.915, and not graphite. The tendency to become converted into graphite is quite independent of the quantity and nature of the mineral matter present. C. H. D.

**Solubility of Carbon Dioxide in Water and Certain Other Solvents at High Pressures.** WILHELM SANDER (*Zeitsch. physikal. Chem.*, 1912, 78, 513—549).—The solubility of carbon dioxide at 20°, 35°, 60°, and 100° in water and in a number of organic solvents has been determined at a series of pressures between 20 and 170 kilog./cm.<sup>2</sup> by means of a Cailletet pressure apparatus.

At low temperatures the relationship between solubility and temperature deviates from Henry's law for all the solvents examined. The solubility of the gas in ethyl and propyl alcohols, benzene, chloro-, bromo- and nitro-benzene, and toluene increases faster with increasing pressure, in ethyl ether, ethyl acetate and water slower, than Henry's law requires. The law in question is more nearly followed when the volume of gas absorbed is referred, not to the volume of the solvent, but to that of the solution.

As would be anticipated, Henry's law is the more nearly followed the higher the temperature, and at 100° the solubility of carbon dioxide in most of the solvents is proportional to the pressure. The solubilities diminish with increasing temperature, except for nitro-benzene, which appears to dissolve the same amount of carbon dioxide at 60° and at 100°.

For solvents which are chemically related, such as benzene and chloro- and bromo-benzene, the solubility of carbon dioxide diminishes with increasing atomic weight.

The isotherms for the saturated solutions of carbon dioxide in ether and of ether vapour in carbon dioxide have been determined at 35°, 60°, and 100°. In the neighbourhood of the critical point, Henry's law is not even approximately valid. G. S.

**Experiments with Liquid Helium. Isotherms of Monatomic Gases, etc. IX. Thermal Properties of Helium.** H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 678—684. Compare Abstr., 1911, ii, 487).—With the aid of the helium cryostat described previously, the author has succeeded in measuring directly the critical temperature 5.25° (abs.). The following vapour-pressure data have also been obtained for liquid helium between the boiling point and the critical temperature:

Temperature .....	4.28°	4.97°	5.10°	5.15°	5.22°	5.25
Pressure (mm. Hg) ...	767	1329	1520	1569	1668	1718

According to these numbers, the vapour pressure increases very rapidly with the temperature above the boiling point. From the above data, the critical volume is calculated to be 0.00271.

H. M. D.

**Monatomicity of Neon, Krypton, and Xenon.** SIR WILLIAM RAMSAY (*Proc. Roy. Soc.*, 1912, A, 86, 100—101).—Measurements

have been made of the wave-lengths of sound in air, neon, krypton, and xenon. From these data the specific heat ratios obtained are: neon 1·642, krypton 1·689, xenon 1·666. Within the limits of experimental error these numbers agree with the value 1·667 required on the assumption that the gases are monatomic. H. M. D.

**The Availability of the Potassium in "Rapakivi" and Pegmatitic Granites.** OSSIAN ASCHAN (*Zeitsch. anorg. Chem.*, 1912, 74, 55—73).—"Rapakivi" is a Finland porphyritic granite, which weathers readily, and leaves large, easily separable masses of orthoclase. Various methods have been proposed for rendering the potassium of these and other silicates available for manures.

[With LAURI LOKKA.]—Estimations of potassium and phosphates in (I) orthoclase from pegmatite at Sörnäs, near Helsingfors; (II) round rapakivi masses from weathered rock near Lovisa; (III) larger and less weathered masses from the same district; (IV) crystals from less weathered rock near Wiborg; (V) finer particles from the same rock; give

	I.	II.	III.	IV.	V.
K <sub>2</sub> O .....	13·44	9·68	10·95	10·16	9·87%
P <sub>2</sub> O <sub>5</sub> .....	0·313	0·197	0·204	0·204	0·178%

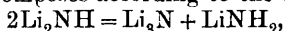
A small part of the potassium is extracted by heating on the water-bath with milk of lime, whilst in a sealed tube at 150—180° as much as 17% of the total potassium is rendered soluble, and at 225° in an autoclave, 22% of the total. Sulphuric acid extracts up to 25%, whilst hydrogen chloride at a red heat removes very little. Fusion with lime and sodium chloride at 900—1000° renders 81% of the potassium soluble. Fusion with calcium chloride has much less effect. The residue has considerable value as a fertiliser. Experiments on the action of soil on the powdered felspar show that in the course of six to twelve months at the ordinary temperature, the potassium increases, but the results are inconclusive, on account of decomposition of the soil, setting free phosphates and potassium salts. C. H. D.

**New Alkali Phosphides of the Type M<sub>2</sub>P<sub>5</sub>.** LOUIS HACKSPILL and ROBERT BOSSUET (*Compt. rend.*, 1912, 154, 209—211).—A description of the preparation and properties of *caesium*, *rubidium*, *potassium*, and *sodium phosphides* having the general formula M<sub>2</sub>P<sub>5</sub>.

Two or three grams of the metal and a large globule of phosphorus are distilled successively into an evacuated tube, and the mixture heated at 400—430°. A black mass is formed containing free metal, but after 100 to 150 hours this is lost by volatilisation and the phosphide becomes reddish-brown. In the case of the sodium salt, it is necessary to heat at 450°. At 0—100° the four phosphides resemble cadmium sulphide in appearance, but become darker at higher temperatures, and are almost colourless when cooled in liquid nitrogen. They melt at about 650° with decomposition and loss of phosphorus. They rapidly decompose in air, and when treated with water yield a solid phosphorus hydride, together with a small amount of phosphine and hydrogen. Potassium phosphide has D 2 approximately.

W. O. W.

**New Compounds of Nitrogen and Hydrogen with Lithium.** FRANZ W. DAFERT and R. MIKLAUZ (*Monatsh.*, 1912, 33, 63—69. Compare Abstr., 1909, ii, 882; 1911, ii, 39).—On exposure to sunlight, lithiumimide decomposes according to the equation:



the reaction being accompanied by the development of a dark red colour. In the action of nitrogen on lithium hydride, of hydrogen on lithium nitride, or of mixtures of nitrogen and hydrogen or ammonia on lithium hydride or nitride, lithiumimide, lithiumamide or trilithiumamide, or mixtures of these three substances are formed, the final product depending on the temperature and other experimental conditions. The amide can be readily obtained by the action of ammonia on amorphous lithium nitride at temperatures between 130° and 350°, or on crystalline lithium nitride from 410° to 430°, or on lithium hydride from 440—460°, the changes taking place according to  $\text{Li}_3\text{N} + 2\text{NH}_3 = 3\text{LiNH}_2$  and  $\text{LiH} + \text{NH}_3 = \text{LiNH}_2 + \text{H}_2$ .

At 450° lithiumimide reacts with hydrogen according to  $3\text{Li}_2\text{NH} + 2\text{H}_2 = 2\text{Li}_3\text{NH}_2 + \text{NH}_3$ . The trilithiumamide thus obtained reacts at about 600° with nitrogen according to  $4\text{Li}_3\text{NH}_2 + \text{N}_2 = 6\text{Li}_2\text{NH} + \text{H}_2$ .  
H. M. D.

**The True Atomic Weight of Silver, Deduced from the Laboratory Determinations of a Century.** GUSTAVE D. HINRICHS (*Compt. rend.*, 1912, 154, 211—213. Compare Abstr., 1908, ii, 573, 574; 1909, ii, 140, 653; 1910, ii, 285, 844; 1911, ii, 1080).—The extent to which values for the atomic weight of silver by Stas, Marignac, Maumené, Gallo, the Harvard school, and others differ from the whole number 108 is shown in diagrammatic form. The author considers that the manner in which these differences are distributed above and below 108 justify the conclusion previously arrived at, that the true atomic weight of silver is 108°.

W. O. W.

**Modifications of Silver. I. Mirror Silver.** VOLKMAR KOHL-SCHÜTTER and EMILIE FISCHMANN (*Annalen*, 1912, 387, 86—145).—True allotropy, characterised by a different energy-content of the modifications, does not occur in silver, but the physical properties of silver differ in a marked degree according to the method of preparation. In the present investigation, the properties of silver mirrors prepared under different conditions are studied.

Potential measurements with ammoniacal silver solutions against silver nitrate show that a part of the silver must be present as hydroxide, and this part is of essential importance in mirror formation. It is shown that the reduction by tartaric acid or sugars always involves the formation of aldehydes, and that in all cases colloidal substances are formed during the reaction. Reduction with ferrous salts or hydrogen causes deposition of the silver on the surface of the containing vessel, but the deposit is black, and does not take the form of a mirror. The reduction potential is not the determining factor, as the substances which yield mirrors include those with both high and low reduction potentials. A low velocity of reduction is favourable,

and the influence of traces of copper and other metallic salts in promoting the formation of mirrors is due to their retarding effect on the reduction. Adsorption of silver hydroxide by the walls of the containing vessel plays an important part, and the formation of a mirror is favoured by prolonged contact with the silver solution, before the reducing agent is added. Experiments with filter paper show that silver hydroxide is adsorbed to a greater extent than the other constituents of the solution. The surface tension is lowered by all the substances which serve as reducing agents, and in some cases the surface tension diminishes with time.

Silver mirrors prepared in presence of traces of metallic salts differ in appearance, but consist in general of pure silver. Thin mirrors are transparent, and are recognisable as colloidal (disperse) by means of the cardioid ultramicroscope. The colloidal character is confirmed by the action of electrolytes, very dilute acids and haloid salts dislodging the film without dissolving it. The electrolytic potential is the same as that of massive silver, but the electrical resistance is greater, and alters with the time, in a manner which is characteristic of the reducing agent used.

Silver films produced by electrical discharge in dilute gases show similar variations with the nature of the gas employed.

C. H. D.

**Gelatin and Other Colloids as Retarders in the Reduction of Silver Chloride.** WILLEM REINDERS and C. J. VAN NIEUWENBURG (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 36—40).—The addition of small quantities of colloidal substances to a ferrous citrate solution has been found to have a very marked retarding influence on the rate at which silver chloride is reduced. The effect is exhibited by gelatin, albumin, agar-agar, gum arabic, and also by certain dyes such as acid-violet-6B. With Ponceau-3R there appears to be little or no retardation, however. In the case of gelatin and albumin, the effect is well developed even in the presence of 0.001% of the colloid. With increasing concentration of the colloid, the retardation increases, and curves are drawn to show the influence of concentration.

Of the two steps which are involved in the reduction process: (a) dissolution of the silver chloride, (b) reduction of the dissolved salt and precipitation of metallic silver, it is shown that the colloids are without influence on the former, and that the observed effect is due to retardation of the second process.

From these experiments it appears that gelatin has a double function in the photographic process. It acts as an accelerator in the photochemical reduction of the silver halide (compare Abstr., 1911, ii, 490) and as a retarder in the subsequent development. H. M. D.

**Double Carbonates of Calcium.** MAURICE BARRE (*Compt. rend.*, 1912, 154, 279—280).—When precipitated calcium carbonate is boiled with a concentrated solution of sodium carbonate, orthorhombic crystals are produced having the composition



and not  $\text{Na}_2\text{CO}_3, \text{CaCO}_3, 5\text{H}_2\text{O}$ , as stated by Fritsche (*J. pr. Chem.*,

1864, 93, 339). The compound is not formed at  $98^{\circ}$  unless the solution contains at least 21.06% of sodium carbonate. Under these conditions, potassium carbonate gives a salt crystallising in prismatic needles, having the composition  $K_2CO_3 \cdot CaCO_3$ . This is readily hydrolysed by water, and at  $19^{\circ}$  is only stable in solutions containing at least 59.25% of potassium carbonate.

Barium and strontium carbonates do not appear to form double salts with the alkali carbonates. W. O. W.

**The Conditions for the Formation of Magnesium Nitride from Air.** CAMILLE MATIGNON and A. LASSIEUR (*Chem. Zeit.*, 1912, 36, 30; *Compt. rend.*, 1912, 154, 63—65).—When magnesium powder is heated to redness in a deep, closed crucible, the upper layer is converted into oxide and the lower into nitride. The reaction with nitrogen, as shown by the fall of pressure in a manometer connected with the vessel containing the magnesium, begins at  $670^{\circ}$ , whilst the reaction with oxygen begins at  $600^{\circ}$  and is more rapid. If air is used, and the vessel is heated to  $620^{\circ}$ , the reaction ceases when all the oxygen has been absorbed. The behaviour in a crucible is thus accounted for. C. H. D.

**Preparation of Magnesium Silicide and its Decomposition by Acids.** ADOLPHE BESSON (*Compt. rend.*, 1912, 154, 116—119).—A mixture of magnesium with half its weight of powdered quartz is stamped into an iron crucible, and the reaction started by lighting some magnesium powder placed on the top. On treating the black mass of silicide with hydrochloric acid, a gas is obtained containing 6—7% of silicon hydrides, whereas Moissan's silicide gives only 4—5%. The amount of silicon hydrides is not increased by using other acids, but may be diminished, as in the case of oxalic, citric, or sulphurous acids which yield only hydrogen. The hydrides are best prepared by decomposing the silicide under water in a large flask by pure hydrochloric acid. A gas containing less than 0.5% of hydride (calculated as tetrahydride) is not spontaneously inflammable, but fumes in air, forming a colourless solid of variable composition,  $H_4Si_2O_3$  or  $H_4Si_2O_4$ . When this is heated in a vacuum, water is lost, and the colourless residue has the composition of a suboxide of silicon. W. O. W.

**Indian and Chinese Zinc.** W. HOMMEL (*Zeitsch. angew. Chem.* 1912, 25, 97—100).—The history of the manufacture of zinc in India and China is dealt with, the author drawing the conclusion that the metal was first obtained in India, the manufacture then being transplanted to China, which country then alone produced it until the middle of the eighteenth century.

The analysis of a specimen of Chinese zinc recovered from the wreck of a ship which sank near Gothenburg in 1745 gave the figures: zinc, 98.990%; iron, 0.675%; antimony, 0.245%. Copper, nickel, silver, arsenic, and lead were not present. T. S. P.

**The Ternary System Cadmium Chloride–Potassium Chloride–Sodium Chloride.** HERMANN BRAND (*Jahrb. Min. Beil. Bd.*, 1911, 32, 627—700).—This system has been investigated as a case of a

ternary system including binary compounds which do not melt without decomposition. The three components have the m. p.'s  $\text{CdCl}_2$   $562^\circ$ ,  $\text{KCl}$   $774^\circ$ ,  $\text{NaCl}$   $798^\circ$ . The binary system cadmium chloride–potassium chloride contains two compounds,  $\text{CdCl}_2 \cdot \text{KCl}$ , m. p.  $431^\circ$ , forming a maximum on the freezing-point curve, and  $\text{CdCl}_2 \cdot 4\text{KCl}$ , which breaks up at  $460^\circ$  into  $\text{KCl}$  and liquid. The two eutectic points occur at  $382^\circ$  and 34 mol. %  $\text{KCl}$ , and at  $390^\circ$  and 63 mol. %  $\text{KCl}$  respectively. The first compound forms rhombic crystals, and eutectic structures are well developed.

In the binary system cadmium chloride–sodium chloride, only a single compound occurs,  $\text{CdCl}_2 \cdot 2\text{NaCl}$ , which breaks up at  $425^\circ$  into sodium chloride and liquid. The eutectic point is at 45 mol. %  $\text{NaCl}$  and  $392^\circ$ . Sodium and potassium chlorides form a continuous series of solid solutions, the freezing-point curve having a minimum at  $654^\circ$  and 50 mol. %  $\text{NaCl}$ . At a lower temperature the solid solution is resolved into its components, the transformation curve having a maximum in the middle at  $400^\circ$ . Equilibrium is not entirely reached after some months at atmospheric temperature.

The compound  $\text{CdCl}_2 \cdot \text{KCl}$  does not form solid solutions, and the ternary system may thus be broken up into two systems  $\text{CdCl}_2$ – $\text{CdCl}_2 \cdot \text{KCl}$ – $\text{NaCl}$  and  $\text{CdCl}_2 \cdot \text{KCl}$ – $\text{NaCl}$ – $\text{KCl}$ . The space-model has been constructed by means of a complete thermal and microscopical analysis of these two systems. There are three ternary eutectic points at  $354^\circ$ ,  $370^\circ$ , and  $373^\circ$  respectively. There are six surfaces of primary crystallisation. Ternary solid solutions are formed with small proportions of cadmium chloride, and the presence of cadmium chloride raises the temperatures at which solid solutions of potassium and sodium chlorides are resolved into their compounds.

The theory of ternary systems of this type is discussed very fully. C. H. D.

**The Binary Systems Cadmium Iodide–Potassium Iodide and Cadmium Iodide–Sodium Iodide.** HERMANN BRAND (*Centr. Min.*, 1912, 26–32).—Cadmium iodide has m. p.  $385^\circ$ , and potassium and sodium iodides have m. p.'s  $678^\circ$  and  $653^\circ$  respectively. The freezing-point curve of mixtures of cadmium and potassium iodides has a eutectic point at  $185^\circ$  and 47.5 mol. %  $\text{KI}$ , whilst the ascending branch has two breaks, corresponding with the formation of the compound  $\text{CdI}_2 \cdot 2\text{KI}$  at  $269^\circ$  from crystals and liquid, and with the transformation of the  $\alpha$  regular crystals of this compound at  $215^\circ$  into the  $\beta$  doubly refracting modification, stable at low temperatures.

The freezing-point curve of mixtures of cadmium and sodium iodides is of a simple form, and a compound is not formed. The eutectic point is at  $287^\circ$  and 47 mol. %  $\text{NaI}$ . The formation of solid solutions is not observed in either case. C. H. D.

**The System Cadmium–Tin.** A. P. SCHLEICHER (*Intern. Zeitsch. Metallographie*, 1912, 2, 76–89).—The freezing-point curve of the alloys of cadmium and tin consists of only two branches, intersecting at the eutectic point at  $177^\circ$  and 67.6 atomic % of tin.  $\gamma$ -Tin holds

up to about 10 atomic % of cadmium in solid solution,  $\beta$ -tin much less. The transformation observed at  $127^\circ$  corresponds with the breaking up of the solid solution into cadmium and  $\beta$ -tin. Cadmium does not retain more than traces of tin in solid solution. C. H. D.

[The Behaviour of Certain Hydroxides towards Solutions of Alkylenediamines.] A Correction. WILHELM TRAUBE (*Ber.*, 1912, 45, 164. Compare this vol., i, 9).—The author points out that Hantzsch and Robertson (*Abstr.*, 1909, ii, 44), and also Dawson (*ibid.*, ii, 1011), have shown that ammoniacal solutions of cupric hydroxide contain the tetrammine base,  $\text{Cu}(\text{NH}_3)_4(\text{OH})_2$ . F. B.

Study of the Atomic Weight of Mercury through the Analysis of Mercuric Bromide. C. W. EASLEY and B. F. BRANN (*J. Amer. Chem. Soc.*, 1912, 34, 137—147).—Easley (*Abstr.*, 1909, ii, 1013; 1910, ii, 957) has determined the atomic weight of mercury by the analysis of mercuric chloride. The constant has now been re-determined by a study of mercuric bromide.

Pure mercuric bromide was prepared by passing a current of nitrogen through liquid bromine, and thus conveying bromine vapour into a chamber containing mercury at  $300^\circ$ . When the whole of the metal had been converted into the bromide, the latter was heated at  $235^\circ$  and nitrogen passed through the apparatus to remove the excess of bromine. The salt was thus obtained in masses of needles and was completely soluble in water.

The analysis of the bromide was effected by treating a solution, containing a weighed amount, with sodium hydroxide and reducing by means of hydrazine hydrate or hydrogen peroxide, so that the mercury was precipitated and the bromine ions left in solution. After the mercury had been removed by filtration, the solution was treated with a slight excess of nitric acid, and silver nitrate was added to precipitate silver bromide. The ratio  $\text{HgBr}_2 : 2\text{AgBr}$  was thus determined.

The results of eleven experiments gave a mean value for the atomic weight of mercury, 200.64 ( $\text{Br} = 79.92$ ;  $\text{Ag} = 107.88$ ), as compared with 200.62 and 200.63 obtained in the experiments with mercuric chloride (*loc. cit.*). E. G.

Fractional Crystallisation of the Picrates of the Rare Earths. LOUIS M. DENNIS and C. W. BENNETT (*J. Amer. Chem. Soc.*, 1912, 34, 7—10).—In attempting to ascertain whether a separation of the rare earths could be effected by the fractional crystallisation of the picrates, it was considered desirable to use mixtures of earths containing members of the yttrium, erbium, and didymium groups. After removing cerium and thorium from such a mixture by chlorination and treatment with hydrogen peroxide, the earths were precipitated as oxalates and the latter converted into the oxides by ignition. The oxides were converted into the hydroxides by dissolving them in hydrochloric acid and adding ammonia. The hydroxides were dissolved in hot solution of picric acid to form a neutral solution. The picrates were fractionally crystallised from the

solution, twenty-five final fractions being obtained. The absorption spectra of these fractions were examined, and the atomic weights determined by precipitating the earths as oxalates and finding the ratio  $R_2O_3:3C_2O_4$ . Curves were constructed to show the changes in the atomic weights and in the intensity of certain bands of the absorption spectra.

The curves show that praseodymium and neodymium concentrated in the first few fractions, but rapidly decreased after the sixth fraction; a remarkable increase in the amounts of these elements, however, occurred in the tenth and nineteenth fractions, and this peculiarity is being further investigated. Erbium and holmium were absent from the first six fractions, but suddenly appeared in the eighth fraction.

It is evident, therefore, that the fractional crystallisation of the picrates enables a rapid concentration of praseodymium and neodymium, free from erbium and holmium, to be effected, and also a concentration of erbium and holmium containing but small amounts of elements of the didymium group.

E. G.

**Preparation and Properties of Metallic Cerium.** ALCAN HIRSCH (*Trans. Amer. Electrochem. Soc.*, 1911, 20, 57—104).—Cerium is best prepared by dehydrating ceric chloride in an atmosphere of hydrogen chloride, and electrolysis the fused chloride in an iron crucible, which serves as cathode, with a graphite anode. Sodium chloride, potassium fluoride, and barium chloride are added in small quantities to the electrolyte to increase the resistance of the bath and check decomposition. The cerium thus obtained contains about 2% of impurities, consisting of iron and of cerium oxide and carbide. It may be purified by amalgamating with boiling mercury, skimming off the undissolved impurities, and distilling in a vacuum in a quartz vessel lined with magnesia. The metal has then  $D_{25}$  6.92, and is almost as soft and malleable as lead. Its alloys with most other metals are hard and brittle, but the alloy with antimony is soft and stable in air. The alloys with iron, nickel, tungsten, manganese, cadmium, and several other metals yield sparks when struck.

C. H. D.

**The Electrical Properties of Aluminium Alloys.** WITOLD BRONIEWSKI (*Ann. Chim. Phys.*, 1912, [viii], 25, 5—125).—Most of the experimental results contained in this paper have been previously published (Abstr., 1910, ii, 128, 715; 1911, ii, 115). The following further compounds are described:  $Al_3Fe$ ,  $Al_3Mn$ , and  $Al_3Ni$ , which are recognised by the electrical methods previously employed. Ternary alloys of copper, aluminium, and silver, obtained by making binary mixtures of the compounds  $AlCu_3$  and  $Al_2Ag_3$ , have also been studied. A series of measurements of alloys of the composition  $AlCu_3$  fix the transition point at  $580^\circ$ .

C. H. D.

**Sinhalese Iron and Steel of Ancient Origin.** SIR ROBERT HADFIELD (*Proc. Roy. Soc.*, 1912, A, 86, 94—100).—Specimens of iron and steel, obtained from the buried cities of Ceylon, have been

analysed, subjected to various mechanical tests, and the micro-structure examined. The analytical data for the three specimens are as follows :

	C.	Si.	S.	P.	Mn.	Fe.	Density.
Steel chisel (fifth century).....	traces	0·12	0·003	0·28	nil	99·3	7·69
Nail (fifth century) .....	traces	0·11	nil	0·32	nil	—	7·69
Native billhook .....	traces	0·26	0·022	0·34	traces	—	7·50

The percentage of silicon is low, that of phosphorus high, whilst the absence of manganese is rather remarkable. The low percentage of sulphur indicates that a very pure fuel, no doubt charcoal, was employed in the production of the material. The micro-photographs and the mechanical tests show that the specimens represent wrought iron and not steel, resembling somewhat the material known as puddled iron. According to the photographs, the specimens contain a large amount of slag, indicating that the material has not been subjected to anything like the amount of squeezing and forging that modern wrought iron undergoes. Some of the micro-photographs show martensitic structure in parts, and the author considers that this affords evidence of quenching.

H. M. D.

**Influence of Painting on the Rusting of Iron.** ERIK LIEBREICH and FRITZ SPITZER (*Zeitsch. Elektrochem.*, 1912, 18, 94—99).—The authors show, by covering iron with a varying number of coats of paint, that a thick coating does not prevent rusting; on the contrary, the greater the number of coats the greater the rusting. The requisite water probably comes, in part at least, from the slow oxidation of the oil of the paint. The source of the oxygen also necessary for rusting has not been discovered, nor has any explanation been found for the fact that rusting is favoured by the thickness of the coating. All the paints tried had the same effect except one containing alkali.

Fresh iron is positive towards painted iron at first, but the positive value gradually diminishes, and finally the fresh iron is negative to the painted iron. This appears to be due to the liberation of hydrogen on the iron.

G. S.

**First Crystallisation and Subsequent Physico-chemical Transformations in Iron-Carbon Alloys containing more than 4% of Carbon.** NICOLAUS M. VON WITTORF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1613—1690).—The principal results of this extended thermal and micrographic study of iron-carbon alloys are as follows.

Fusions containing 6·2—10% of carbon begin to crystallise at 2000—2380°, with separation of a phase rich in carbon (?FeC<sub>2</sub>), which in unetched sections has a pale sulphur-yellow colour and a silvery reflexion. This phase is etched very slowly by nitric acid (1 : 4), and becomes coated with copper when treated with very dilute copper sulphate solution; after the action of nitric acid, a dark residue is obtained. The same carbide crystallises when the fusion is heated to 2600° and graphite dissolved in it. From somewhat below 2000° down to 1700°, the first substance separating is pure cementite.

In the temperature region 1650—1330°, burning of the fusion takes place, this being particularly marked with a carbon-content of about 7%; stirring of the fusion is accompanied by the appearance of thin, tabular crystals (?FeC) at the surface, whilst in fusions heated to about 1600° these crystals assume the form of long arrows with angular projections.

Fusions heated below 1700° always contain a metallic phase surrounding the arrows or a compound rich in carbon (?FeC<sub>2</sub>), forming dendritic masses on a eutectic-like foundation. This compound is not appreciably etched by 4% alcoholic picric acid solution or by aqueous sulphuric acid (1:10 by weight) if the mass is hardened at a temperature not below 1160°, but, unlike cementite, it is etched energetically by 1:4 nitric acid. The quantity of this compound separating initially increases from 0 to 100% with increase in the concentration of the carbon from 4.1% to 5%. In fusions containing 6% or 7% of carbon, the basic mass of metal consists of this compound and of the arrow-like residuum (?FeC), its composition being expressed by the formula Fe<sub>4</sub>C (5.02% C). The carbide, Fe<sub>4</sub>C, decomposes into  $\gamma$ -solution and graphite below 1130°.

Crystallisation of the stable eutectic in fusions containing more than 4.1% of carbon proceeds at about 1180°.

The phases crystallising above 2000° (?FeC<sub>2</sub>) and at 1600—1400° (?FeC) decompose with separation of graphite.

The points of disagreement between these results and those of Ruff and of Ruff and Goecke (Abstr., 1911, ii, 897), which were published after the completion of the author's investigations, are discussed.

T. H. P.

**Triferro-carbide (Cementite), Fe<sub>3</sub>C.** OTTO RUFF and EWALD GERSTEN (*Ber.*, 1912, 45, 63—72).—Owing to the uncertainty as to the heat of formation of iron carbide, the authors have carried out further work on the subject. The carbide was prepared as follows: A mixture of 1000 grams of iron (C, 4.13%; Si, 0.074%; S, 0.006%; Mn, 0.15%; P, 0.20%; Cu, 0.005%) with 100 grams of powdered arc-lamp carbon was heated for one hour at a white heat, and the fused mass then poured on to a large iron plate. After removing oxide and dross, the cold fused mass was finely powdered and digested at the ordinary temperature with *N*-acetic acid for four weeks, and then for several weeks with *N*/5-hydrochloric acid. Any remaining carbon was then removed by levigation, and the residual carbide washed with alcohol and ether, and dried in a vacuum; it contained 6.69% C and 93.28% Fe (theory, 6.67 and 93.33 resp.). In appearance it was dark grey, and consisted, for the most part, of fragments of globular aggregates of needle-shaped crystals; it was very brittle, and could be powdered on the hand. The hardness lies between 3.2 and 3.3, so that it cannot, itself, be the cause of the hardness of rapidly cooled steel, which is probably due to the solid solution of the carbide in  $\gamma$ -iron:  $D^{21} = 7.396$ , the molecular volume being 24.34.

The molecular heat of combustion, determined in a bomb calorimeter, was found to be 375.1 Cals., the products of combustion being carbon dioxide and ferrosiferrous oxide. In the actual combustions, a mixture

of ferrous and ferrosiferrous oxide is produced, from the analysis of which and the knowledge of the heat of combustion of ferrous oxide to magnetic oxide, the necessary correction to be applied to the observed heat of combustion of the carbide can be calculated.

The molecular heat of formation of ferrosiferrous oxide was found to be 265.2 Cal. Pure Swedish iron (Fe, 99.745%), and iron prepared from pure ferric chloride were used in these experiments, allowance being made for the heat of combustion of the traces of impurities present in the Swedish iron.

From the molecular heats of formation of ferrosiferrous oxide and of carbon dioxide (from graphite = 94.8 Cal.), and from the molecular heat of combustion of iron carbide to ferrosiferrous oxide and carbon dioxide, the heat of formation of iron carbide ( $\text{Fe}_3\text{C}$ ) is found to be -15.1 Cal.

T. S. P.

**Chromic and Aluminium Nitrates.** MILORAD Z. JOVITSCHITSCH (*Monatsh.*, 1912, 33, 9—18).—By dissolving strongly heated chromic oxide in hot concentrated nitric acid of D 1.4, a solution is obtained from which the hydrate,  $\text{Cr}_2(\text{NO}_3)_6 \cdot 15\text{H}_2\text{O}$ , crystallises on cooling in the form of dark brown prisms [ $a:b:c=1.4250:1:1.1158$ ;  $\beta=93^\circ 10'$ ]. In contact with dry air, the crystals lose  $6\text{H}_2\text{O}$ , with the formation of the grey-coloured hydrate,  $\text{Cr}_2(\text{NO}_3)_6 \cdot 9\text{H}_2\text{O}$ .

Under similar conditions, the solution of strongly heated alumina in concentrated nitric acid gives rise to the nitrate,  $\text{Al}_2(\text{NO}_3)_6 \cdot 15\text{H}_2\text{O}$ . These crystals, like those of the corresponding chromic salt, are quite stable when exposed to the ordinary air.

Crystals of aluminium nitrate containing a smaller proportion of water appear to separate from solutions of alumina in fuming nitric acid, but these are very hygroscopic, and the composition could not be determined.

H. M. D.

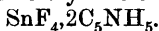
**Preparation and Properties of Some Perchlorates.** H. GOLDBLUM and F. TERLIKOWSKI (*Bull. Soc. chim.*, 1912, [iv], 11, 103—111).—The perchlorates were prepared by dissolving the appropriate carbonate or hydroxide in perchloric acid, and evaporating the solution obtained until crystallisation occurred. Analyses of the nickel and cobalt salts were made, the metals being determined electrolytically after conversion into sulphates. The acid was estimated by electrolysis of a dilute solution of the perchlorate, using a current of 0.1 ampere and 2.4 volts, and titrating the solution, when deposition of the metal was complete.

*Nickel perchlorate*,  $\text{NiClO}_4 \cdot 5\text{H}_2\text{O}$ , m. p.  $149^\circ$ , forms long, green, hygroscopic needles, and is soluble in water, alcohol, or acetone. When heated at  $103^\circ$ , it becomes only partly soluble in these solvents; the insoluble matter is yellow and crystalline, and is probably a basic salt. When kept in aqueous solution even at  $0^\circ$ , the perchlorate undergoes hydrolysis, depositing a flocculent precipitate of nickel hydroxide. *Cobalt perchlorate*,  $\text{CoClO}_4 \cdot 5\text{H}_2\text{O}$ , m. p.  $143^\circ$ , forms long, red needles, and resembles the nickel salt in properties, but is more stable, not being decomposed when heated at  $103^\circ$ , nor when the aqueous solution is boiled. *Chromium perchlorate* forms short, green,

deliquescent needles, and is very soluble in alcohol. *Didymium perchlorate* forms hopper-shaped aggregates of cubic crystals, and is less soluble in alcohol than the other three perchlorates. T. A. H.

**Some Reactions and Compounds of Tin Tetrafluoride.** LUDWIG WOLTER (*Chem. Zeit.*, 1912, 36, 165).—Pure tin tetrafluoride is a snow-white, very hygroscopic, crystalline compound. Gaseous ammonia combines with it at 43°, forming a white compound,  $\text{SnF}_4 \cdot \text{NH}_3$ , which loses very little ammonia even at 400°. When tin tetrafluoride and ammonia are heated together in a sealed tube at 120–130°, strongly refracting crystals of a second compound,  $\text{SnF}_4 \cdot 2\text{NH}_3$ , are obtained. Both compounds dissolve in water, the solutions gradually becoming turbid.

The *pyridine* compound, obtained by heating the components in a reflux apparatus, forms white crystals of the composition



Quinoline and aniline yield white additive compounds. Liquid hydrogen sulphide decomposes tin tetrafluoride in a sealed tube, according to the equation:  $\text{SnF}_4 + 2\text{H}_2\text{S} = \text{SnS}_2 + 4\text{HF}$ . Chlorine compounds of phosphorus bring about an exchange of chlorine and fluorine. Metals react violently, liberating tin, and the formation of a difluoride is not observed. C. H. D.

**Arsenic-Antimony Alloys.** NICOLA PARRAVANO and PIETRO DE CESARIS (*Intern. Zeitsch. Metallographie*, 1912, 2, 70–75).—Only alloys containing from 0 to 40% of arsenic can be prepared under the ordinary pressure. Within this range, a continuous series of solid solutions is formed, the freezing-point curve having a minimum at 612° and 17.5% of arsenic. The alloys are microscopically homogeneous. The compound  $\text{Sb}_2\text{As}$  (Descamps, *Abstr.*, 1878, 705) does not exist. C. H. D.

**Hydrosols of Columbic and Tantalac Acids and the Separation of Columbium and Tantalum according to the Method of Weiss and Landecker.** OTTO HAUSER and A. LEWITE (*Zeitsch. angew. Chem.*, 1912, 25, 100–103).—The hydrosols of columbic and tantalac acids are readily prepared by fusing columbium or tantalum pentoxides with alkali, dissolving the fused mass in water, and dialysing the solution, whereby a neutral liquid can be obtained. The hydrosols are comparatively stable, remaining unchanged for weeks when preserved in stoppered flasks; by concentration over sulphuric acid, solutions were obtained which contained 1.346 grams of tantalum pentoxide and 2.571 grams of columbium pentoxide per litre. The disperse phase is negatively charged, and the various precipitation reactions are described. It is specially noteworthy that they are very sensitive to sulphate, chloride, sulphite, or nitrate ions, and that the hydrosol of tantalac acid is readily precipitated by a current of carbon dioxide, whereas that of columbic acid remains stable, at all events for twenty-four hours.

The sensitiveness towards the nitrate ion explains why Foote and Langley (*Abstr.*, 1911, ii, 72) were not able to obtain good results in

the separation of columbium and tantalum by the method of Weiss and Landecker (Abstr., 1909, ii, 942), since according to this method potassium nitrate is added to the sodium carbonate used in the fusion. The authors find that satisfactory results are obtained when sodium carbonate alone is used. T. S. P.

**Coagulation of Gold Hydrosols.** ANT. GALECKI (*Zeitsch. anorg. Chem.*, 1912, 74, 174—206).—The coagulation of gold hydrosols on addition of small quantities of electrolytes has been examined by means of the ultra-microscope and by measurements of the movements of the particles in an electric field. From these, the conclusion is drawn that there is no essential connexion between the colour of the colloidal solutions and the size of the disperse particles. On the other hand, the curves which are obtained when the calculated electric charges carried by the particles are plotted against the concentration of the electrolytes, show that the electrostatic effects accompanying the coagulation process vary in a marked manner with the nature of the electrolyte. H. M. D.

**Platinum, Rhodium, and Hydrogen.** ADOLF SIEVERTS and E. JURISCH (*Ber.*, 1912, 45, 221—229).—Using the method described previously (Abstr., 1911, ii, 990), the authors have determined the solubility in platinum wire of hydrogen at atmospheric pressure and at temperatures up to 1340°. The solubility increases with rise in temperature; platinum which has been saturated with hydrogen at a high temperature retains practically none of the gas when cold. At room temperatures, massive platinum dissolves no measurable quantity of hydrogen.

The absorptive power of platinum for hydrogen is much less than that of an equal weight of iron or nickel, and is considerably less than that of copper; at 409°, 100 grams of platinum wire dissolve 0.006, and at 1342°, 0.084 mg. of hydrogen at atmospheric pressure.

At constant temperature and under varying pressure, the quantity of hydrogen absorbed by platinum wire is proportional to the square-root of the pressure.

Carbon monoxide and sulphur dioxide are insoluble in platinum.

Precipitated rhodium, when heated in a vacuum, gives off a considerable volume of gas, consisting of a mixture of carbon dioxide, oxygen, hydrogen, and water vapour. Four grams of the metal which had been heated to a red heat did not dissolve a measurable quantity of hydrogen or carbon dioxide between 420° and 1020°. T. S. P.

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### Mineralogical Chemistry.

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A Suggestion for Mineral Nomenclature. HENRY S. WASHINGTON (*Amer. J. Sci.*, 1912, [iv], 33, 137—151).—A suggestion for a system of names (to supplement the present nomenclature  
18—2

retained for ordinary use) which would indicate, not only chemical and crystallographic characters, but also indicate mineral relationships. The nature of this suggestion may be best indicated by selecting a few examples.

*Pyrite Group* (pyrides,  $R(S, As, Sb)_2$ ; cubic, pyritohedral):

Pyrite .....	$FeS_2$ .....	Iron sulphyride.
Hauerite .....	$MnS_2$ .....	Manganese sulphyride.
Smaltite .....	$CoAs_2$ .....	Cobalt arsenpyride.
Cobaltite .....	$Co(S, As)_2$ .....	Cobalt sularsenpyride.

*Marcasite Group* (marcasides,  $R(S, As)_2$ ; orthorhombic):

Marcasite .....	$FeS_2$ .....	Iron sulmarcaside.
Rammelsbergite .....	$NiAs_2$ .....	Nickel arsenmarcaside.

*Spinel Group* (spinelates,  $R''R'''_2O_4$ ; cubic):

Spinel .....	$MgAl_2O_4$ .....	Magnesium aluminospinelate.
Magnetite .....	$FeFe_2O_4$ .....	Ferrous ferrispinelate.
Chromite .....	$FeCr_2O_4$ .....	Ferrous chromispinelate.

*Datolite Group* (datolates,  $R''_3R'''_2Si_2O_{10}$ ; monoclinic):

Datolite .....	$H_2Ca_2B_2Si_2O_{10}$ ..	Acid calcium bori-datolite.
Euclase .....	$H_2Gl_2Al_2Si_2O_{10}$ ..	Acid glucinum alumi-datolite.
Gadolinite .....	$FeGl_2Y_2Si_2O_{10}$ ..	Ferro-glucinum yttri-datolite.

*Apatite Group* (apatates,  $R''_5(F, Cl)([P, As, V]O_4)_3$ ; hexagonal):

Apatite .....	$Ca_5(F, Cl)(PO_4)_3$ ..	Calcium phosphapatate.
Minnetite .....	$Pb_5Cl(AsO_4)_3$ .....	Lead arsenapatate.
Vanadinite .....	$Pb_5Cl(VO_4)_3$ .....	Lead vanadapatate.

L. J. S.

**Paraffins from a Yorkshire Coal Seam.** JULIUS B. COHEN and CORNELIUS P. FINN (*J. Soc. Chem. Ind.*, 1912, 31, 12—14).—Analyses of a dark brown, semi-solid material obtained from the Haigh Moor seam of the Hemsworth Collieries showed that the substance consisted of a mixture of liquid and solid paraffins. The liquid fractions obtained on distillation under low pressure contained probably members of the series from  $C_{10}H_{22}$  to  $C_{16}H_{34}$ ; from the solid fractions the following paraffins were isolated:  $C_{20}H_{42}$ ,  $C_{22}H_{46}$ ,  $C_{23}H_{48}$ ,  $C_{24}H_{50}$ ,  $C_{25}H_{52}$ ,  $C_{26}H_{54}$ , and  $C_{32}H_{66}$ .  
W. P. S.

[Goldfeldite and Famatinite from Goldfield, Nevada.] FREDERICK LESLIE RANSOME (*Zeitsch. Kryst. Min.*, 1912, 50, 188—189; from *Prof. Paper, U.S. Geol. Surv.*, 1909, No. 66, 1—258).—In a monograph on the geology and ore-deposits of this district, the following mineral analyses are given. The name *goldfeldite* is proposed for a massive, lead-grey mineral with bright metallic lustre and conchoidal fracture;  $H = 3-3\frac{1}{2}$ . Analysis I, by Palmer, corresponds with the formula  $5Cu_2S, (Sb, Bi, As)_2(S, Te)_3$ :

	S.	Te.	Sb.	As.	Bi.	Cu.	Fe.	Au.	Ag.	Insol.	Total.
I.	21.54	17.00	19.26	0.68	6.91	33.49	—	0.51	0.18	2.00	101.57
II.	30.5	—	11.3	10.2	—	44.8	3.2	—	—	—	100.0

A massive, reddish-grey mineral is shown by analysis II, by Schaller, to be in composition midway between enargite and famatinite. An

analysis is also given of crystallised bismite (Schaller and Ransome Abstr., 1910, ii, 220).  
L. J. S.

**Lorandite from Wyoming.** AUSTIN F. ROGERS (*Amer. J. Sci.*, 1912, [iv], 33, 105—106).—This thallium mineral,  $\text{TlAsS}_2$ , previously known only from Allchar, in Macedonia, is recorded from the Rambler mine, near Encampment, in southern Wyoming. A single, small, deep red crystal was found with realgar and orpiment on a matrix of iron-pyrites and barytes. The identity of the mineral is proved by crystallographic measurements and by chemical and spectroscopic tests.  
L. J. S.

**The Chemical Constitution of Titaniferous Iron Ores.** WILHELM MANCHOT and B. HEFFNER (*Zeitsch. anorg. Chem.*, 1912, 74, 79—85).—It has not been decided whether titaniferous iron ores have the constitution  $\text{FeO} \cdot \text{TiO}_2$  or  $\text{Fe}_2\text{O}_3 \cdot \text{Ti}_2\text{O}_3$ , on account of the difficulty of determining the state of oxidation of the titanium. Two specimens have now been examined: (I) a coarse, titaniferous ore from Ekersund, and (II) a large crystal of ilmenite from Ural. The titanium is estimated by fusion with potassium hydrogen sulphate, reduction of the iron with sulphurous acid, and precipitation of titanous acid by boiling. The total iron is estimated in a solution reduced by sulphurous acid, and the ferric iron iodometrically in a solution prepared by means of hydrochloric acid in absence of air:

	Ti.	Total Fe.	Fe'''.	Mg.	Ca.	S.
I. ....	16.12	44.50	22.76	0.66	0.25	0.28
II. ....	29.81	34.71	9.38	—	—	0.08

The ratio  $\text{Ti}:\text{Fe}'':\text{Fe}'''$  is, for I, 1:1.1147:1.215, and for II, 1:0.7312:0.2706. The ferric iron in II is probably due to secondary oxidation, and the ratio  $\text{TiO}_2:\text{FeO}$  thus approaches 1:1 in both cases.

It has been shown by Manchot and Richter (Abstr., 1906, ii, 172) that compounds containing tervalent titanium evolve hydrogen with alkalis. Hydrogen is not, however, evolved by the action of alkalis on ilmenite. The reaction of ilmenite with sulphuric acid is also quite similar to that of a mixture of titanous acid and a ferrous salt. The conclusion is drawn that titaniferous iron ores contain only titanium dioxide, and not titanous compounds.  
C. H. D.

**Chemico-mineralogical Section of the Older Salt Beds in the Berlepsch Mine at Stassfurt.** OTTO RIEDEL (*Zeitsch. Kryst. Min.*, 1912, 50, 139—173).—Samples of the salts were taken at intervals of a few metres ranging from the top to the bottom of the deposit (a total thickness of 184 metres), and representative of the various well-known zones. The materials, being mixtures of various minerals, are regarded as rocks, and as such are subjected to a combined mechanical and chemical analysis, with the object of determining the relative proportions of the several minerals present. In the mechanical analysis the powdered materials were fractionated according to density by a heavy liquid (tetrabromoethane and toluene).

The separated grains were identified by means of their optical characters and by micro-chemical tests, and, after drying at 44–45°, the different fractions were analysed. The chemical and mineralogical results obtained with thirty-six samples are tabulated, and curves are drawn. The mineral species identified include halite, anhydrite, polyhalite, kieserite, carnallite, loewite, vanthoffite, langbeinite, and sylvite.

An analysis of vanthoffite ( $3\text{Na}_2\text{SO}_4, \text{MgSO}_4$ ) gave the following results; the calcium is due to a little intermixed polyhalite, and some loewite is also perhaps present:

$\text{SO}_4$ .	Na.	Mg.	Ca.	K.	Total.
70·81	24·46	4·83	0·09	0·10	100·29

The conditions of formation of the deposits are discussed, and the conclusion is drawn that the temperature was not less than 72°. The order of crystallisation of the various minerals was much influenced by the supersaturation of the solution.

L. J. S.

**Pickeringite from Thuringia.** H. HESS VON WICHENDORFF (*Centr. Min.*, 1912, 42–43).—White or yellowish-white balls of pickeringite, consisting of fine silky fibres, occur in crevices in the slates quarried near Lehesten in the duchy of Saxe-Meiningen, D 2·2, anal. I and II. Similar material has also recently been observed in the alum-shales of the Wetzelsstein near Saalfeld; anal. III by Eyme. These analyses agree closely with the usual formula  $\text{MgSO}_4, \text{Al}_2(\text{SO}_4)_3, 22\text{H}_2\text{O}$ :

	$\text{SO}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	MnO.	MgO.	$\text{H}_2\text{O}$ .	Total.
I. ....	37·76	12·14	—	trace	4·55	45·45	99·90
II. ....	38·09	12·22	—	trace	4·62	45·44	100·37
III. ....	37·31	11·22	1·66	—	5·04	44·88	100·11

The mineral has been produced by the action of sulphuric acid, formed by the decomposition of iron-pyrites, on the shale. L. J. S.

**The Melting Point of Spodumene.** KURD ENDELL and REINHOLD RIEKE (*Zeitsch. anorg. Chem.*, 1912, 74, 33–47).—Lithium silicates have in general a high velocity of crystallisation. The data referring to the melting point of spodumene,  $\text{Li}_2\text{O}, \text{Al}_2\text{O}_3, 4\text{SiO}_2$ , are very divergent. The only temperature which can be regarded as the true melting point is that at which the mineral passes from the anisotropic to the isotropic-amorphous condition, the liquefaction of the amorphous substance, and diminution of its viscosity, being a gradual process. The mineral has been examined by heating to various definite temperatures, cooling rapidly, and determining certain of the physical properties.

The specific gravity is unaltered by heating to 920°, but is diminished from 3·147 to 2·370 at 980°. Double refraction disappears after heating the powder to 980°, or with very fine powder at 950°. Sections of the mineral remain almost unchanged even after heating to 1000°. The mean refractive index of crystalline spodumene is 1·66, and that of the glass 1·519, the discontinuity occurring at 920–980°. The heating curve shows a marked discontinuity at 950°.

Spodumene glass has, at the melting point, a viscosity almost

equal to that of the crystals, and it is only at 1250—1300° that the viscosity diminishes so far as to show softening of the glass. The melting point is therefore 950°, and natural spodumene, which is always monoclinic, must have been formed below 950°. C. H. D.

[Bentonite from Laramie, Wyoming.] NELSON HORATIO DARTON and C. E. SIEBENTHAL (*Zeitsch. Kryst. Min.*, 1912, 50, 187—188; from *Bull. U.S. Geol. Surv.*, 1909, No. 364, 1—81).—In an account of the geology and mineral resources of the Laramie basin, the following analyses are given of a kind of clay called bentonite. This is pale yellow to pale olive-green, with a waxy lustre and a conchoidal fracture; it becomes dull on exposure to air. It forms beds with sometimes a thickness of 5 feet.

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MgO.	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
59·78	15·10	2·40	4·14	0·73	—	—	16·26	98·51
58·25	24·70	2·61	1·30	1·61	—	—	11·00	94·47
66·5	23·9	3·1	1·0	0·5	—	—	5·0	100·0
64·0	24·0	3·2	1·5	0·6	—	—	6·7	100·0
60·18	26·11		2·54	—	0·80		10·26	99·63
60·18	26·58		1·01	0·23	1·23	—	10·26	99·49

L. J. S.

**Allophanoids.** STANISLAUS J. THUGUTT (*Centr. Min.*, 1912, 35—41; from *Spraw. Tow. Nauk. Warszawa*, 1911, 4, 222—228. Compare Abstr., 1911, ii, 210).—A reply to Stremme (Abstr., 1911, ii, 406). It is maintained that the allophanoids (that is, clays of the allophane, halloysite, and montmorillonite groups) represent definite compounds, and are not merely mechanical mixtures of colloidal hydrated alumina and silica. Analyses are given of pseudomorphs after augite from Bilin, Bohemia, consisting of mixtures of cimolite and anauxite.

L. J. S.

**Lavas of the Active Volcano at Reunion.** ALFRED LACROIX (*Compt. rend.*, 1912, 154, 251—257).—A number of analyses were carried out to ascertain whether the predominance of vitreous lavas at the summit of a volcano and the greater abundance of crystalline ones near the base is associated with differences in the chemical composition of the two varieties. I. Mean of analyses of three normal ancient lavas and five modern ones, three being crystalline and the others vitreous. II. An abnormal modern lava very rich in peridot.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	TiO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O.	Total.
I.	48·22	14·74	2·24	9·38	7·01	12·26	2·23	0·89	2·72	0·36	0·06	100·11
II.	43·82	10·10	2·98	10·44	20·89	7·66	1·44	0·62	2·07	0·21	0·02	100·25

The results show that the crystalline condition of the lava is independent of the chemical composition.

The abnormal lava resembles more closely certain Tahiti rocks than any hitherto described. It appears to be a felspathic picrite rather than a basalt, and is distinguished by the abundance of very large, macled crystals of olivine, containing grains of magnetite. The mineralogical characteristics of highly crystalline stalactites and

stalagmites of lava are described. Chemically they do not differ from the normal rock, but probably owing to more rapid cooling, are lacking in crystals of olivine. W. O. W.

**Composition of the Mineral Water of Bad Dürkheim**  
G. RUPP (*Zeitsch. Nahr. Genussm.*, 1912, 23, 56—59).—An analysis is recorded showing the quantities of mineral constituents in this water. The results obtained agree with those found by analyses in the year 1860 as regards the chief constituents, but the earlier analyses make no mention of the appreciable quantities of arsenic present in the water; as the general composition of the water has not changed, arsenic has probably been present in the water for some time. The amount of arsenic found in the present analysis was 0·01735 gram of arsenic trioxide per kilo. of the water (compare Abstr., 1907, ii, 485). W. P. S.

**New Analyses of Water from the Dead Sea.** A. FRIEDMANN (*Chem. Zeit.*, 1912, 36, 147. Compare Stutzer and Reich, Abstr., 1907, ii, 791).—The samples were taken by the author, (I) at a depth of half-a-metre, and (II) at a depth of 3 metres, near the north-west end of the Dead Sea, the temperature of the water being 27°, and that of the air 34°. In a 30 cm.-high measuring cylinder both samples of water were clear and transparent, with a tinge of blue colour; they possessed a bitter, saline taste, were alkaline to litmus, and lead acetate paper was blackened when held near the mouth of the cylinder. Analysis gave (percentage by weight):

		Total solids after drying at 140°.	NaCl.	KCl.	CaCl <sub>2</sub> .	MgCl <sub>2</sub> .	NaBr.	CaSO <sub>4</sub> .	CaCO <sub>3</sub> , iron, org. matter.
D <sup>15</sup> .									
I.	1·1241	23·8500	7·8550	1·5208	3·6800	10·0299	0·5200	0·1460	trace
II.	1·1336	24·1309	7·9325	1·4318	3·6903	10·3125	0·5212	0·1412	trace

T. S. P.

### Physiological Chemistry.

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**Action of Iron on the Mobile Oxygen of Blood.** GIUSEPPE ROCCHI (*Chem. Zentr.*, 1911, ii, 1870; from *Arch. Farm. speriment.*, 1911, 12, 317—324).—That portion of the oxygen in blood which is combined with hæmoglobin, and may be estimated by reducing agents, is termed mobile oxygen by the author. Results of experiments on dogs showed that the injection of iron (6 to 12 mg. per kilo. of body-weight) resulted in a diminution of the mobile oxygen during the first thirty minutes, followed by an increase in the next two hours. Experiments *in vitro* also proved that the addition of ferrous sulphate to blood increased the quantity of mobile oxygen. Probably the activity of the oxydases is increased.

W. P. S.

**Iron in Blood.** HERMANN W. FISCHER and E. BRIEGER (*Zeitsch. physikal. Chem.*, 1912, 78, 582—628. Compare Abstr., 1910, ii, 856).—The paper does not deal directly with iron in blood, but with certain colloidal systems containing iron salts and “protective” substances which favour the retention of iron compounds in the colloidal condition. It is shown that in many respects these solutions behave like solutions of hæmoglobin. Their behaviour towards hydrogen peroxide (which may be regarded as oxygen under high pressure) has been investigated in detail. The rate of decomposition of the peroxide was followed by measuring the oxygen evolved, and in most of the experiments the solutions were not shaken. The results are only qualitative.

The decomposition of hydrogen peroxide in acid and alkaline “protected” solutions was investigated. As protective agents, glycerol and other hydroxyl compounds were used. In acid solution, the protective substance is oxidised and the iron reduced; in slightly alkaline solution, on the other hand, the protective substance is not attacked, but the iron is oxidised to ferrate. The iron compounds obtained in acid solution are unstable, and have characteristic colours. One of these compounds, which is deep violet in colour, appears to be intermediate in composition between ferrous and ferric salts; in other words, it corresponds with magnetic oxide of iron. A number of experiments with different protective agents are described.

The ferrate solutions, obtained by oxidation in weak alkaline solution, are so similar in behaviour to hæmoglobin with regard to colour, power of absorbing oxygen, etc., that it is assumed that the mechanism of oxygen absorption is similar in the two cases. On this basis it is suggested that the capacity of hæmoglobin to take up oxygen, forming a peroxide, depends on its being nearly neutral. When the blood reaches a part of the body where carbon dioxide is being given off, it becomes more acid; the peroxide is then unstable, and decomposes, giving up oxygen. This theory is also applied to the action of muscles.

G. S.

**The Glucose of Blood-serum.** LEONIDAS DOXIADES (*Biochem. Zeitsch.*, 1912, 38, 306—309).—When 20—30% dextrose solutions are treated with blood-serum, there is an increase in the optical rotation, and a diminution of the reducing power for Allihn's copper solution. These facts, together with certain results obtained by the isolation of the osazones, lead the author to believe that maltose is produced, and that the blood-serum contains a synthesising enzyme. S. B. S.

**A Simple Coagulometer.** HENRY H. DALE and PATRICK P. LAIDLAW (*J. Path. Bact.*, 1912, 16, 351—362).—The coagulation time can be accurately determined in a drop of human blood drawn from a finger prick. It is collected in a capillary tube containing a shot; the end point is the moment when the shot no longer moves when the tube is held vertically. In comparative observations, the bore of the tube, the size of the shot, and the temperature must be constant. The time so determined in normal individuals only varies by a few seconds. Administration of calcium salts, or of adrenaline, and a milk diet made no appreciable difference. W. D. H.

**Gastric Acidity.** JUSTIN WINTER (*Compt. rend.*, 1912, 154, 71—73. Compare Abstr., 1910, ii, 786).—The author quotes the results of experiments carried out on a dog. After special test meals the stomach contents were removed by a sound, and their acidity and hydrochloric acid content determined. The conclusions drawn are that hydrochloric acid is produced in three successive stages, the first of which involves formation of neutral organic hydrochlorides, the second corresponding with the acidification of these substances, and the third to their dissociation, with production of free hydrochloric acid. The last stage does not occur when the animal is fed on water or sugar solution alone, but requires a stronger stimulus, such as that supplied by meat or other nitrogenous material, or by the irritation caused by experimental gastric fistulæ. The effect of the latter has not hitherto been taken sufficiently into account in such observations.  
W. O. W.

**The Hourly Chemical and Energy Transformations in the Dog after an Abundant Meat Diet.** H. B. WILLIAMS, J. A. RICHE, and GRAHAM LUSK (*Proc. Amer. physiol. Soc.*, 1911, xxxiii—xxxiv; *Amer. J. Physiol.*, 29).—A calorimeter of great accuracy (Atwater-Rosa type) was used. A dog was fed on 700 grams of meat at noon, and next day its metabolism measured between 10 and 11 a.m. At mid-day it received 1200 grams of meat, and it was returned to the calorimeter. Heat production and other factors were then determined hourly for twenty hours. Direct and indirect calorimetry agreed perfectly. Heat production rose largely, and this was proportional to the nitrogen eliminated in the urine, and not to the quantity of material in the intestine. The carbon which was retained from the protein must have been retained as glycogen, for if it had been retained as fat, oxygen absorption would have been 10% less than it was. Glutamic acid added to a standard diet did not increase heat production.  
W. D. H.

**Creatine and Creatinine Metabolism.** CHARLES G. L. WOLF (*J. Biol. Chem.*, 1912, 10, 473—478).—A discussion of previous results from which the conclusion is drawn that a disturbance of carbohydrate metabolism (emphasised by Mendel and Rose), or a disturbance of liver functions (as in dogs with Eck's fistula), will not alone explain the excretion of creatine. The other processes which contribute to this end will be considered later.  
W. D. H.

**Creatine and Creatinine Metabolism in Dogs During Feeding and Inanition, with Special Reference to the Function of the Liver.** C. TOWLES and CARL VOEGTLIN (*J. Biol. Chem.*, 1912, 10, 479—497).—The view is taken that the liver does not play the important rôle in creatine metabolism which is ascribed to it. Sometimes creatine appears in the urine after the administration of creatinine; occasionally it is the other way round; possibly the reaction is a reversible one. On a fixed diet, creatinine excretion is kept constant by an adjustment between its production in katabolism and its destruction by enzymes. The portion excreted by the kidney is the part which is not destroyed.  
W. D. H.

**Katabolism of Histidine.** HENRY D. DAKIN and ALFRED J. WAKEMAN (*J. Biol. Chem.*, 1912, 10, 499—502).—It has been shown previously that acetoacetic acid can arise from aromatic amino-acids, such as tyrosine. It is derived from four adjacent carbon atoms, two in the side-chain and two in the cyclic nucleus. The histidine molecule shows four carbon atoms similarly placed, and that it also may form acetoacetic acid is confirmed by experiments on the perfusion of dogs' livers; the perfusion fluid consisted of blood to which histidine carbonate was added; after fifty minutes there was a slight increase in the acetoacetic acid of the issuing fluid. The histidine molecule is probably first resolved into ammonium carbonate (which may then form urea) and acetoacetic acid (which may then undergo further oxidation, reduction, or hydrolysis) and a urea group derived from the nitrogen atoms of the ring. This would accord with the experiments of Abderhalden and Einbeck, and of Kowalewsky, who found that when histidine is given to dogs, urea was apparently the only katabolic product excreted.  
W. D. H.

**Protein Metabolism from the Standpoint of Blood and Tissue Analysis.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1912, 11, 87—95).—Many observers consider that the fate of amino-acids after absorption is mysterious, because so little is discoverable in the blood. As a matter of fact, the non-protein nitrogen of the blood does rise and fall in reference to absorption, but the amino-acids pass rapidly to the tissues, and for a time accumulate there. Their deamidation in the liver does not occur so rapidly as some observers have considered. In the present preliminary paper, experiments are described which give analyses of the blood and certain tissues, especially muscle, after the absorption of urea, glycine, the abiuretic products of pancreatic digestion and egg-albumin from the intestine. There is also a comparison of the blood (portal and systemic) in fasting and fed cats. The increase of non-protein nitrogen is quite manifest after absorption. The new note struck is that the tissues act as a storehouse or reservoir for a time, and this will have to be reckoned as an important factor in theories of protein metabolism. The full publication of methods, etc., is deferred.  
W. D. H.

**Rôle of Proteins in Growth.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL (*Proc. Amer. physiol. Soc.*, 1911, xii; *Amer. J. Physiol.*, 29. Full details in *Publication 156, Part II, Carnegie Inst. of Washington*, 1911).—Some proteins are adequate for maintenance and growth; others are not. Maintenance and growth, moreover, must be distinguished. The experiments were made on rats, and single proteins were added to their diet (protein-free milk). In promoting growth, casein, lactalbumin, egg-albumin, edestin, glycinin, and glutenin are adequate; zein, gliadin, and hordein are inadequate. Gliadin and hordein are adequate for maintenance, zein is not. The inadequate proteins are all deficient in two or more of the usual amino-acid complexes.  
W. D. H.

**Studies in Nutrition. IV. The Utilisation of the Proteins of the Legumes.** LAFAYETTE B. MENDEL and MORRIS S. FINE (*J. Biol. Chem.*, 1912, 10, 433—458. Compare *Abstr.*, 1911, ii, 1109; this vol., ii, 63).—In comparison with the other vegetable proteins

investigated, the legume proteins are less well utilised. This is explained in part in the case of soy bean flour, and a preparation from white beans by the presence of cellulose and hemicellulose; but this explanation cannot apply to phaseolin (a protein isolated from the white bean) or to globulin separated from the pea. W. D. H.

**Studies in Nutrition. V. The Utilisation of the Proteins of Cotton Seed.** LAFAYETTE B. MENDEL and MORRIS S. FINE (*J. Biol. Chem.*, 1912, 11, 1—3).—Fraps states that 88% of the proteins of cotton seed are utilised by steers and sheep. A lower figure (67—75%) was obtained in the present experiments on dogs.

W. D. H.

**Studies in Nutrition. VI. The Utilisation of the Proteins of Extractive-free Meat Powder; the Origin of Faecal Nitrogen.** LAFAYETTE B. MENDEL and MORRIS S. FINE (*J. Biol. Chem.*, 1912, 11, 5—26).—The meat residue employed was supplied by Armour & Co., and was a light brown powder. The utilisation of its nitrogen by dogs was distinctly lower than that of fresh meat. The faeces were relatively rich in nitrogen, which indicates a loss through the excrements.

On ordinary meat diet, protein utilisation is at least 95%, and the resulting faeces are for the most part of metabolic origin. Very little nitrogen comes from the intestinal juices, for these are mainly re-absorbed. This, however, will depend on the rate of peristalsis, and that in time is influenced by the mass and character of the intestinal contents. Hence if indigestible material is added to meat, peristalsis is accelerated, and more metabolic products will escape absorption. If the material added is non-nitrogenous, the nitrogen % of the faeces will be lower; but if the comparatively indigestible material is nitrogenous, the nitrogen concentration will be higher. If both types are present, the amount of nitrogen may be indistinguishable from that found in meat faeces.

W. D. H.

**The Formation of Organic Phosphorus Compounds from Inorganic Phosphates in the Animal Body.** GUSTAV FINGERLING (*Biochem. Zeitsch.*, 1912, 38, 448—467).—The animals experimented on were ducks, which were fed during one season on foodstuffs nearly free from organic phosphorus compounds with addition of organic phosphates, and in another season on foodstuffs rich in organic phosphorus compounds. The weights of the egg laid and their content in lecithin-phosphorus and nucleic acid-phosphorus were estimated. From the results little difference was observed in both the quantity and composition of the eggs laid under different conditions, from which the conclusion was drawn that the organism can synthesise organic phosphorus compounds from inorganic phosphates.

S. B. S.

**Absorption of Fat by the Stomach in the Salmon.** CHARLES W. GREENE (*Proc. Amer. physiol. Soc.*, 1911, xxxvi—xxxvii; *Amer. J. Physiol.*, 29).—Young salmon were fed with olive oil per rectum.

Subsequent microscopic examination after suitable fixation and staining showed that fat globules were present in the surface epithelium of both the cardiac and pyloric regions of the stomach.

W. D. H.

**Absorption of Fat by the Mammalian Stomach.** CHARLES W. GREENE and WILLIAM F. SKAER (*Proc. Amer. physiol. Soc.*, xxxvii—xxxviii; *Amer. J. Physiol.*, 29).—In dog, cat, and rat, the evidence that fat absorption occurs in both regions of the stomach is similar to that adduced in the case of the salmon (see preceding abstract).

W. D. H.

**Data from Two Fasts Each Exceeding One Hundred Days in Length in the Same Dog.** PAUL E. HOWE and PHILIP B. HAWK (*Proc. Amer. physiol. Soc.*, 1911, xiv; *Amer. J. Physiol.*, 29).—The initial fast gave the animal a sort of resistance which enabled it to resist more successfully the demands made on it by the second. The loss of weight and the rapidity of the loss were much less in the second period of inanition.

W. D. H.

**How do Isotonic Sodium Chloride Solution and other Parthenogenic Agents Increase Oxidation in the Sea Urchin's Egg?** J. F. McCLENDON and PHILIP H. MITCHELL (*J. Biol. Chem.*, 1912, 10, 459—472).—The main conclusion reached is that hydroxyl ions in the medium increase the rate of oxidation in the egg-cells.

W. D. H.

**The Differences in the Composition of the Brain Substance in Normal and Starving Animals.** RAFFAELE PALADINO (*Biochem. Zeitsch.*, 1912, 38, 443—447).—In experiments carried out on dogs, it was found that the water content in the brain of fasting animals was higher than that of normal animals. Parallel with the increase of water there is a diminution of ether-soluble substances. No differences could be detected in the quantities of the other brain constituents (cholesterol, proteins, lecithin).

S. B. S.

**The Liver and Regeneration of Fibrinogen.** WALTER J. MEEK (*Proc. Amer. physiol. Soc.*, 1911, xix—xx; *Amer. J. Physiol.*, 29).—Fibrinogen was estimated as fibrin. Dogs were bled, the blood whipped, and then re-injected; fibrinogen is regenerated rapidly, and 100% increase was noted in three hours. After an Eck fistula and ligature of the portal vein, this occurred more slowly; but if the other blood supply, the hepatic artery, was also tied, regeneration did not occur, and the fibrinogen left in the blood rapidly disappeared. Whether the liver itself forms fibrinogen, or by means of a hormone influences the formation of this substance elsewhere, is uncertain.

W. D. H.

**The Effect of Eck's Fistula on Bile Formation.** SAMUEL A. MATTHEWS (*Proc. Amer. physiol. Soc.*, 1911, xxvii—xxviii; *Amer. J. Physiol.*, 29).—Dogs become jaundiced after ligature of the bile ducts, and generally die within a fortnight. If, however, a biliary

fistula is also made, no jaundice develops, although the animals suffer from digestive troubles. If, further, an Eck's fistula is established, bile flows from the biliary fistula for five or six days and then ceases, and no jaundice comes on. If the ducts are ligatured, and then after the onset of jaundice an Eck's fistula is established, the jaundice clears off and the dogs become fairly healthy in a few days. It therefore appears that the portal blood contains the substance out of which the liver makes bile, or which stimulates it so to do.

W. D. H.

**The Place of Retention or Reconjugation of the Amino-acids in the Body.** ALBERT WOELFEL (*Proc. Amer. physiol. Soc.*, 1911, xxxviii—xxxix; *Amer. J. Physiol.*, 29).—If the mediation of the liver or of the intestinal mucosa is necessary for the regeneration of protein out of its cleavage products, then after shunting these organs out of the circulation, introduction of amino-acids should lead to increase of amino-acid or of ammonia in blood and urine.

Dogs were used with Eck's fistula, and the hepatic artery tied; solutions of amino-acids were then introduced into the washed-out intestines; two hours later the animals were killed, and the blood and urine collected. Small increases of amino-acid nitrogen were found in both fluids, which were far from commensurate with the amounts absorbed. The same results were obtained from dogs with coeliac axis and mesenteric arteries tied, the amino-acids being introduced intravenously. In other words the tissues in general manifest an avidity for amino-acids, and presumably use them for the regeneration of their protein constituents.

W. D. H.

**Chemistry of the Dog's Spleen.** HARRY J. CORPER (*J. Biol. Chem.*, 1912, 11, 27—35).—Estimations of water, nitrogen, ether-soluble material, phosphorus, etc., are given in averages from the examination of three normal dogs' spleens. The purines obtained per kilo. of spleen were:

	In fresh spleen. Gram.	After autolysis in absence of air.	After autolysis in presence of air.
Guanine .....	1.09	—	—
Adenine .....	0.62	—	—
Hypoxanthine .....	0.15	0.017	0.004
Xanthine .....	0.04	1.69	0.09
Uric acid .....	—	—	1.69

Oxydase, guanase, and adenase are present, but uricase was absent.

W. D. H.

**The Ash of Smooth Muscle.** LEON A. RYAN and EDWARD B. MEIGS (*Proc. Amer. physiol. Soc.*, 1911, xv; *Amer. J. Physiol.*, 29).—The smooth muscle of the pig's stomach contains less potassium and phosphorus, and somewhat more sodium and chlorine than the striated muscle of the same animal, but the differences are not great.

W. D. H.

**The Absorption of Fat in the Salmon's Muscles, and its Resorption During the Migration Fast.** CHARLES W. GREENE (*Proc. Amer. physiol. Soc.*, 1911, xxxix—xl; *Amer. J. Physiol.*, 29).—The salmon stores large quantities of fat in its tissues before it begins

to fast on entering fresh water. The storage is chiefly in the muscles, and the stored fat gradually diminishes until the animal dies after spawning, but it is never wholly consumed. The storage in the constantly active fin muscles is slight, and is chiefly inter-muscular. Fat is thrown into the fibres of the great lateral muscle, and kept there in strikingly uniform amount during the entire migration period. This is no doubt used by the muscle as a source of energy.

W. D. H.

**Studies on Chicken Fat. I. Occurrence and Permanence of Lipase in the Fat of the Common Fowl (*Gallus domesticus*).** MARY E. PENNINGTON and JOSEPH S. HEPBURN. II. **Oxidation of Chicken Fat by means of Hydrogen Peroxide.** JOSEPH S. HEPBURN (*J. Amer. Chem. Soc.*, 1912, 34, 210—222).—Experiments are described which show that lipase occurs in the fat of fowls, and is the cause of the fat becoming hydrolysed. Immediately after the bird has been killed, the fat exhibits little or no lipolytic activity, and it is therefore probable that during life the lipase exists in its zymogenic form. After death, however, the enzyme becomes active, and the acidity of the fat increases. The change occurs less rapidly below 0° than above that temperature. It has been found that the lipase still retains its activity after the fowls have been frozen for as long as eighty-nine months.

When fowls are kept in the frozen state, the saponification and Hehner numbers of the fat both increase, and this change must be due to oxidation. In view of Dakin's work (*Abstr.*, 1908, i, 119) on the oxidation of ammonium salts of fatty acids with hydrogen peroxide, experiments have been made on the action of this reagent on the fat of fowls. It was found that the acidity of the fat always increased, and that the saponification and Hehner numbers also increased simultaneously, the effect produced being thus the same as that which takes place in the fat when submitted to prolonged freezing. The increase of the saponification value is attributed to the formation of slightly lower homologues of the acids of the fresh fat, and that of the Hehner number to the formation of aldehydes and ketones. The corresponding changes in the fat on prolonged freezing are probably due to the action of enzymes.

E. G.

**The Origin and Destiny of Cholesterol in the Animal Organism. VIII. The Cholesterol Content of the Liver of Rabbits Under Various Diets and During Inanition.** GEORGE W. ELLIS and JOHN A. GARDNER (*Proc. Roy. Soc.*, 1912, B, 84, 461—470).—The total free and combined cholesterol per kilo. of body-weight is remarkably constant in rabbits fed entirely on bran which has been extracted with ether, and may be taken as representing the normal cholesterol content of the liver under conditions in which the body-weight is kept constant, but no cholesterol or phytosterol is absorbed with the food.

After a period of feeding on green food, a small increase is noticed, indicating that some phytosterol has been absorbed from the food and appeared in the liver in the form of cholesterol. A marked increase

in the total cholesterol of the liver is noticeable when cholesterol is administered either with the food or by injection into the peritoneal cavity, and also when the animals are kept in a state of inanition and are living on their own tissue.

These experiments afford further support for the hypothesis previously formulated (Abstr., 1909, ii, 498), that cholesterol is a constituent constantly present in all cells, and that when the cells are broken down in the life process, the cholesterol is not excreted as a waste product, but is utilised in the formation of new cells.

W. J. Y.

**The Course of the Daily Excretion of Chlorides in the Urine.** ADOLF HERRMANNSDORFER (*Pflüger's Archiv*, 1912, 144, 169—228).—The excretion of chlorine rises in the morning, but is independent of breakfast or the previous evening meal. Meals produce a rise about half an hour later, and this is followed by a fall accompanying the formation of the hydrochloric acid of gastric juice. An hour later the curve again rises, due to the alkali content of the food. Administration of solutions of sodium chloride has no influence on the excretion; the organic substances in the diet have also no effect. The alkali of the food is all excreted within twenty-four hours. Potassium ions produce a sinking of the urinary chlorides; this element is held fast by the body, especially if it is previously poor in chlorine. Chlorine and water excretion were parallel. Abnormally large intake of protein produces diuresis and increase of urinary chlorides.

W. D. H.

**The Influence of Magnesium Salts and Sodium Acetate on the Acidity of the Urine.** L. DE JAGER (*Biochem. Zeitsch.*, 1912, 38, 294—305).—It has been shown by the author that after ingestion of calcium salts a double decomposition takes place with the sodium phosphate, the calcium phosphate formed being stored up in the body. At the same time alkali is withdrawn from the body, and to restore equilibrium the urine becomes acid. A similar action follows the ingestion of magnesium salts. In this case the author assumes that double decomposition takes place between magnesium salt and calcium phosphate in the alimentary tract, as a consequence of which (in the case of magnesium sulphate) magnesium phosphate and calcium sulphate are formed, of which the former is more readily resorbed. The magnesium phosphate in the intestines exerts an acid action, as a consequence of which alkali is withdrawn and the urine becomes acid. In the case of ingestion of sodium sulphate, calcium sulphate and sodium phosphate will be formed. Of these, the latter is more readily absorbed, and on the first day of the experiment, the content of urine in ammonia, free acid, and total acidity showed marked diminution, whereas there was an increase of phosphoric acid. Similar results were previously obtained after ingestion of sodium phosphate. After ingestion of magnesium oxide, the first effect was that due to alkalis generally, after which the effect was that of a magnesium salt.

S. B. S.

**Elimination of Amino-nitrogen from the Depancreatised Dog.** HENRI LABBÉ and L. VIOLLE (*Compt. rend.*, 1912, 154, 73—75. Compare this vol., ii, 69).—As a result of about three hundred experiments on normal dogs fed on lean meat, the daily urinary excretion of nitrogen in the form of amino-acids was found to vary from 0.053 to 0.065 gram. In the case of a dog from which the pancreas had been almost completely removed, the daily elimination corresponded with four to seven times this amount. The ratio of amino-acid nitrogen and total nitrogen, moreover, was about four times greater with the depancreatised animal than in the normal dog. These results are of clinical interest in connexion with pancreatic disease. W. O. W.

**Metabolism in an Experimental Fever with Special Reference to Creatinine Elimination.** VICTOR C. MYERS and G. O. VOLOVIC (*Proc. Amer. physiol. Soc.*, 1911, xviii—xix; *Amer. J. Physiol.*, 29).—Fever was produced in rabbits by inoculation with the bacillus of hog-cholera. The excretion of creatine ran parallel to body-temperature; so also did total nitrogen and urea. Creatinine elimination increased by 30%, reaching its climax with the highest temperature. Creatinine excretion followed the crisis. The increased creatinine elimination is regarded as representing endogenous protein metabolism, which is abnormally intense, owing to the rise in temperature. The presence of creatine suggests the exhaustion of the normal glycogen store of energy, and perhaps measures the amount of abnormal endogenous protein metabolism. W. D. H.

**Cell Stimulation by Prolonged Ingestion of Alkaline Salts.** FREDERICK P. WILSON (*Bio-Chem. J.*, 1912, 6, 162—170).—In mice fed on food mixed with sodium hydrogen carbonate or alkaline sodium phosphate, marked wasting occurred; post mortem, the testis was found to be the only organ affected, the cells showing evidence of great stimulation. In female mice, there was no corresponding change in the ovaries. In rabbits, wasting also occurred, but there were no changes in the generative organs. W. D. H.

**Calcium Resorption and Calcification.** MASAHIKO TANAKA (*Biochem. Zeitsch.*, 1912, 38, 285—293).—In continuation of the former work (*Abstr.*, 1911, ii, 907) the author, from histological investigations of animals, after injection of calcium salts, finds that the calcifications are of the character of metastasis, that is to say, the calcium salts were either taken up by the blood and spread about, or the dissolved calcium salts were resorbed and a secondary decomposition then took place, either in the immediate neighbourhood of the injection area, or at greater distances from it. In the latter case, the striated muscular tissue showed a special disposition for the formation of calcium deposits. In the kidneys, the calcifications had the appearance of secretion deposits. The chemical nature of the salts had no effect on the character of the calcifications, and the inflammation and formation of the giant cells surrounding calcifications appeared to be ordinary inflammatory reactions. S. B. S.

**The Relation of Calcium to the Cardio-Inhibitory Function of the Vagus.** H. H. HAGAN and J. K. ORMOND (*Proc. Amer. physiol. Soc.*, 1911, xi; *Amer. J. Physiol.*, 29).—In frogs and turtles, the presence of calcium in the perfusion fluid is essential for the production of vagus inhibition of the heart. If the amount of calcium in the solution of sodium chloride is too small for the purpose, vagus action is restored by the addition of a small amount of potassium chloride.  
W. D. H.

**Pharmacological Action of Vanadium.** D. E. JACKSON (*Proc. Amer. physiol. Soc.*, 1911, xxiii—xxiv; *Amer. J. Physiol.*, 29).—Vanadium produces gastro-intestinal irritation, increased intestinal peristalsis, and a rise of blood-pressure, more lasting but less pronounced, than that caused by adrenaline. Constriction of the arterioles is present in kidney, intestine, and spleen, but not in the leg. This action is peripheral, not central.  
W. D. H.

**Physiology of Allyl Compounds.** E. WACE CARLIER (*Bio-Chem. J.*, 1912, 6, 182—199).—The effects of allyl compounds on respiration, blood pressure, and heart are illustrated by numerous graphic records. The toxic action is very great, and is due to the allyl in the compounds, but is increased in some cases, and lessened in others, by the substances with which it is combined.  
W. D. H.

**Carbamido-acid Formation.** WALTER WEILAND (*Biochem. Zeitsch.*, 1912, 38, 385—392).—When leucine and other amino-acids are treated with carbamide, they readily form carbamido-acids. If leucine is added to urine and the solution boiled, carbamido-leucine is formed. A certain amount of the carbamido-acid is also formed when the solution is evaporated at a temperature not exceeding 42—45°. The author suggests that certain amino-acids can be identified by the preparation of these derivatives, which are in some cases more readily prepared than the naphthalenesulphonyl compounds.

S. B. S.

**The Synthetic Formation of Amino-acids in the Liver. II.** GUSTAV EMBDEN and ERNST SCHMITZ (*Biochem. Zeitsch.*, 1912, 38, 393—406).—By perfusing the ammonium salts of  $\alpha$ -keto-acids through the liver, the corresponding  $\alpha$ -amino-acids are formed. By the perfusion of the ammonium salt of pyruvic acid, alanine was obtained, whilst the ammonium salt of phenylpyruvic acid yielded phenylalanine, that of *p*-hydroxyphenylpyruvic acid, tyrosine, and that of  $\alpha$ -hydroxyisohexoxic acid and the corresponding keto-acid, leucine. Tyrosine and alanine were isolated in the form of the naphthalylsulphonyl derivative, and leucine and phenylalanine in the form of the corresponding carbamido-acids (see preceding abstract). The surviving livers of dogs and dog's blood were employed in the experiments, the perfusion apparatus already described being used, and the perfusion lasted generally ninety minutes. Full details as to the methods of preparation of the substances perfused and the methods of isolating the products formed are given by the authors. The amino-acids were obtained in optically active forms.  
S. B. S.

**The Synthetic Formation of Amino-acids in the Liver.**  
 III. **The Formation in the Liver of Amino-acids not Obtainable by Protein Hydrolysis.** KURA KONDO (*Biochem. Zeitsch.*, 1912, 38, 407—413).—In addition to amino-acids which are obtained by the hydrolysis of proteins of the body, other amino-acids can be synthetically formed in the liver by the perfusion of the corresponding  $\alpha$ -keto-acids. The author has succeeded in this way in obtaining  $\alpha$ -amino-*n*-butyric and  $\alpha$ -amino-*n*-hexoic acid by the perfusion of the ammonium salts of  $\alpha$ -ketobutyric and  $\alpha$ -ketohehexoic acids. For the preparation of the latter substance the method of Bouveault and Locquin was used. The butyric acid derivative was isolated in the form of the naphthalenesulphonyl compound, and the hexoic acid derivative in the form of the carbamido-compound. Both the synthetic acids were optically active. The technique employed was the same as that described in the preceding papers. S. B. S.

**The Synthetic Formation of Amino-acids in the Liver.**  
 IV. **The Formation of Alanine from Glycogen.** HANNI FELLNER (*Biochem. Zeitsch.*, 1912, 38, 414—420).—As it is known that the  $\alpha$ -hydroxy-acids and the corresponding keto-acids give rise to amino-acids by perfusion of the ammonium salts through the liver, it was also conceivable that amino-acids could be formed directly from carbohydrates, which on perfusion through the liver by themselves give rise to  $\alpha$ -hydroxy-acids (lactic acid) if ammonium salts were at the same time present. The author has, in fact, succeeded in obtaining alanine by perfusing livers containing abnormally large amounts of glycogen, the amino-acid being formed, if at all, only in very small quantity when a glycogen-poor liver is perfused. S. B. S.

**The Behaviour of *d*- $\alpha$ -Glucoheptonic Acid in the Organism of the Rabbit, Dog, and Man.** KOHSHI OHTA (*Biochem. Zeitsch.*, 1912, 38, 421—433).—The investigations with this acid were undertaken in view of the fact that its lactone is a sweet substance, which has been employed instead of sugar in the case of diabetes. The acid on treatment with dilute hydrochloric acid is readily converted into its optically active lactone, and by determining the polarisation of urine after this treatment, the amount excreted could be readily ascertained. The acid was also in certain cases directly isolated. In the various experiments on man, 12.3% up to 50% of the acid was excreted unchanged; in the case of dogs, up to 70% was burnt up in the body, although there were considerable individual differences. In the case of rabbits, there were also considerable individual variations, but more than 80% was utilised in the organism. S. B. S.

**The Physiological Action of the Four Isomeric Piperonyl-acrylbutylamides.** HERMANN THOMS and F. THÜMEN (*Biochem. Zeitsch.*, 1912, 38, 492—496).—The *isobutyl* derivative has been shown by the authors to exist in the root-bark of *Fagara xanthoxyloides* (this vol., i, 115). It has also been obtained synthetically. In addition the authors have also prepared the corresponding normal, secondary, and tertiary butylamides, and have submitted these

substances to physiological investigation by Kobert and Rost, a summary of whose report is communicated. All substances act in a similar way, exerting a narcotic action. S. B. S.

**Antagonism between Salts and Anæsthetics. I. The Conditions of the Anti-stimulating Action of Anæsthetics and of their Protective or Antitoxic Action.** RALPH S. LILLIE (*Amer. J. Physiol.*, 1912, 29, 372—397).—Isotonic solutions of sodium chloride cause in *Arenicola* larvæ strong muscular contractions and a loss of pigment; anæsthetic concentrations of ether, chloroform, alcohol, and chloretone prevent both; that is, they prevent stimulation and increase of permeability. This protective or antitoxic action resembles that of calcium or magnesium chloride. Chloral hydrate, urethane, benzene, xylene, and toluene act in the same direction, but less powerfully and more gradually. W. D. H.

**The Metabolic Influence of Ether Anæsthesia.** E. L. ROSS and PHILIP B. HAWK (*Proc. Amer. physiol. Soc.*, 1911, xvii—xviii; *Amer. J. Physiol.*, 29).—Ordinary and “dehydrated” ether both produce in dogs, after two hours’ inhalation, a glycosuric condition if the carbohydrate of the diet is entirely replaced by meat; but when the diet contains 3.3 to 4.1 grams of carbohydrate per kilo. of body-weight this does not occur. W. D. H.

**Narcotics and Local Anæsthetics. III. The Stability of the Bases of Local Anæsthetics in Solution.** OSKAR GROS (*Arch. exp. Path. Pharm.*, 1912, 67, 126—131).—Cocaine is rapidly decomposed in solution, and so if kept will produce a smaller effect on nerve than the hydrochloride; this will probably explain how Symes and Veley (*Abstr.*, 1911, ii, 508) obtained results which differ from the author’s. Alypin and novocaine are more stable in the free state. W. D. H.

**Narcotics and Local Anæsthetics. IV. The Action of Novocaine Salts.** OSKAR GROS (*Arch. exp. Path. Pharm.*, 1912, 67, 132—136).—Experiments on the frog’s sciatic nerve show that the salts of novocaine act more powerfully as anæsthetics the more they are hydrolysed in solution, that is, the more base is liberated. Arranged in order of activity the salts investigated were borate, hydrogen carbonate, secondary phosphate, acetate, and chloride. W. D. H.

**The Action of Protracted Cocaine Administration in Animals.** JULIUS GRODE (*Arch. exp. Path. Pharm.*, 1912, 67, 172—190).—Although there is evidence that in man, habituation to the use of cocaine occurs, the present experiments on dogs, cats, and guinea pigs show that in these animals there is not only no habituation, but there is an increase in their sensitiveness towards the drug. W. D. H.

**The Influence of Various Alkaloids on the Capacity of the Liver for the Formation of Urea in vitro.** GIOVANNI BATTISTA ZANDA (*Chem. Zentr.*, 1912, i, 156; from *Arch. Farm. speriment.*, 1911, 12, 418—423).—The amount of urea formed by the liver

*in vitro* is increased by cocaine when present in the fluid to the extent of 0·1—0·25% ; quantities of 0·5% have no influence, whereas 1—2% has an inhibitory action. Morphine (even in doses of 0·1%), quinine, quinidine, and strychnine exert an inhibitory influence. S. B. S.

**Action of Adrenaline on Blood-vessels.** S. OGAWA (*Arch. exp. Path. Pharm.*, 1912, 67, 89—110).—Experiments on the frog and on isolated organs (kidney, intestine, skin, and muscle) show that the typical action of adrenaline is constriction of blood-vessels, but in very low concentrations the effect may be dilatation, or dilatation may follow the primary constriction ; this is probably due to an action on the vaso-dilator nerves. The action of *d*-adrenaline is weaker than that of *l*-adrenaline. W. D. H.

**Glycosuria Produced by Subcutaneous and Intra-muscular Injections of Adrenaline.** I. S. KLEINER and SAMUEL J. MELTZER (*Proc. Amer. physiol. Soc.*, 1911, xxvi—xxvii ; *Amer. J. Physiol.*, 29).—Intravenous injections of adrenaline is the least favourable method of producing glycosuria. The view that any method which favours rapid absorption of this substance into the blood is unfavourable to the production of glycosuria is supported by experiments which show that intra-muscular injections (rapid absorption) in rabbits produce less glycosuria than subcutaneous injections (slow absorption). W. D. H.

**The Toxic Effect of Oxalates and the Physiological Action of Calcium.** OSCAR LOEW (*Biochem. Zeitsch.*, 1912, 38, 226—243).—Neutral potassium oxalate is poisonous to the lowest animal organisms, and also to plants, with the exception of the very low species of algæ and moulds, which have no physiological needs for calcium. There appears, therefore, to be a relationship between the toxicity of oxalates and the physiological function of the calcium. Observations show that the toxic action takes place in the nucleus and chloroplasts, from which the conclusion is drawn that a combination with the calcium takes place in these parts. Physiological facts indicate that this combination also takes place in the cell nucleus of animal organisms. S. B. S.

**Toxicity of Arsenic Compounds Employed in Therapeutics.** ANTOINE MOUNEYRAT (*Compt. rend.*, 1912, 154, 284—286. Compare Abstr., 1903, ii, 444).—Experiments on rabbits with injections of salts of diaminodihydroxyarsenobenzene and its dichloro- and di-iodo-derivatives show that other conditions being the same, the danger of a fatal result increases as the interval between successive injections is diminished. After death, arsenic is found in the liver and muscles, but is specially localised in the nervous centres. W. O. W.

**Grayanotoxin, the Poisonous Constituent of Leucothoe Grayana Max.** O. KUBO (*Arch. exp. Path. Pharm.*, 1912, 67, 111—117).—Grayanotoxin was separated from the leaves of the

ericaceous Japanese plant named above. It is neither a glucoside nor an alkaloid. It crystallises in colourless needles, melts at 222—223°, and has the empirical formula  $C_9H_{14}O_8$ .

It causes fibrillary twitchings in frog's voluntary muscles, and finally paralyzes motor nerve-endings. It acts on the frog's heart like aconitine. It is easily absorbed in the rabbit, and in the dog causes vomiting, however administered. It causes motor paralysis, and kills by stopping the respiration.

W. D. H.

Cynanchotoxin, the Poisonous Constituent of *Cynanchum caudatum* Maxim., and Phytolaccotoxin. K. IWAKAWA (*Arch. exp. Path. Pharm.*, 1912, 67, 118—125).—*Cynanchotoxin* is prepared from the root of the plant, and is used therapeutically in Japan. It belongs to the picrotoxin group. It produces convulsions, and slowing and finally stoppage of the heart, acting on centres in the central nervous system. Experiments on frogs and warm-blooded animals are described, and details given of the lethal doses.

Phytolaccotoxin, previously-described as the active constituent of *Phytolacca acinosa*, is the same substance. Doubt, however, has been thrown on its presence in *P. acinosa*, and there is some reason to think that the plant from which it was obtained was in reality *C. caudatum*.

W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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The Bacterial Production of Acetylmethylcarbinol and  $\beta\gamma$ -Butylene Glycol from Various Substances. ARTHUR HARDEN and DOROTHY NORRIS (*Proc. Roy. Soc.*, 1912, *B*, **84**, 492—499).—Both acetylmethylcarbinol and  $\beta\gamma$ -butylene glycol are produced by *B. lactis aërogenes* and *B. cloacae* when these organisms are grown in a peptone solution containing either dextrose, lævulose, mannose, galactose, arabinose, isodulcitol, mannitol, or adonitol.

*B. lactis aërogenes* under similar conditions produces  $\beta\gamma$ -butylene glycol, but no acetylmethylcarbinol, from glycerol, ethylene glycol, and acetaldehyde. In all these cases a carbon synthesis is involved, analogous to the production of butyric acid from glycerol and lactic acid. Neither substance was produced from citric and malic acids, dihydroxyacetone, or peptone water. W. J. Y.

The Chemical Action of *Bacillus cloacæ* (Jordan) on Dextrose and Mannitol. JAMES THOMPSON (*Proc. Roy. Soc.*, 1912, *B*, **84**, 500—504).—When *B. cloacae* is grown in peptone water containing dextrose or mannitol, the same products are obtained as were found by Harden and Walpole (*Proc. Roy. Soc.*, 1906, *B*, **77**, 399) in the case of *B. lactis aërogenes* under similar conditions, namely, acetic lactic, succinic and formic acids, ethyl alcohol, carbon dioxide, hydrogen,  $\beta\gamma$ -butylene glycol, and acetylmethylcarbinol.

The relative proportions of the products of fermentation with both substances differed considerable from those obtained with *B. coli communis* and in a less degree from those obtained from *B. lactis aërogenes*.  
W. J. Y.

**The Gelatinase of *Bacillus prodigiosus*.** FRANZ VON GRÖER (*Biochem. Zeitsch.*, 1912, 38, 252—284).—The most active gelatinase preparations are obtained from bouillon cultures of the organism, which are freed from the bacteria by centrifugalisation. The gelatinase is very sensitive towards sodium fluoride and acids, and is very, although not completely, resistant to high temperatures. Gelatin protects the enzyme against fluoride action and the deleterious action of heat. The reaction rate with not too small quantities of ferment and 5% gelatin solution is a constant. By increasing the temperature 10°, the reaction rate is increased comparatively little. The enzyme action was measured by determining the changes in the viscosities of the mixtures.  
S. B. S.

**The Action of Some Benzene Derivatives on the Development of *Penicillium glaucum*.** JACOB BÖESEKEN and H. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 608—622. Compare this vol., ii, 306).—The authors have examined the influence of a considerable number of benzene derivatives on the development of *Penicillium glaucum*, and have, in many cases, determined the division factor of these substances between olive oil and water. In all cases they have noticed a distinct parallelism between the retarding action and the value of the division factor.  
H. W.

**Influence of Light on the Fermentation of Grape Juice.** W. LUBIMENKO and A. FROLOFF-BAGREIEF (*Compt. rend.*, 1912, 154, 226—229).—Experiments on a culture of natural grape yeast are described, showing that the energy of fermentation in grape juice is greater in darkness than in light. The amount of alcohol, glycerol, and carbon dioxide formed is greater in obscurity, and the proportion of volatile acids is smaller. The amount of esters formed seems to be independent of the illumination.  
W. O. W.

**Formation of Glycogen in Yeast Cells.** DIANA BRUSCHI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 54—60).—The paper records experiments designed to elucidate the mechanism of the production of glycogen in yeast cells. Narcotics, like ether and chloroform, stop the production of glycogen only when added in sufficient quantity to prevent fermentation. Thymol and formaldehyde stop the formation of glycogen when they arrest fermentation, but smaller quantities have no effect on either process. Potassium hydrogen sulphite in small amount increases both fermentation and the production of glycogen, whilst with a larger quantity the fermentation is increased, but the production of glycogen is diminished. The addition of ethyl alcohol to a yeast in full growth causes an immediate production of glycogen, but when enough has been added to stop the fermentation, the production of glycogen soon ceases also, so that the alcohol seems

to act merely as a nutrient or stimulant. Plasmolysis of the cells frequently stops the production of glycogen, but it recommences when they return to their normal state. When the acidity of a culture is neutralised, the formation of glycogen increases.

It was eventually found possible to separate to some extent the fermentative activity from the process leading to the production of glycogen. When cultures in full fermentation are neutralised and treated with enough alcohol greatly to diminish fermentation, no glycogen is formed; if after fermentation has ceased the liquid is replaced with fresh medium to which ether has been added, it does not recommence, and the cells do not multiply, but they remain alive, and after three days granules of glycogen appear in them. In another case the liquid was removed from a culture in which glycogen had formed and redissolved, and was replaced by the liquid from another culture in which an abundant formation of glycogen had been caused by the addition of alcohol and an excess of sucrose; ether was also added, and glycogen gradually appeared, although fermentation and multiplication did not recommence. Further experiments showed that, in order to observe the production of glycogen in this manner in the absence of fermentation, it is necessary to choose cells at a particular stage in their growth.

The results indicate that the glycogen is formed from some intermediate product in the fermentation, so that its production is due to a secondary process which is a partial reversal of one of the processes in the chain of reactions which constitute the fermentation.

R. V. S.

**Action of Dissolved Substances on the Auto-fermentation of Yeast.** ARTHUR HARDEN and SYDNEY G. PAINE (*Proc. Roy. Soc.*, 1912, *B*, 84, 448—459).—The rate of auto-fermentation of pressed yeast is largely increased by the addition of a number of soluble substances, such as salts, alcohol, etc. As this rate is controlled by the rate at which sugar is formed from the glycogen of the cell by the enzyme glycogenase, an increase in rate of auto-fermentation indicates a greater activity of this enzyme.

It is found that only those substances which plasmolyse the yeast cell cause increase in the rate of auto-fermentation. Substances like urea, which even in concentrated solution do not produce plasmolysis, have no accelerating effect.

This effect is probably a direct result of the concentration of the cell contents due to plasmolysis, since a similar acceleration is obtained with yeast which has been partly dried in a vacuum or in a current of dry air. A similar acceleration is produced by toluene, but in this case other factors, such as disorganisation of the cell, or a hormone action, may be concerned.

W. J. Y.

**The Fermentation of the Different Tartaric Acids.** LASZLÓ KARCZAG (*Biochem. Zeitsch.*, 1912, 38, 516—518).—*d*-Tartaric acid on fermentation with yeast yields more carbon dioxide, especially in the earlier stages, than the *l*-acid, the *dl*-acid being in this respect intermediate between the two. The *meso*-acid and the inactive acid

act in a similar way to the *d*-acid. Hefanol scarcely attacks the free acid, but acts on the potassium salts, especially that of the *d*-acid.

S. B. S.

**Copper Fungicides.** SPENCER U. PICKERING (*J. Agric. Sci.*, 1912, 4, 273—281. Compare *ibid.*, 3, 171; Trans., 1909, 1411; Gimingham, this vol., ii, 75).—From the results of investigations of the products of the action of lime on copper sulphate, the conclusion was drawn that the fungicidal action of such products depends on the amount of copper rendered soluble by atmospheric carbon dioxide. When lime is deficient, a lower basic sulphate is obtained, from which larger amounts of copper are rendered soluble by carbon dioxide than is the case with the highly basic sulphates in Bordeaux mixture. The compound  $10\text{CuO}\cdot\text{SO}_3$ , obtained by adding lime water, just short of alkalinity, which, theoretically, should be rendered soluble to the extent of 10% of the copper by carbon dioxide, is found in practice, owing to the presence of calcium sulphate, to furnish a far larger proportion of soluble copper.

Although the copper present in Woburn Bordeaux paste ( $10\text{CuO}\cdot\text{SO}_3$ ) is only soluble to the extent of 0.5 per million, it was found that, in ten hours, rods of bright iron immersed in a liquid containing the basic sulphate, through which a current of air was passed, removed 10.9% of the copper, and that this rate of action could be nearly maintained by using fresh iron rods. When ordinary Bordeaux mixture was employed, the iron remained perfectly bright until the whole of the lime was converted into carbonate by the carbon dioxide of the air. Addition of calcium sulphate to Bordeaux mixture increases the action six-fold, whilst calcium chloride only doubled the action, and calcium carbonate had no effect at all.

Whilst an atmosphere of carbon dioxide enormously increases the action of Woburn Bordeaux, the action is retarded by small amounts; by removing carbon dioxide from the air its action is increased 9%.

The results obtained by Gimingham, showing that ordinary Bordeaux is effective in absence of carbon dioxide, are attributed to the fungicidal action of the free lime (compare Freeman, Abstr., 1911, ii, 222).

N. H. J. M.

**Comparison of Oxidation Phenomena in Galls and the Normal Homologous Organs.** MARIN MOLLIARD (*Compt. rend.*, 1912, 154, 68—70).—The respiratory coefficient of elm galls and of the normal leaves is the same in darkness, whereas in light the galls fix more oxygen than the leaves. The oxydases of the parasitic growth are much more active than those of the normal leaves, although, contrary to expectation, the leaves contain a higher proportion of iron and manganese. Analyses show wide differences in the mineral composition of the two organs, the galls containing about one-third as much silica, one-half as much calcium oxide, 3.5 times more phosphorus, and four times as much potassium and sodium as the leaves.

Similar results have been obtained with other plant galls.

W. O. W.

**Nitrate and Nitrite Assimilation.** New Hypothesis of the Formation of the Precursors of Proteins in Plants. OSKAR BAUDISCH (*Centr. Bakt. Par.*, 1912, ii, 32, 520—540. Compare Abstr., 1911, ii, 523).—When a mixture of nitromethane and formaldehyde is subjected to the action of mercury light, nitrous oxide, hydrogen, carbon dioxide, and carbon monoxide, are given off, whilst the solution yielded crystals of isonitrobutylglycerol. The conclusion is drawn that the compound  $\text{CH}_2\text{:NO}\cdot\text{OH}$ , aci-nitromethane, is first formed, and that it reacts with the excess of formaldehyde with production of nitrous oxide and carbon dioxide. Formhydroxamic acid is also produced by the action of light on nitromethane and formaldehyde.

It is conceivable that in plants dihydroxyacetoneoxime may be formed from isonitrobutylglycerol, and both compounds react with potassium nitrite in presence of light.

Starting with isonitrobutylglycerol, it is shown how the production of various amino-acids, citric acid, pentoses, and hexoses may be accounted for.

When plants are supplied with ammonium salts, it is probable that the ammonia is first oxidised by plant oxydases, or is converted by the oxidising action of ultra-violet rays, in presence of formaldehyde, into aci-nitromethane. N. H. J. M.

**Assimilation of Nitrates in Plant Cells.** OSCAR LOEW (*Chem. Zeit.*, 1912, 36, 57—58).—In reference to Baudisch's theory of nitrate assimilation (preceding abstract), it is pointed out that experiments with barley plants supplied with nitrate and sugar showed that the nitrates disappeared when the plants were kept in darkness, whilst plants which had no sugar showed a strong nitrate reaction (Suzuki, Abstr., 1899, ii, 323). The conclusion is drawn that light does not directly bring about the reduction of nitrates, but only indirectly, the nitrates being reduced by the action of the living protoplasm in conjunction with carbohydrates formed in the leaves. N. H. J. M.

**The Effects of Caffeine on the Germination and Growth of Seeds.** FRED RANSOM (*Bio-Chem. J.*, 1912, 6, 151—155).—Caffeine in 1% aqueous solution retards, or may even stop, the germination and growth of seeds. W. D. H.

**The Action of Caffeine on the Germination and Growth of Seeds.** FRED RANSOM (*Bio-Chem. J.*, 1912, 6, 156—161).—Caffeine when added in the proportion of from 1% to 0.01% to water, in which seeds are then sown, retards germination and growth. In the former concentration germination may be completely inhibited. No evidence that caffeine acts as a stimulant to plant life was discovered.

W. D. H.

**Grape Stones.** GIULIO PARIS (*Chem. Zentr.*, 1912, i, 40; from *Staz. sperim. agrar. ital.*, 1911, 44, 669—727).—The residue of freshly pressed grapes consists of 25—30% stalks, 50—60% skins and fibres, and 15—20% stones. The stones, after being dried at 100°,

consist of 12% proteins, 22% fat, 0.12% phytosterol, 0.12% lecithin, 0.72% phytin, 4.95% tannin, 3.16% sugar, 9.66% starch, 9.66% hemi-celluloses, 25.63% lignin, etc., 10.77% cellulose, and 3.00% ash. The proteins yielded 11.63% arginine, 1.18% histidine, and 0.26% lysine.

Grape seed oil has  $D_{25}^{15}$  0.9502, acid number 16.8, esterification number 179.8, iodine number 96.0, and acetyl number 143.1. It contains 8.9% glycerol, 13% of solid and 80% of liquid fatty acids, and 0.5713% of phytosterol, m. p. 132—133°,  $[\alpha]_D^{15}$  -32.8° (acetyl derivative, m. p. 120—121°). Erucic, linoleic, oleic, stearic, and palmitic acids have been identified among the fatty acids. C. S.

**Is Humus a Direct Source of Carbon for the Higher Green Plants?** MARIN MOLLIARD (*Compt. rend.*, 1912, 154, 291—294).—Experiments were conducted on horse-radish plants grown in vegetable mould in order to compare the total increase in the amount of carbon of the plant with the amount directly assimilated from the atmosphere as carbon dioxide. The experiments were complicated by the fact that, even after heating for six hours at 120°, the soil was still capable of evolving measurable amounts of carbon dioxide. The results seem to show that if humus is directly absorbed by plants, the amount assimilated must be extremely small.

W. O. W.

**The Condition of Chlorophyll in Plants and Colloidal Chlorophyll.** AMEDEO HERLITZKA (*Biochem. Zeitsch.*, 1912, 38, 321—329).—If the leaves of plants are mixed with kieselguhr and sand, and then submitted to pressure in the Buchner press, most of the chlorophyll will remain absorbed on the solid cake, and but little will appear in the expressed juice. If, however, the plant is mixed with sand alone and then pressed, the chlorophyll will be found in the expressed juice. In this juice it appears to be in the same condition as it exists in the plant, and differs from that obtained by the ordinary extraction methods. It is in the condition of an electronegative dispersoid, and this fact accounts for the difference in the spectroscopic and other characters of the colloid in plants to the chlorophyll preparations obtained by the ordinary methods.

S. B. S.

**Betaines of Plants. II.** ERNST SCHULZE and GEORG TRIER (*Zeitsch. physiol. Chem.*, 1912, 76, 258—290).—The supposition (Abstr., 1910, ii, 743) that betaines are widely distributed in plants is confirmed. Betaine is present in the seeds of *Helianthus annuus*, and in the leaves and stalk of *H. tuberosus*. The tubers of *Dahlia variabilis* and *Scorzonera hispanica* contain very small quantities of trigonelline. In *Cichorium intybus* there is neither betaine nor trigonelline.

The leaves and stalk of *Stachys tubrifera* contain stachydrine; *S. sylvatica* contains trigonelline and betonidine, which are also found in *Betonica officinalis*. *Salvia pratensis* does not contain betaine. *Vicia sativa* contains betaine, and *Pisum sativum* contains trigonelline.

The method of formation of betaines in plants and their significance are discussed (compare Stanek, Abstr., 1910, ii, 336; 1911, ii, 1124).

They are regarded as waste products of metabolism like the alkaloids ; the evidence is against their being made use of during the life of the plant. E. F. A.

**Rôle of Oxydases in the Formation of Certain Constituents of Essential Oils.** I. BENJAMIN T. BROOKS (*J. Amer. Chem. Soc.*, 1912, 34, 67—74).—In a study of the essential oil of *Michelia champaca* (Abstr., 1911, i, 1001), the presence of an oxydase was discovered in the flowers, and it was suggested that the formation of aldehydes and ketones in essential oils is largely due to the activity of such enzymes. A further study has now been made of this question.

Oxydases have been detected in green caraway seeds (*Carum carvi*) and in the inflorescence of the peppermint (*Mentha piperita*). It is probable that all the mints contain an oxydase, as active extracts were prepared from the flower stalks of *Mentha viridis*, *M. crispa*, *M. sylvestris*, and *M. gentilis*, as well as from the inflorescences of *Satureja montana* and *Calamintha officinalis*. Oxydases are also present in the leaves of the tansy (*Tanacetum vulgare*) and in those of *Thuja occidentalis*, but could not be detected in rose petals or in the leaves of *Andropogon schoenanthus*.

Peppermint flowers and the leaves of rue (*Ruta graveolens*) contain a catalase.

The development of the characteristic odour of valerian roots is due to the action of a lipase.

The presence of an oxydase probably accounts for the fact that the perfumes of many flowers rapidly deteriorate after picking, especially if they are bruised. E. G.

**Phosphorus and Nitrogen in the Alcoholic Extract of Leaves.** JOSEF SESSL (*Zeitsch. landw. Vers. Wesen. Oesterr.*, 1911, 14, 886—893).—An account of experiments with the tabulated results of numerous estimations of phosphorus and nitrogen in the alcoholic extracts of leaves picked under varying conditions of growth and in various stages of development during the period between May and November.

In some cases the ratio  $P_2O_5 : N$  increased during the later stages of growth, notably in *Aesculus hippocastanum*, where this ratio increased from about 1 : 4 to 1 : 8 ; in other cases there was a decrease during the period of growth, that in *Quercus robur* being from 1 : 5·19 to 1 : 3·19.

F. M. G. M.

**The Hæmagglutinating and Precipitating Properties of the Bean, *Phaseolus multiflorus*.** EDWARD C. SCHNEIDER (*J. Biol. Chem.*, 1912, 11, 47—59).—The proteose prepared from scarlet runner beans is an active agglutinating agent. Hæmagglutinin is also adsorbed in small amount by the other proteins of the bean. It is not a product of autolysis. As the seedling develops, it gradually disappears from the cotyledons simultaneously with the stored food material. Extracts of root, stem, and leaves of the plant have no agglutinating properties. The clear extract of the beans produces a

flocculent precipitate when added to rabbits' serum; this is chiefly associated with phaseolin, a globulin. W. D. H.

**Allantoin, a Constituent of Comfrey Rhizome (*Symphytum officinale*).** ARTHUR W. TITHERLEY and N. G. S. COPPIN (*Pharm. J.*, 1912, [iv], 34, 92—94).—An aqueous infusion of this drug has long been used as an application to sores and ulcers, and recent clinical observations by Macalister (*Brit. Med. Journ.*, 1912, 1, 10) and Bramwell (*loc. cit.*, p. 12) having established its efficacy, the authors undertook its investigation in order to isolate the active constituent. Its remedial action is due to allantoin.

An aqueous infusion of the rhizome contains allantoin, a reducing sugar, giving a phenylosazone, m. p. 205—208°, gum, and dextrin-like carbohydrates, but no starch, glucosides, or alkaloids. A substance giving a green coloration with ferric chloride and one yielding an intensely yellow solution with alkalis are also present. Alcohol extracts all these substances, except the gum and carbohydrates, and in addition a small amount of essential oil, some resin and tannins, resembling those present in catechu, and a small quantity of an organic acid.

The allantoin was isolated to the extent of from 0.55 to 0.79% by extracting the rhizome with hot 95% alcohol, from which it separated along with some sugar on concentration, and was purified by washing with a little cold water and recrystallisation from boiling water. T. A. H.

**Lactarinic, Lactaric, and Stearic Acids in Fungi.** J. BOUGAULT and CHARLES CHARAUX (*J. Pharm. Chim.*, 1912, [vii], 5, 65—71. Compare Abstr., 1911, i, 835, 949).—By the method described already (*loc. cit.*) the following minimum percentages of free lactarinic acid, expressed on dry material, have been isolated from the species named: *Lactarius uvidus*, 2.9; *L. theiogalus*, 2.3; *L. lilacinus*, 2.25; *L. subdulcis*, pale variety, 2.15; *L. plumbeus*, 2.1; *L. pyrogalus*, 1.80. The following species yield free stearic acid; the figures, where given, are minimum percentages expressed on dry material. *L. azonites*, 3.0; *L. vellereus*, 1.2; *L. controversus*, 1.1; *L. deliciosus*, 0.9; *L. piperatus*, *L. subdulcis*, *L. torminosus*, *Russula delica*, 0.5 to 0.6; *R. Queletii*, 0.5 to 0.6. In both cases more acid must be present in a combined condition. The latex of *L. piperatus* contains at least 5% of stearic acid, or 25% expressed on dry material. The lactaric acid described by Thörner (Abstr., 1880, 44), Bissinger (Abstr., 1884, 480), and Chodat and Chuit (Abstr., 1890, 80) is identical with stearic acid (compare Gérard, Abstr., 1891, 606). Phytosterols have been found in some of the species of fungi mentioned above, and also in a number of species belonging to other genera (compare Goris and Mascré, this vol., ii, 79).

T. A. H.

**Is Iron a Catalyst in the Oxidation of Phenols by the Peroxydase of Horse-radish?** H. COLIN and A. SÉNÉCHAL (*Compt. rend.*, 1912, 154, 236—237. Compare Abstr., 1911, ii, 795—872).—The catalytic activity of horse-radish juice may be due to the presence

of salts of iron with organic acids analogous to the artificial peroxy-dasic ferrocyanide of iron. On the other hand, many substances capable of undergoing oxidation in presence of the artificial oxydase are not affected by the natural enzyme. The author considers, therefore, that the active agent in the horse-radish is a compound of the hæmoglobin type containing a very small proportion of iron.

W. O. W.

**Carbohydrates of the Mangold Leaf.** A. V. CAMPBELL (*J. Agric. Sci.*, 1912, 4, 248—259).—Analyses of mangold leaves collected every two hours, day and night, on Sept. 16—17, indicated that the amounts of dextrose and lævulose with other reducing substances do not vary very much; the percentage is fairly constant during the night and somewhat higher in the day-time. Sucrose varied from 0.5 to 2.5%, and seems to be produced during periods of light; the commencement of the increase coincided with the time of sun-rise; the fluctuations of the starch resembled those of the sucrose, the chief difference being that, whilst the sucrose begins to decrease in the afternoon, the increase of starch continued until 11 p.m. Maltose fluctuated considerably, in the reverse sense to sucrose, the increase commencing at 8 p.m. and continuing until the first dawn.

As regards the effect of manures on the amounts of sugars in the leaves, it is shown that leaves from a plot which received no potassium sulphate contained about twice as much dextrose and lævulose (10.91—11.70%) as leaves from a plot which had potash (5.53—5.75%), whilst the amounts of sucrose and maltose were much higher under the influence of potassium sulphate than on the plot which received no potassium salt. The leaves on the latter plot are always attacked by *Uromyces*, and are very dark to coloured and unhealthy (compare Massee, *Phil. Trans.*, B, 197, 7).

Old leaves were found to contain much less dextrose, lævulose, and maltose than young leaves collected at the same time.

N. H. J. M.

**Bark, Latex, and Seed of Nerium Oleander.** A. LEULIER (*J. Pharm. Chim.*, 1912, [vii], 5, 108—116. Compare *J. Pharm. Chim.*, 1891, [vii], 4, 157).—The author has already (*loc. cit.*) isolated from the bark a bitter, highly poisonous glucoside very similar to strophanthin, which he now proposes to call *l*-strophanthin. This may be identical with Schmiedeberg's neriin, isolated from the leaves of the same plant (*J. Pharm. Chim.*, 1890, [vi], 22, 356). This glucoside is also present in the seeds, which also contain a phytosterol, m. p. 134—135°, crystallising in colourless needles.

The latex of the plant contains a second glucoside, m. p. 179—180°, which crystallises from boiling water in long, silky needles, and is hydrolysed by dilute sulphuric acid, forming a reducing sugar and a colourless, crystalline, bitter substance, which decomposes at 230° (approx.). This second glucoside is far less toxic than the *l*-strophanthin obtained from the bark and seeds (compare Dubigadoux and Durieu, *Abstr.*, 1899, ii, 325).

T. A. H.

**Proteins of Rice.** S. KAJIURA (*Bio-Chem. J.*, 1912, 6, 171—181).—The proteins of “white rice” as used for dietary purposes in Japan consist to a very small extent of albumins and globulins; the amount of alcohol-soluble protein is negligible. The main protein, *oryzenin*, belongs to the glutelin class (proteins soluble in dilute alkali). In its nitrogen partition (Hausmann’s method) it differs from wheat glutenin (the only other glutelin so far studied) very considerably.

W. D. H.

**Hydrolysis of Vegetable Oils by Emulsion of *Ricinus communis*.** DAVID SOMMERVILLE (*Bio-Chem. J.*, 1912, 6, 203—204).—Emulsion of castor oil beans acts on castor oil and cotton-seed oil, hence is not specific in its action. Addition of acetic acid or manganese sulphate produced no increase in the amount of fatty acid liberated. The active enzyme rapidly loses its activity when mixed with water, alcohol, or acetone, but not when mixed with ether or benzene. The bean does not lose its lipolytic power by heating to 100° (dry heat), but in the form of emulsion, heating to 60° destroys the enzyme. No separation into two constituents was found, similar to that described for pancreatic lipase. If cotton oil and castor oil are neutralised and freed from proteins, no hydrolysis takes place.

W. D. H.

**Influence of Atmosphere Oxygen on the Work of Proteolytic Enzymes in Dead Plants.** WLADIMIR I. PALLADIN and Y. A. KRAULE (*Bull. Acad. Sci. St. Petersburg*, 1912, [vi], 83—93).—Experiments on the extent of proteolytic action in dead mushrooms and etiolated bean-leaves give the following results.

The autolysis of protein in dead plants rich in respiratory chromogens is considerably retarded by the oxygen of the air, the amount of this retardation increasing with the porosity of the tissues of the organ investigated. In the compact pileus of the mushroom, absence of oxygen increases the degradation of the protein to the extent of 15%; whilst in the porous tissues of the gills of the mushroom, and in thin etiolated leaves of the bean, the increases are 34% and 122% respectively. This relation of autolysis to atmospheric oxygen is, however, only indirect, as it is found that the actions of the enzymes in dead plants are not co-ordinated. “Enzymes in dead cells resemble soldiers without a leader; they act independently, one of the other, and hence without understanding.” One enzyme may destroy another, either directly or with the help of the products it forms.

In the investigation of the work of any enzyme in a dead animal or vegetable organ, it is not sufficient to create conditions favourable to the action of the particular enzyme; attention must be paid to the injurious influence of the other enzymes present.

T. H. P.

**Chemistry of Cheddar Cheese.** MAXIMILIAN NIERENSTEIN (*J. Agric. Sci.*, 1912, 4, 225—244. Compare Abstr., 1911, ii, 326).—From cheddar cheese, about four years old, the following amounts of the various constituents were obtained: glycine, 0·4; alanine, 0·31; valine, 0·17; leucine, 0·12; *isoleucine*, 0·32; tyrosine, 3·8; lysine.

0.85; aminobutyric acid, 0.43, and aminovaleric acid, 0.14%. Glutamic acid (about 0.7%), phenylalanine, serine, and tryptophan were also found, whilst arginine was not detected, and the presence of aspartic acid was doubtful.

Glycine has not been so far definitely proved to be present in caseinogen (compare E. Fischer, *Abstr.*, 1901, i, 780), and it may be derived from other proteins, such as lactalbumin, lactoglobulin, and opalescin, which also occur in cheese.

The absence of arginine may be due to its being produced in the early stages of ripening, and to its subsequent decomposition.

The free aminovaleric acid previously obtained from old cheese (*loc. cit.*) is probably a mixture of the  $\alpha$ - and  $\delta$ -acids, the former predominating.

N. H. J. M.

**The Awakening of the Earth.** ACHILLE MÜNTZ and HENRI GAUDECHON (*Compt. rend.*, 1912, 154, 163—168).—The awakening of the soil to reproductive activity at the beginning of spring appears to coincide with a considerable increase in the nitrifying activity of the organisms in the soil. Direct experiments on the nitrifying power of soil in Paris shows the existence of a well-marked maximum occurring between March 28th and April 25th. This is especially intense in vegetable mould, and is followed by a considerable diminution in activity, after which a second rise occurs, but to a much smaller extent than that represented by the first maximum.

W. O. W.

**Adsorption Capacity of the Soil.** JOHANNES H. ABERSON (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 13—22).—The adsorption of ammonium chloride from its aqueous solutions by various samples of soil has been examined. The data show that the phenomenon is not due to chemical action, but resembles closely the adsorption of substances from solution by charcoal, wool, and silk. If chlorides of calcium, magnesium, or potassium are added to the ammonium chloride solutions before treatment with the soil, the adsorption of the ammonium salt is diminished. Since these substances are formed as a result of chemical interaction when pure ammonium chloride solutions are brought into contact with the soil, it seems probable that the deviations from the exponential law, which are exhibited by the experimental data for such solutions, are due to the disturbing effect of double decomposition. If the final concentration of the displaced cations (Ca, Mg, and K) is constant in a given series of experiments, the quantity of ammonium chloride adsorbed is proportional to the amount of soil used in the different experiments, that is to say, is proportional to the surface of the soil colloids.

There appears to be some connexion between the adsorption capacity of a soil and its hygroscopicity, but the two quantities are not proportional. With rise of temperature the adsorptive capacity of soil diminishes, as has been observed in the case of other colloidal substances.

H. M. D.

**Chemical Nature of the Organic Nitrogen in the Soil. II.** S. L. JODIDI (*J. Amer. Chem. Soc.*, 1912, 34, 94—99).—In continua-

tion of the work described previously (Abstr., 1911, ii, 820), further samples of soil from plots on the Wisconsin Drift have been investigated. Each plot had been heavily manured, and during the next three years had been planted with oats, clover, and maize. The nitrogen of the soil was found to consist almost entirely of organic compounds; 48.65—52.14% was present in the form of amino-acids, 14.18—19.90% as diamino-acids, and 33.19—33.59% as amides. The amount of ammoniacal nitrogen was insignificant. On the whole, these results confirm those recorded in the earlier paper (*loc. cit.*).

E. G.

**Isolation of Creatinine from Soils.** EDMUND C. SHOREY (*J. Amer. Chem. Soc.*, 1912, 34, 99—107. Compare Sullivan, this vol., ii, 86).—A detailed account is given of methods of isolating creatinine from soils and effecting its identification. The possibility of this substance being formed from some more complex compound during the treatment has been considered, and the conclusion drawn that the creatinine is probably present as such in the soil. The results of the investigation indicate that creatinine is probably a normal constituent of all soils.

E. G.

**Phosphate Nutrition of Plants.** ALLAN BAGULEY (*J. Agric. Sci.*, 1912, 4, 318—322).—Pot experiments in which oats, peas, and swedes were grown in purified white sand, manured with tricalcium, ferric, and aluminium phosphates, and with superphosphate respectively as sources of phosphoric acid, in addition to calcium carbonate (3%), ferric hydroxide (0.5%), potassium nitrate, magnesium sulphate, and sodium chloride.

Iron and aluminium phosphates gave on the whole similar results. They produced stronger oat plants and larger and more healthy swedes than superphosphate. In the case of peas, the plants ripened later, and produced less seed when manured with iron and aluminium phosphates than when superphosphate was employed.

Oats manured with tricalcium sulphate failed to utilise the manure, and were not better than plants which received no phosphate. Peas grew moderately well with tricalcium phosphate, but ripened early and gave a poor crop. The swedes were later in making a start, but subsequently recovered, and finally produced good, healthy plants.

Further experiments are described in which the plants were manured with ignited ferric and calcium phosphates. The results show that the availability of the phosphoric acid is considerably reduced by ignition and extraction with boiling water, and that, in the case of oats, insoluble calcium phosphate is distinctly less effective than insoluble ferric phosphate.

N. H. J. M.

## Analytical Chemistry.

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**Hydrolysis of Sodium Oxalate and its Influence on the Test for Neutrality.** WILLIAM BLUM (*J. Amer. Chem. Soc.*, 1912, 34, 123—136).—Sørensen (Abstr., 1898, ii, 185; 1903, ii, 684, 750) has suggested the use of sodium oxalate as a standard in volumetric analysis, but its general adoption has been hindered by the difficulty of obtaining the salt of a sufficient degree of purity. A study of sodium oxalate has now been carried out in order to investigate certain points of uncertainty in Sørensen's method.

Solutions of pure sodium oxalate are alkaline. It has been found that *N*/20-sodium oxalate causes a coloration with phenolphthalein equivalent to 4% transformation of the indicator, and that a *N*/10-solution gives a coloration equivalent to 6% transformation. The most probable values of  $[H^+]_{18}$  for such solutions are  $2.5 \times 10^{-9}$  and  $2.0 \times 10^{-9}$  respectively. The value of the ionisation constant *K* for phenolphthalein is probably less than  $1.7 \times 10^{-10}$  for solutions in which it is transformed to an extent of less than 8%. Sodium oxalate solutions do not undergo decomposition to an appreciable extent on boiling. They readily attack glass, and, of various kinds tested, "Durax" glass was the least affected. Commercial specimens of sodium oxalate even after being heated at 240° may contain sodium hydrogen carbonate or occluded carbon dioxide.

The test for neutrality is best carried out by evaporating 200 c.c. of water in a quartz or "Durax" glass flask to 150 c.c. in a current of air, free from carbon dioxide, adding 0.2 c.c. of 1% phenolphthalein solution in alcohol and 4 grams of the sodium oxalate, and boiling for ten minutes. If the salt is pure, the solution should have a pink colour, equivalent to 6% transformation of the phenolphthalein. The solution is now titrated with *N*/100-acid or alkali hydroxide until a standard colour is obtained, indicating the presence of about 0.04% of sodium hydrogen carbonate or 0.03% of sodium hydrogen oxalate.

The salt can usually be purified by one or two recrystallisations from water in a platinum dish.

E. G.

**New Burettes with Automatic Zero.** HEINTZ (*Chem. Zeit.*, 1912, 36, 171).—The upper end of the burette is drawn out to a point, which is sealed into a bulb, provided with two tubes to which rubber tubing may be attached. The inflow tube, above the stopcock, is also provided with two branches, one of which is connected with the upper bulb, and the other with the storage vessel. The burette is filled in the usual way, the overflow escaping into the bulb. When this has become partly filled with solution, the clip closing the descending tube may be opened, when the solution descends and enters the burette. In a modification for use with liquids which attack rubber, the storage vessel is below, and the solution is forced up into the burette by a pressure bulb.

C. H. D.

**Jointless Stock-Bottle-Support Burette.** NORMAN ROBERTS (*J. Amer. Chem. Soc.*, 1912, 34, 49—51).—Apparatus is described which may be made by drawing out obliquely the upper part of a tall, open-mouthed, glass cylinder, and fusing it to an opening in the side of a burette near the top. It may be strengthened by sealing a piece of glass rod between the lower end of the burette and the side of the cylinder. The upper opening of the burette is fitted with a glass stopper, beneath which the tube is somewhat constricted. For certain purposes, the glass stopper may be replaced by a rubber stopper carrying a tube of soda-lime. The liquid can be transferred from one vessel to the other by tilting the apparatus into a nearly horizontal position with that limb uppermost from which the liquid is to flow.

The advantages of the apparatus are its simplicity, and the ease with which the liquid can be transferred in either direction without exposure to the air. It is particularly recommended for solutions of alkali hydroxides. E. G.

**Estimation of Solid Material in Aqueous Suspension.** VON NOBLE and MARC LARCHEVÉQUE (*Sprechsaal*, 1911, 44, 428—430).—Mathematical; the author deduces a formula, and exhibits curves by which he is enabled to estimate the solid matter present in the slimes and sludges employed in the ceramic and other allied industries. The suspended matter must be insoluble, and the water have retained its normal chemical and physical properties. F. M. G. M.

**Estimation of Fluorine as Calcium Fluoride.** GUNNAR STARCK and E. THORIN (*Zeitsch. anal. Chem.*, 1912, 51, 14—18).—The solution of the fluoride is slightly acidified with acetic acid, and a solution of ammonium oxalate of known strength is added in such quantity that it will produce an amount of calcium oxalate about equal to the calcium fluoride expected. After heating, the solution is precipitated by an excess of calcium chloride, the precipitate, which settles readily owing to the admixed oxalate, is collected on a weighed asbestos filter, washed, dried at 210°, and weighed.

From the weight is then deducted that of the calcium oxalate; the difference represents calcium fluoride. L. DE K.

**Gases Dissolved in Solids.** MARCEL GUICHARD (*Bull. Soc. chim.*, 1912, [iv], 11, 49—50. Compare *Abstr.*, 1911, ii, 803).—The object of this work was to obtain greater exactness in the estimation of oxygen, and to determine the error due to the absorption or liberation of gases from the solids used as absorbents.

Phosphorus (10 grams), after sublimation several times under reduced pressure, shows a vapour tension of only 0.01 mm., corresponding with 0.02 c.c. of gas, but this material is unsatisfactory as an absorbent, since it and its oxides give off vapours, which preclude its use in apparatus connected to mercury pumps.

Cadmium, after repeated sublimation, gives a vapour tension of 0.01 mm. (approx.), but it is not a good absorbent for oxygen, probably because its oxide dissociates easily. Zinc, even after sublimation five times under reduced pressure, gives off 2 c.c. of gas per 100 grams of

metal. Potassium also liberates considerable quantities of gas after repeated distillation. Lead, after heating for eleven hours at 750° and eight hours at 550° under reduced pressure, still evolves 0.1 c.c. of gas per 100 grams of metal per hour. T. A. H.

**Estimation of Sulphur in Pyrites. II.** ARNOLD HECZKO (*Zeitsch. anal. Chem.*, 1912, 51, 1—14).—A combination of Dennstedt's process (compare this vol., ii, 89) and Raschig's benzidine volumetric process for sulphates (Abstr., 1903, ii, 572, 691). L. DE K.

**Detection of Nitric Acid in Presence of an Excess of Nitrous Acid.** HEMENDRA K. SEN and BIRMAN B. DEY (*Zeitsch. anorg. Chem.*, 1912, 74, 52—54. Compare Abstr., 1911, ii, 822).—When hydrazine sulphate reacts with soluble nitrites, the whole of the nitrite is destroyed, and if pure nitrite is used, nitrates cannot be detected in the solution by the sensitive diphenylamine test. The method may therefore be used to remove an excess of nitrites before testing for nitrates. It is superior to the carbamide method, which requires the addition of acid, as traces of nitrate are then always produced in the reaction. C. H. D.

**Estimation of Nitrates in Urine.** HUBERT CARON (*Ann. Chim. anal.*, 1912, 17, 9—13).—Schloesing's method was found to yield trustworthy results when applied to concentrated urine, but Bush's "nitron" method (Abstr., 1905, ii, 282) was less satisfactory. The colorimetric estimation with diphenylamine gave approximately correct results. Urines examined by the author contained, generally, from 0.1 to 0.2 gram of nitrate (calculated as potassium nitrate) per litre; a few samples contained up to 0.4 gram, whilst others yielded but a mere trace of nitrate. W. P. S.

**A Simple Apparatus for the Estimation of Small Quantities of Arsenic.** W. N. IWANOFF (*Chem. Zeit.*, 1912, 36, 31—32).—The generating flask is fitted with a cork, through which a funnel passes. A capillary tube is fitted into this funnel by means of rubber tubing, and the end is bent down, so as to dip into a *N*/10-solution of lead acetate contained in the funnel. The top of the funnel is closed by a plug of glass wool, over which a filter paper is tightly stretched, and moistened with a drop of an alcoholic solution of mercuric chloride. The gas evolved bubbles through the lead solution, which removes hydrogen sulphide, and the arsenic stain becomes visible on the filter paper. For quantitative purposes, control spots are prepared by placing different quantities of the arsenic solution in the apparatus, and oxidising with permanganate, before evolving the gas. The stained papers are coated with collodion, and may then be kept in paper in a desiccator for a year. C. H. D.

**Fractional Burning of the Constituents in the Analysis of Coal Gas.** LEO UBBELOHDE and DE CASTRO (*J. Gasbeleuchtung*, 1911, 54, 810—814).—A sketch of the apparatus and description of the method by which coal gas can be fractionally burnt with heated

copper oxide. This method has been previously advocated by Jäger and by Nesmjeloff (Abstr., 1909, ii, 519); the hydrogen and carbon monoxide burn at 265—270°, the methane and ethane at 800—900°, and the nitrogen at still higher temperatures. F. M. G. M.

**A New Apparatus for Gas Analysis.** HOHENSEE (*J. Gasbeleuchtung*, 1911, 54, 814—817).—A discussion of the apparatus and methods of Ubbelohde and de Castro (see preceding abstract), with a sketch, and description of the author's methods of conducting gas analysis. F. M. G. M.

**Organic Analysis by Combustion without the Use of an Oxygen-Carrier.** J. MAREK (*J. pr. Chem.*, 1911, [ii], 84, 713—731).—Hitherto it has been generally assumed that in the combustion of organic substances complete oxidation of the carbon to carbon dioxide cannot be effected without the use of an oxygen-carrier. From numerous analyses the author shows that complete combustion may be obtained without the use of a carrier, provided that the tube is heated strongly, and a sufficient excess of oxygen is supplied during the combustion.

The analyses were carried out in a 55 cm. tube, provided with the mercury seal previously described (Abstr., 1909, ii, 617), 10 cm. of the tube being maintained at a bright red heat.

In many cases complete combustion was obtained even at a dull red heat.

Analyses are also quoted to show that the combustion is often complete when only 5 cm. of the tube are heated to bright redness.

In order to secure regular and rapid volatilisation, the substance to be analysed is placed in a small tube, closed at one end, and provided with a lateral constriction to prevent the molten substance from flowing out of the tube.

A new form of apparatus for absorbing the carbon dioxide is also described. F. B.

**Simple Apparatus for Estimating Carbon Dioxide.** ERWIN RUPP (*Chem. Zeit.*, 1912, 36, 59—60).—The apparatus consists of a 160 c.c. Erlenmeyer flask containing a 15 c.c. pipette, the upper end of which passes through the india-rubber cork, and is closed with a glass cap. The flask is provided, by means of a second hole in the cork, with a straight calcium chloride tube.

In estimating carbonates, the pipette is filled with 20% acid, the weighed substance added, and the apparatus and contents weighed. The acid is then allowed to flow out of the pipette, and the contents of the flask heated to boiling. The pipette stopper is then replaced by a second calcium chloride tube, and air drawn through the apparatus, which, when cold, is again weighed.

A sketch of the apparatus is given.

N. H. J. M.

**Estimation of Alkalies in Silicates by Fusion with Calcium Chloride.** EERO MÄKINEN (*Zeitsch. anorg. Chem.*, 1912, 74, 74—78).—Alkalies are conveniently estimated in silicates by the following

method. Half a gram of the powdered silicate is mixed with 7 grams of dry, purified calcium chloride, and heated to fusion in a platinum crucible, the upper half of which is kept cool by an asbestos screen. Finally, the temperature is raised to bright redness, but without the use of a blowpipe. The mass is then treated as in Lawrence Smith's method. The calcium carbonate must be twice precipitated, and the filtrate is evaporated to dryness, redissolved in very little water, and freed from traces of calcium by ammonia and ammonium carbonate. The extraction of alkali by this method is more complete than by Lawrence Smith's method, and the details of working are simpler. C. H. D.

**Estimation of Potassium as Potassium Platinichloride.** RUD. TRNKA (*Zeitsch. anal. Chem.*, 1912, 51, 103).—Fiechter's process (Abstr., 1911, ii, 933), reduction of potassium platinichloride by means of metallic magnesium, is not a novel idea, but has been known for many years. L. DE K.

**Rapid Estimation of Zinc.** K. VOIGT (*Zeitsch. angew. Chem.*, 1912, 25, 205—206).—A reply to Hassreidter (*ibid.*, 1911, 24, 2471), who states that the author's process (this vol., ii, 93) must yield unsatisfactory results owing to a recombination of a portion of the zinc with the hydrated silica on adding ammonia.

The author states that no zinc is lost in that way. By following the exact directions and titrating with ferrocyanide in acid solution with ammonium molybdate as external indicator, good results are obtained. L. DE K.

**Two New and Very Delicate Tests by Use of the Reagent, "Tetramethyl Base."** ROBERT J. CARNEY (*J. Amer. Chem. Soc.*, 1912, 34, 32—35).—Trillat (Abstr., 1903, ii, 512) has shown that a solution of tetramethyldiaminodiphenylmethane gives a deep blue coloration with the oxides of lead and manganese, thus affording a delicate test for these metals. A modification of Trillat's method of applying the test is now described, in which citric acid is used instead of acetic acid.

When a very dilute solution of gold chloride is treated with the reagent, a beautiful purple coloration is developed, which soon changes to blue and then disappears, but reappears on warming. The reaction is interfered with by free mineral acids, and the solution should therefore be neutralised and rendered slightly acid with acetic or citric acid before applying the test. In a solution containing gold only, 0.01 mg. can be detected in 50 c.c.

The reagent can also be employed for the detection of ammonia, the test depending on the fact that hydrogen peroxide does not react with a manganous salt in absence of alkali hydroxide, whilst in presence of even a trace of alkali hydroxide, the manganese is instantly converted into a brown oxide. The solution to be tested is boiled with sodium hydroxide in a flask fitted with a rubber stopper through which passes a glass tube bent at right angles. A piece of filter paper is moistened with 1% solution of manganous sulphate containing hydrogen peroxide, and is then held in the steam issuing from the glass tube. If ammonia

is present, a brown stain appears on the paper. On moistening this stain with the solution of tetramethyldiaminodiphenylmethane, a deep purple colour appears. When ammonia is present in exceedingly small quantity, the brown stain is not produced, but a purple coloration is obtained on adding the reagent. In this way it is possible to detect 0.01 mg. of ammonia. E. G.

**Estimation of Copper in Steels.** S. ZINBERG (*Zeitsch. anal. Chem.*, 1912, 51, 19—20).—Three to five grams of the sample are heated with dilute sulphuric acid in a current of carbon dioxide. The iron dissolves and the copper is not in the least attacked; it is finally ignited and weighed as oxide. A special apparatus is described and figured. L. DE K.

**Rapid Method for the Estimation of Manganese in Ferrotungsten.** PAUL SLAWIK (*Chem. Zeit.*, 1912, 36, 106).—One gram of the finely-divided alloy is fused in a porcelain crucible with 10 grams of sodium peroxide; the mixture should be heated gently at first, and afterwards maintained in a molten condition for three minutes. When cold, the fused mass is dissolved in water, acidified with a large excess of hydrochloric acid, and boiled for three minutes. The solution is now treated with a small excess of zinc oxide, and titrated in the usual way with permanganate solution. The results agree with those obtained by the ordinary precipitation method.

W. P. S.

**Dimethylglyoxime as a Sensitive Reagent for Ferrous Salts.** PAUL SLAWIK (*Chem. Zeit.*, 1912, 36, 54).—If tartaric acid is added to a drop of a solution of a ferrous salt, followed by 1 c.c. of alcoholic dimethylglyoxime, and an excess of ammonia, an intense red coloration is produced, which rapidly disappears through atmospheric oxidation, but is restored by reducing agents. This is the most delicate reaction for ferrous salts. C. H. D.

**The Estimation of Ferrous Iron in Silicates.** MAX DITTRICH and A. LEONHARD (*Zeitsch. anorg. Chem.*, 1912, 74, 21—32).—When rocks and minerals are attacked by heating with sulphuric and hydrofluoric acids in absence of air, and the ferrous iron estimated by titration with permanganate, the end-point is sometimes indistinct, the coloration gradually disappearing. The effect is partly due to the presence of manganese and of hydrofluoric acid, and it has been proposed to add precipitated silica (Fromme, *Abstr.*, 1910, ii, 351). It is shown that manganese salts are without influence, but that in presence of hydrofluoric acid they increase the quantity of permanganate required. The addition of manganese salts to the solutions obtained from minerals is without influence on the titration. Good results are also obtained with ilvaite, containing 2.3% MnO, and the addition of pyrites, which has also been suggested as a source of error, does not affect the result. The cause of the irregularities is now shown to be titanium. Addition of titanous salts gives a high result on titration, and the colour disappears after a time, owing

to the action of titanous salts on ferric salts. Titanium thus occurs in some minerals and rocks in the form of  $Ti_2O_3$ .

The determination of ferrous iron in rocks is best carried out by weighing 0.8 to 1 gram of the powdered rock, with the addition of 0.5 gram of powdered quartz if necessary, heating with 2 c.c. of concentrated sulphuric acid in a platinum crucible, stirring, and adding at once 8 c.c. of hydrofluoric acid, and heating on the water-bath, covering with a short funnel, through the opening of which the stirrer passes. Ten grams of precipitated silica are then placed in a 600 c.c. beaker with 100 c.c. of water, 2 c.c. of concentrated sulphuric acid, and 23–25 grams of potassium sulphate. The crucible is emptied into the beaker and rinsed with boiled water, and the whole is rapidly titrated with  $N/10$ -permanganate. C. H. D.

**A Simple Method of Estimating Vanadium in Ferrovanadium.** PAUL SLAWIK (*Chem. Zeit.*, 1912, 36, 171).—Vanadium may be estimated, without previous removal of iron, by titration with permanganate; 0.5 gram of the alloy is dissolved in 15–20 c.c. of nitric acid, D 1.2, evaporated to dryness, baked, and taken up with hydrochloric acid and again evaporated several times. It is finally taken up with hydrochloric acid, 30 c.c. of sulphuric acid (1:2) are added, and heated until fumes are evolved. After dilution, 30 c.c. of phosphoric acid, D 1.3, are added, and the whole is diluted to 500–700 c.c., boiled, and titrated with permanganate while hot. The vanadium factor is obtained by multiplying the iron factor by 0.916. Chromium is without influence on the titration.

C. H. D.

**Volumetric Estimation of Vanadic Acid with Potassium Ferrocyanide.** ERICH MÜLLER and OTTO DIFENTHÄLER (*Zeitsch. anal. Chem.*, 1912, 51, 21–23).—Twenty c.c. of the solution containing about 0.09 gram of vanadium are mixed with 60 c.c. of molar  $N$ -potassium ferrocyanide, and then with 10 c.c. of molar  $N$ -sulphuric acid. Three grams of potassium iodide and 15 c.c. of zinc sulphate (15 grams in 100 c.c.) are next added, and, after diluting to 200 c.c., the iodine liberated by the ferricyanide formed in the reaction, which represents the vanadic acid, is titrated with  $N/20$ -thiosulphate with starch as indicator. L. DE K.

**A Modification of the Gold Dust Test.** ROLAND STERNER-RAINER (*Oesterr. Zeitsch. Berg. Huttenw.*, 1911, 59, 461–462).—Good results are obtained by dissolving the product supposed to contain gold in nitric acid (32° Bé), thoroughly boiling, and allowing to remain for some time; the liquid is then carefully poured away, water and a drop of mercury added, and the mixture boiled, when an amalgam is formed from which the gold is again separated by heating with concentrated nitric acid. F. M. G. M.

**Estimation and Elimination of Sulphur Compounds in Commercial Benzene.** J. G. ELLERTON (*J. Soc. Chem. Ind.*, 1912, 31, 10–12).—Of the many sulphur compounds occurring in com-

mercial benzene, carbon disulphide and thiophen predominate. The former may be estimated by shaking the benzene with alcoholic potassium hydroxide solution, and titrating the potassium xanthate which is formed with *N*/10-copper sulphate solution after the xanthate solution has been acidified with acetic acid; potassium ferrocyanide is used as the indicator. Thiophen is estimated by dissolving the benzene in methyl alcohol, adding a concentrated mercuric sulphate solution, collecting the precipitate, and drying it at 115° before weighing. For the estimation of the total sulphur in benzene, the latter should be diluted with alcohol and burnt in an ordinary spirit lamp, the top of which is surrounded with ammonium carbonate; the latter, together with condenser liquid, is dissolved in water, filtered, and oxidised with bromine, the resulting sulphate being then estimated in the usual way. The method yields concordant, but low, results, and the approximately correct result is found by multiplying the result obtained by 1.8. The method described by Lomax (*Abstr.*, 1906, ii, 123) yields low results. Carbon disulphide may be removed from benzene by fractional distillation, whilst thiophen is best eliminated by treatment with concentrated sulphuric acid. The latter process involves considerable loss (up to 12%) of benzene, but is far more efficient than treatment with oxidising substances, such as ozone, hydrogen peroxide, etc.

W. P. S.

**The Nitrosite of Caoutchouc and its Application in Analysis.** KURT GOTTLÖB (*Chem. Zentr.*, 1911, ii, 1712; from *Gummi-Zeit.*, 1911, 25, 1561—1562).—In reply to criticisms by Alexander (*Abstr.*, 1911, i, 389), the author asserts that he has never stated that Harries' method gives a quantitative yield of nitrosite; on the contrary, he has found that the impure nitrosites (1 and 2) do not have a uniform composition, but that, on further purification, their composition becomes approximately uniform. The employment of considerable quantities of nitrogen tetroxide leads to the formation of by-products. The author also points out that the crude nitrosite, when freed from solvent and nitrous acid, does not melt or decompose below 120°.

W. P. S.

**Estimation of Caoutchouc.** JULES BOCK (*Rev. gén. Chim. pure appl.*, 1911, 14, 209—221).—A discussion of the work of Budde, Harries, Schneider, Fendler, Jacobsen, and others, with an account of the author's experiments on the analysis of caoutchouc; he draws the conclusion that the Fendler and Kuhn modification of Budde's method is the most satisfactory, and that the preparation of tetrabromide is not influenced by the presence of resins, but is to some extent by proteins, which, however, are only detrimental when gravimetric methods of analysis are employed.

F. M. G. M.

**Detection of Methyl Alcohol** WILHELM SAILER (*Pharm. Zeit.*, 1912, 57, 93).—Into a 100 c.c. Erlenmeyer flask is placed, by way of a check, 0.5 gram of sodium salicylate and 1 gram of pure spirits of wine, and into a similar flask 0.5 gram of sodium salicylate and 1 gram of the spirit to be tested. Into both flasks are now dropped

twenty drops of sulphuric acid in four portions at an interval of one minute. If methyl alcohol is present, a perceptible odour of methyl salicylate is noticed. On adding an emulsion of 0.4 gram of quick lime in 2 c.c. of aqueous sodium hydroxide, a strong odour resembling phenyl methyl ether is developed after a minute.

L. DE K.

**The Recovery of Alcohol from Animal Tissues.** PAUL J. HANZLIK (*J. Biol. Chem.*, 1912, 11, 61—65).—The procedure differs from methods at present in use by the following points: (1) phosphoric acid is added to liberate the alcohol and facilitate the distillation; (2) the distillate is automatically filtered to remove volatile solid products which would interfere with specific gravity determinations, and (3) a modification of Anstie's ring test is made more delicate to determine the completion of the distillation. The results obtained are accurate within 1%. The dichromate-sulphuric acid test reveals the presence of alcohol in dilutions of 1 in 10,000.

W. D. H.

**The Testing of Dynamite Glycerol.** FRANZ HOFWIMMER (*Chem. Zeit.*, 1912, 36, 41—42).—Glycerol intended for the manufacture of dynamite is best tested by nitration and estimation of the quantity of glyceryl nitrate formed. An apparatus is described for the rapid performance of this test. The nitration vessel is a thin-walled cylinder, surrounded by a cooling jacket, and terminating below in a long graduated tube, provided with a tap at its lower end. The vessel is filled with nitrating acid ( $55\% \text{HNO}_3 + 45\% \text{H}_2\text{SO}_4$ ) to a mark and cooled to  $15^\circ$ , and 10 grams of the glycerol are run in slowly from a special pipette, whilst a current of dry air is bubbled through the mixture through the lower tube. When the nitration is complete, fifteen minutes are allowed for separation from the acid, and the volume of glyceryl nitrate is read.

C. H. D.

**The Estimation of Phenol and *p*-Cresol in Mixtures.** MAX SIEGFRIED and R. ZIMMERMANN (*Biochem. Zeitsch.*, 1912, 38, 434—442).—A reply to the criticisms of Ditz and Bardach (this vol., ii, 98).

S. B. S.

**Estimation of Cholesterol by Ritter's Method.** Influence of Autolysis on Cholesterol. HARRY J. CORPER (*J. Biol. Chem.*, 1912, 11, 37—45).—The presence of excess of sodium ethoxide over that necessary for saponification of fats and esters prevents a complete extraction of the cholesterol from the salt mixture by means of ether. The error may vary from 5 to 20% in the case of a normal tissue when there is an excess of from 1 to 5 c.c. of a 5% solution of sodium ethoxide used in saponifying 1—5 grams of alcohol-ether extract.

No marked change was found in the amount of cholesterol present in the dog's spleen after autolysis. The steer spleen contains about 0.4% of its moist weight as cholesterol.

W. D. H.

**Phosphotungstic Acid as a Clarifying Agent in Urine Analysis.** CLARENCE E. MAY (*J. Biol. Chem.*, 1912, 11, 81—83).—Phosphotungstic acid is advised for the removal of protein from, and

clarifying of, urine. The details of the method are different from those adopted by Oppler (this vol., ii, 100). If the urine has subsequently to be analysed for sugar, the results obtained either by Fehling's method or the polarimeter are sharp and accurate.

W. D. H.

**Composition of the Fehling [Copper] Solution.** O. LÜNING (*Chem. Zeit.*, 1912, 36, 121).—The author states that when preparing the Fehling solution there is no need, as a rule, to take the exact weights of crystallised copper sulphate (34.639 grams) and sodium hydroxide (51.6 grams per litre) as directed. These figures may safely be rounded off.

L. DE K.

**Unification of Reducing Sugar Methods. (A Correction.)** PERCY H. WALKER (*J. Amer. Chem. Soc.*, 1912, 34, 202—209).—The tables given in an earlier paper (Abstr., 1907, ii, 585) showing the relation between cuprous oxide and lactose were erroneous. The figures have therefore been re-calculated and the correct results are tabulated.

E. G.

**Volume-Condition of Alcoholic Sugar Solutions and the Indirect Determinations of the Extract.** I. and II. WILHELM FRESSENIUS and LEO. GRÜNHUT (*Zeitsch. anal. Chem.*, 1912, 51, 23—52, 104—123).—The paper is mainly devoted to a criticism of Tabarié's process and formula for the indirect estimation of alcohol and extract respectively. The formula leads to erroneous results in the case of liquids rich in alcohol or extract. In order to obtain correct results, the liquid should be freed from alcohol without previous neutralisation, and after restoring the original volume, the specific gravity is determined and the extract found by referring to a table. From this, however, should be deducted the amount, divided by 20, of any inverted sugar formed during the evaporation, that is, in excess of the amount existing originally. Another modification of the process is described, based on neutralisation, and allowing for the amount of alkali added.

L. DE K.

**A Gravimetric Method for the Estimation of Sucrose by Oxidation with Chromic Acid.** ADOLF WECHSLER (*Chem. Zentr.*, 1912, i, 163; from *Oster.-ung. Zeitsch. Zucker.-Ind. Landw.*, 40, 683—703).—The method consists in oxidising the sugar by means of a mixture made by dissolving 100 grams of chromium trioxide in 300 c.c. of water, to which solution is added 500 c.c. of concentrated sulphuric acid. The reaction is carried out in a specially designed apparatus ("oxydimeter"), and the sugar is estimated by weighing the apparatus before and after oxidation, and determining thus the loss of carbon dioxide. As substances other than sugar are oxidised in this way, the process can be employed for ascertaining whether other substances are present if the polarisation of the mixture is also carried out at the same time.

S. B. S.

**Estimation of Crystal Sugar in Raw Sugar.** ALEXANDER HERZFELD and HERMANN ZIMMERMANN (*Zeitsch. Ver. deut. Zuckerind.*, 1912, 166—183).—The existing methods for the separation of sugar

crystals from the accompanying syrup are discussed, and a method is described in detail which obviates many of the sources of error criticised. The crude sugar is agitated with at least five times its weight of a sugar solution carefully and accurately saturated at the working temperature, care being taken not to warm the vessel. The mixture is then filtered on the pump, the funnel consisting of a special metal cylinder, and the vessel and crystals washed with more of the saturated sugar solution. The funnel and its contents are run in a suitable centrifugal machine for five minutes. The sugar crystals are removed, weighed, dried, and weighed again, the sugar corresponding with the water expelled is deducted from the dry weight of the crystals. The method is still regarded as under trial ; numerous analytical results are quoted. E. F. A.

**A Spurious Reaction for Cellulose and Quinine Bark.** WALTER J. DILLING (*Pharm. J.*, 1912, [iv], 34, 30).—Two associated reactions for the detection of cellulose and true quinine bark are given in Merck's "Reagenzien Verzeichniss." The first, Batka's reaction, is stated to depend on the production of red fumes when cellulose, or related substances, such as starch, dextrin, gum, etc., is heated in a dry test-tube with any of the four common cinchona alkaloids (quinine, cinchonine, quinidine, and cinchonidine). Similarly, Grahe's reaction for the detection of quinine bark consists in heating the bark in a test-tube, when red fumes are evolved. The reaction is, however, not due to the presence of cellulose, as the red fumes are obtained when the alkaloids themselves are heated ; Batka's reaction is, therefore, of no value for the detection of cellulose, and the presence of bark is not essential to Grahe's reaction, as a spurious bark mixed with a small quantity of the alkaloids would give a similar result. W. P. S.

**Refractometric Determination of the Strength of Formaldehyde Solutions.** LODEWYK TH. REICHER and F. C. M. JANSEN (*Chem. Weekblad*, 1912, 9, 104—109).—The authors have employed the immersion refractometer and Abbe's refractometer to determine the percentage strengths of solutions of commercial formaldehyde, and give a table from which the percentage can be calculated from refractometric readings, taken at 15°. A. J. W.

**Estimation of Acetaldehyde in [Official] Paraldehyde.** R. RICHTER (*Pharm. Zeit.*, 1912, 57, 125—126. Compare Abstr., 1911, ii, 776).—The process is based on the fact that acetaldehyde reacts with sodium sulphite with liberation of sodium hydroxide ; paraldehyde is not affected.

Ten grams of the sample are dissolved in 100 c.c. of water and neutralised with *N*-alkali, with phenolphthalein as indicator. Twenty c.c. of sodium sulphite solution (25 grams of the crystallised salt in 100 c.c.) are added, and the solution is titrated with *N*-hydrochloric acid. A blank experiment is also made, using the same quantity of sodium sulphite. The difference represents the acetaldehyde ; 1 c.c. of *N*-acid equals 0.044 gram of the same. L. DE K.

**Estimation of Furfuraldehyde by means of Fehling's Solution.** LEWIS EYNON and J. HENRY LANE (*Analyst*, 1912, 37, 41—46).—Flohil (Abstr., 1911, ii, 160) estimates pentosans by means of the furfuraldehyde formed on distillation with strong hydrochloric acid. The neutralised liquid is then heated, with certain precautions, with Fehling solution, and the cuprous oxide is weighed, or the excess of copper may be estimated iodometrically.

The authors state that Flohil was wrong in assuming that the copper reduction power of furfuraldehyde is constant, namely, that 1 mol. of furfuraldehyde = 4 atoms of copper. The reduction power depends on the concentration, and the furfuraldehyde-copper ratio varies fact from 0.362 (0.01 gram of furfuraldehyde) to 0.452 (0.05 gram of same).

In using the process, therefore, reference should be made to the author's directions and tables. It is assumed that 8 grams of sodium chloride are present in the liquid, as this affects the Fehling solution. Reduction of cuprous oxide to metallic copper seems superfluous.

L. DE K.

**Reactions of Lactic Acid.** C. REICHARD (*Pharm. Zentr.-h.*, 1912, 53, 51—56).—If a small quantity of powdered potassium dichromate is placed on a glass slip and moistened with a drop of lactic acid, a brown coloration is at first obtained; the colour then changes to bluish-green, and finally to bright green. A similar green coloration is obtained with ammonium molybdate. When ammonium tungstate is moistened with lactic acid, a colourless solution is obtained, and on the addition of sulphuric acid, a gelatinous precipitate of tungstic acid is formed; this precipitate becomes tinged with blue after the lapse of about ten hours. A characteristic crystalline deposit is obtained when bismuth subnitrate is treated with lactic acid and the emulsion set aside for ten hours. Colourless crystals, mixed with red crystals, are formed when lactic acid and cobalt nitrate solution are heated together and then cooled. Reactions of lactic acid with many other substances are also described.

W. P. S.

**Colorimetric Estimation of Salicylic Acid and Copper.** F. SCHOTT (*Zeitsch. Nahr. Genussm.*, 1911, 22, 727—728).—*Salicylic Acid.*—In small tubes of the same diameter and marked at 5 c.c. are introduced the liquid to be tested, and varying quantities (0, 0.2, 0.4, 0.6, 0.8, 1.0 c.c.) of a solution containing 0.1 gram of salicylic acid per litre. After adding 2 c.c. of Fehling's copper sulphate solution (ten times diluted), five drops of 2% potassium nitrite solution, and five drops of 10% acetic acid, the solutions are made up to the mark, and heated for forty-five minutes in the water-bath. After cooling, the tubes are compared as to colour. When applying the process to milk, 25 c.c. of the sample are mixed with 10 c.c. of Fehling's copper solution, and so much *N*-sodium hydroxide that the solution is only very feebly acid (1.5—2 c.c.); 15 c.c. of the filtrate are then mixed with five drops of 10% potassium nitrite and five drops of 50% acetic acid, and treated as directed. As comparison fluids various amounts of a solution of salicylic acid (0.16 gram per litre) are used.

*Copper*.—The reverse process is employed. As comparison liquids are used various quantities of copper sulphate solution (0.1 gram of Cu per litre). To cause the red colour to appear, 0.3 c.c. of 0.5% dilute alcoholic solution of salicylic acid is added, also five drops of 2% potassium nitrite and five drops of 10% acetic acid are added, and, after diluting up to the mark, the tubes are heated in the water-bath as directed.

L. DE K.

**A Biochemical Method for the Determination of Small Quantities of Salicylic Acid in the Presence of an Excess of *p*-Hydroxybenzoic Acid.** JACOB BÖSEKEN and H. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 604—607).—The authors find that whilst *p*-(and also *m*)-hydroxybenzoic acid can be used as carbon nutriment by *Penicillium glaucum*, the presence of salicylic acid in quantities of more than 1% causes a retardation in the growth of the organism.

By comparing the effect on *Penicillium glaucum* of the mixture under investigation with that of standard mixtures of salicylic acid and *p*-hydroxybenzoic acid, they claim to be able to determine, with an accuracy of a trifle over 1%, quantities of salicylic acid varying from 1 to 10% in an excess of *p*-hydroxybenzoic acid.

H. W.

**Estimation of Glycyrrhizic Acid in Commercial Ammonium Glycyrrhizates.** H. CORMIMBEUF (*Ann. Chim. anal.*, 1912, 17, 47—50).—Two grams of the sample are dissolved in 50 c.c. of hot water, the insoluble matter is collected on a filter, and washed with 50 c.c. of hot water. To the filtrate and washings are added 5 c.c. of *N*/1-sulphuric acid, and, after the lapse of twelve hours, the liquid is decanted through a filter and the precipitated glycyrrhizic acid washed by decantation, small quantities of water being used. The filtrate is now evaporated almost to dryness, the residual solution is mixed with a small quantity of water, and the further quantity of glycyrrhizic acid thus obtained is collected on a filter and washed. Both precipitates are then dissolved in ammonia, the united solutions are evaporated to dryness, the residue is dried at 100°, and weighed. The amount of gums present in the sample may be estimated by rendering the filtrate from glycyrrhizic acid ammoniacal, evaporating the solution, and drying the residue to constant weight. The 5 c.c. of *N*/1-sulphuric acid yield 0.330 gram of ammonium sulphate, and this quantity is subtracted from the weight of the residue so as to obtain the actual weight of the gums.

W. P. S.

**Detection of Added Water in Milk (Detection of Nitrates).** J. TILMANS (*Chem. Zeit.*, 1912, 36, 81).—The presence of added water containing nitrates may be detected in milk by shaking 5 c.c. of the sample with about 20 c.c. of a solution of diphenylamine in sulphuric acid. Should the milk contain more than 3 mg. of nitric acid ( $N_2O_5$ ) per litre, a green coloration is obtained. Milk free from nitrates yields a pink or yellowish-red coloration.

W. P. S.

**New Method of Determining the Melting Points of Fats.** RÉMY PROUZERGUE (*Ann. Chim. anal.*, 1912, 17, 56—58).—The lower end of a glass tube, 5 mm. in diameter, is drawn out into a fine jet which is filled with the molten fat. When the fat has solidified in the jet, the tube is about one-half filled with water, to which a few drops of phenolphthalein solution have been added, and the tube is attached to a thermometer which is immersed in a very dilute sodium hydroxide solution contained in a test-tube. The latter is then placed in a beaker of water, and the temperature is raised gradually. When the melting point of the fat is reached, the alkaline solution in the test-tube flows upwards past the melted fat in the jet, and produces a red coloration with the phenolphthalein in the narrow tube. W. P. S.

**Testing Lecithin.** SEIDLER (*Chem. Zentr.*, 1911, ii, 1885; from *Apoth. Zeit.* 1911, 26, 912—913).—The test described by Casanova (*Abstr.*, 1911, ii, 673) is not practicable, as the ethereal solution does not mix with the ammonium molybdate solution. It is recommended that a small portion of the substance should be mixed with ammonium molybdate solution, and then poured on the surface of concentrated sulphuric acid. If lecithin is present in the substance, a blue coloration is obtained immediately. W. P. S.

**Analysis of Lecithin.** SATTLER (*Chem. Zentr.*, 1911, ii, 1885; from *Apoth. Zeit.*, 1911, 26, 930).—A method, proposed by Thierfelder, is recommended for the estimation of phosphorus in lecithin. A quantity of about 0.5 gram of the lecithin is heated with 20 c.c. of a mixture consisting of equal volumes of sulphuric and nitric acids; afterwards 20 c.c. of nitric acid are added drop by drop, and the mixture is heated to remove the excess of nitric acid. The solution is then diluted with 150 c.c. of water, 50 c.c. of 50% ammonium nitrate solution are added, and the phosphoric acid is precipitated with ammonium molybdate solution. The precipitate is washed by decantation until the greater part of the acid has been removed, then dissolved in a definite quantity of  $N/2$ -sodium hydroxide solution, the ammonia is expelled by boiling the mixture, and the excess of alkali is titrated. The number of c.c. of  $N/2$ -sodium hydroxide solution used, when multiplied by 0.554, gives the amount (in mg.) of phosphorus present. W. P. S.

**The Proposed Method of Micro-sublimation for the Detection of Æsculin and the Identification of Gelsemium.** FRANK TUTIN (*Pharm. J.*, 1912, [iv], 34, 157).—Chiefly a criticism of a paper published recently by Tunmann (compare this vol., ii, 104). It is shown that gelsemium does not contain æsculin, and that the sublimate obtained by Tunmann from gelsemium must have consisted of scopoletin (compare *Trans.*, 1910, 2223; 1911, 1043). Scopoletin yields a distinctly crystalline sublimate at a temperature of 150°, whilst æsculin gives a slight tarry sublimate; on raising the temperature, æsculin gradually decomposes, giving a further quantity of tarry sublimate together with crystals of æsculetin. Æsculin was found to have *m. p.* 200—202°. W. P. S.

**Estimation of Mustard Oil in Feeding Cakes and in Mustard.** CH. BRIOUX (*Ann. Chim. anal.*, 1912, 17, 3—9).—Twenty-five grams of the cake or mustard are heated with 500 c.c. of water in a flask for one hour at 37°, 2 grams of sodium fluoride being also added to inhibit the action of micro-organisms. After the addition of 25 c.c. of alcohol, the mixture is distilled, 150 c.c. of distillate being collected in a 250 c.c. flask containing 10 c.c. of ammonia. The ammoniacal distillate is then treated with 50 c.c. of *N*/10-silver nitrate solution, heated for one hour to a temperature of 80°, cooled, and diluted with water to a volume of 250 c.c. After filtration, 125 c.c. of the filtrate are acidified with nitric acid, and the excess of silver is titrated in the usual way with thiocyanate solution. One molecule of crotonylthiocarbimide yields 1 molecule of silver sulphide, and the amount of the mustard oil (as crotonylthiocarbimide) may, therefore, be calculated from the quantity of silver used. Rape seed cakes were found to contain from 0.50 to 0.86% of crotonylthiocarbimide.

W. P. S.

**Colour Reactions of Amino-compounds in Presence of Mineral Acids and Potassium Dichromate.** HENRI AGULHON and PIERRE THOMAS (*Bull. Soc. chim.*, 1912, [iv], 11, 69—73).—The behaviour of a long series of amino-compounds with (a) sulphuric acid and potassium dichromate and (b) nitric acid and potassium dichromate, has been examined with a view to ascertaining whether these reagents can be used to distinguish between various classes of amino-compounds (compare *Abstr.*, 1911, ii, 1140).

The first reagent, at 100°, divides amino-compounds into four main groups, namely, those which give (1) no coloration, (2) a bright green tint, (3) an olive-green colour, (4) a brownish-green solution, with a few which give brown or reddish colours. The following general conclusions are drawn. The oxidisability of amino-compounds is a function of the number of carbon atoms in the molecule, for example, among the aliphatic amines all below diethylamine give no coloration. The presence of the group  $\text{NH}_2 \cdot \text{CO}_2\text{H}$  renders the compound less liable to oxidation. The presence of a benzene ring leads to the formation of an olive or brownish-green colour.

With the second reagent, only glucosamine gives a coloration in the cold, and comparatively complex amines only give a coloration on warming at 100°.

In the purine group, adenine, hypoxanthine, and parabanic acid give no coloration with either reagent; xanthine, guanine, and allantoin give a green with the first reagent at 100°; uric acid, theobromine, caffeine, and alloxan give colours with the first reagent both in the cold and at 100°, and dialuric acid and alloxanthine give colours with the first reagent in the cold and at 100°, and also at 100° with the second reagent.

T. A. H.

## General and Physical Chemistry.

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The "Constant of Refraction." F. SCHWERS (*Bull. Acad. roy. Belg.*, 1912, 55—80. Compare Abstr., 1910, ii, 913; 1911, ii, 92, 949).—The value of  $A$  in the equation  $C_n = AC_v$  has been calculated, from figures recorded by other observers, for non-aqueous binary mixtures. It varies from one system to another, as in the case of aqueous mixtures, and diminishes slightly with diminution in the wave-length of the light used. The values of  $A$  are, in general, very different from those obtained for aqueous solutions, and are often less than unity. In most of the examples quoted, carbon disulphide was one of the liquids in the mixture, although figures are also given for alcoholic solutions, mixtures of two acids, and mixtures of two liquids of the cyclic series. The author criticises the work of, and values recorded by, Zecchini (compare Abstr., 1897, ii, 470). W. G.

Molecular Refraction, Molecular Volume, and Dissociation in Non-aqueous Solvents. FRITZ RÖHRS (*Ann. Physik*, 1912, [iv], 37, 289—329).—Measurements have been made of the densities and refractive indices of solutions of potassium iodide, cadmium iodide, succinic acid, and mercuric chloride in ethyl alcohol, and of the three former substances in acetone. For the density determinations the displacement method was employed, and it has been found that this affords results of the same degree of accuracy as are obtained in the case of aqueous solutions. Hallwachs's double cell refractometer method was used in the optical measurements, the results thus obtained being accurate to about 0.03%.

As the solutions are diluted, the molecular volume of the dissolved substance diminishes, the falling off being more marked than in aqueous solutions. This diminution is attributed to increasing ionisation.

In a similar way, the molecular refraction of the various substances increases very considerably as the dilution is increased. This variation in the refractivity is probably conditioned by the corresponding change in the molecular volume, and is therefore only indirectly due to the alteration in the degree of ionisation of the solute.

Reference is made to the two groups which are obtained when the differences between the refractivities of acid and their sodium salts are compared. For the weak acids these differences are much greater than for the strong acids. It is shown that the differences in the volume relationships are essentially responsible for the differences in question. H. M. D.

Molecular Refractions of Organic Compounds for Light of Infinite Wave-length. DIMITRI K. DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1—65. Compare Abstr., 1910, ii, 93, 94; 1911, ii, 458).—The author has calculated the molecular refraction for light of infinite wave-length for several hundreds of organic compounds of

different types by means of the formula  $M(K-1)/(K+2)D$ , where  $M$  is the molecular weight and  $K$  the dielectric constant. The values of  $K$  and  $D$  are taken partly from his own measurements and partly from those of other authors. The investigation represents an extension of that of Landolt and Jahn (Abstr., 1893, ii, 57) and Jahn and Moeller (Abstr., 1894, ii, 265).

A large number of detailed conclusions are drawn from the numbers obtained, the principal ones being as follows.

The molecular refraction for light of infinite wave-length exhibits a marked constitutive character, so that the corresponding atomic refractions for the various elements are by no means constant in value. Additive character is very faintly shown, and is much less appreciable than with the molecular refraction for  $D$ - or  $\alpha$ -light.

The increase of  $MR_{\infty}$  corresponding with the increment of  $\text{CH}_2$  in homologous series varies widely in different series, and does not always remain constant in one and the same series. As a rough approximation, it may be said that the values of this increase approach either the value 6—8 ("small difference") found in the case of esters or the value 12 ("large difference") found for the ketone series. Sometimes such values as double the large difference or half the small difference are found, but intermediate numbers rarely occur.

The influence of unsaturation on the value of  $MR_{\infty}$  seldom corresponds with that observed with  $MR_D$  or  $MR_{\alpha}$ . In benzene the three double linkings have virtually no effect, but in other cases unsaturation nearly always produces a negative effect.

No two isomerides are known with identical values of  $MR_{\infty}$ , and isomerism exerts considerable influence on this magnitude, this influence being, in general, similar to that observed with the dielectric constant itself (*loc. cit.*).

T. H. P.

**Refractometric Investigations.** JOHAN F. EYKMAN (*Chem. Weekblad*, 1911, 8, 651—667. Compare Abstr., 1909, i, 718).—A large number of organic compounds, chiefly ring compounds, have been prepared in a pure condition, their refractivities for a number of lines have been measured, and the refraction constants calculated according to the formulæ of Gladstone and Dale, of Lorenz and Lorentz, and of the author. Below are given the names of the compounds investigated, their densities, boiling and melting points where given (some of the compounds have not previously been prepared in a pure condition), and the molecular refraction constants for the  $\alpha$ -line,  $MR_{\alpha}$ , calculated according to the Lorenz formula.

1 : 4-Dimethylcyclohexane, m. p.  $-32^{\circ}$  to  $-33^{\circ}$ , b. p.  $120.0$ — $120.2^{\circ}$ /768 mm,  $D^{22.2}$   $0.7620$ ,  $MR_{\alpha}$   $37.067$ ; 1 : 3 : 5-trimethylcyclohexane, m. p. about  $-50^{\circ}$ , b. p.  $136$ — $140^{\circ}$ ,  $D^{15.7}$   $0.7744$ ,  $MR_{\alpha}$   $41.760$ ; 1 : 2-dimethylcyclohexane, b. p.  $124.5^{\circ}$ /731 mm.,  $D^{14.25}$   $0.7880$ ,  $MR_{\alpha}$   $36.816$ ; 1 : 2 : 4-trimethylcyclohexane, b. p.  $141.5$ — $143^{\circ}$ /759 mm.,  $MR_{\alpha}$   $41.538$ ; pulegane, b. p.  $141.5$ — $142^{\circ}$ /758 mm.,  $D^{15.2}$   $0.7799$ ,  $MR_{\alpha}$   $41.518$ ; cyclopentanecarboxylic acid, m. p.  $3.5^{\circ}$ , b. p.  $92$ — $93^{\circ}$ /7 mm.,  $D^{15.5}$   $1.0555$ ,  $MR_{\alpha}$   $29.207$  (compare Perkin, *Trans.*, 1894, 65, 99); cyclopentylacetic acid,  $D^{34.0}$   $1.0083$ ,  $MR_{\alpha}$   $33.840$ ; cyclohexanecarboxylic acid,  $D^{33.8}$   $1.0258$ ,  $MR_{\alpha}$   $33.801$ ; cyclohexylacetic acid,  $D^{33.5}$   $1.0012$ ,  $MR_{\alpha}$   $38.468$ ; heptoic

acid,  $D^{34.0}$  0.90565,  $MR_a$  36.006; *cyclobutanecarboxylic acid*, m. p.  $-2^\circ$ , b. p.  $74-75^\circ/2-2.5$  mm.,  $D^{14.4}$  1.0656,  $MR_a$  24.953; *pinic acid*,  $D^{109.4}$  1.0925,  $MR_a$  45.384; *azelaic acid*,  $D^{110.6}$  1.0291,  $MR_a$  47.008; *l-pinonic acid*, m. p.  $99^\circ$ ,  $D^{110.7}$  1.0257,  $MR_a$  47.86;  $\alpha$ -pinonic acid, m. p.  $105^\circ$ ,  $D^{109.1}$  0.9975,  $MR_a$  48.434;  $\alpha$ -thujaketonic acid,  $D^{79.6}$  1.0115,  $MR_a$  48.648; *pulegenic acid*,  $D^{17.5}$  1.0036,  $MR_a$  47.543; *puleganic acid*, m. p.  $-18^\circ$  to  $-19^\circ$ ,  $D^{80.4}$  0.9169,  $MR_a$  47.852; *ethyl puleganate*, b. p.  $145^\circ/4$  mm.,  $D^{11.8}$  0.9178,  $MR_a$  56.909; *puleganonitrile*,  $D^{16.2}$  0.8814,  $MR_a$  45.820; *puleganolactone*,  $D^{21}$  1.0146,  $MR_a$  45.391;  $\Delta^{4:8}$ -menthen-1-ol,  $D^{80}$  0.8948,  $MR_a$  47.378;  $\Delta^{3:9}$ -menthen-1-ol,  $D^{79.8}$  0.8703,  $MR_a$  47.198; *fenchone*,  $D^{14.5}$  0.9488,  $MR_a$  44.068;  $\alpha$ -fencholeneamide,  $D^{17.9}$  0.9331,  $MR_a$  49.216;  $\beta$ -fencholenic acid, m. p.  $68^\circ$ ,  $D^{76.1}$  0.9638,  $MR_a$  47.617;  $\beta$ -fencholamide,  $D^{108.2}$  0.9072,  $MR_a$  49.758; *fencholic acid*, m. p.  $18.8^\circ$ , b. p.  $119-120^\circ/1$  mm.,  $MR_a$  47.531.

Some of the conclusions drawn from the optical data are as follows. A comparison of the methylcyclohexanes with their homologues show that in these compounds the increment in the refraction constant for  $CH_2$  is normal (about 4.6 according to the Lorenz formula). The data given for the next series of compounds (the pentyl and hexyl acids) shows that the carboxyl group with the five and six-membered rings and the  $CH_2 \cdot CO_2H$ -group associated with the five-membered ring brings about no optical exaltation which is not already present in the corresponding aliphatic acids. The high values for the optical constant of  $\alpha$ -pinonic acid, as compared with that for *l*-pinonic acid, confirm the view of Bayer that the former contains a *cyclobutane* ring. The results obtained with the terpeneols (menthenols) prove that in the case of a semicyclic double bond the ring is to be brought into calculation as two side-chains. The conclusion of Brühl, that ring-closing has practically no effect on the value of the optical constants is discussed.


1 : 2- and 1 : 4-Dimethylcyclohexanes as well as 1 : 3 : 5- and 1 : 2 : 4-trimethylcyclohexanes were prepared by hydrogenating the corresponding hydrocarbons in presence of nickel. Pulegane (1-methyl-3-*isopropylcyclopentane*) was obtained as a by-product in the conversion of pulegenic acid into puleganic acid by hydrogenation. The following derivatives of puleganic acid are also described: *chloride*, b. p.  $89-90^\circ/11$  mm.; *amide*, m. p.  $147^\circ$ ; *anilide*, m. p.  $149-150^\circ$ . *cyclopentanecarboxylic acid* was prepared by eliminating the elements of water from *cyclopentane-2-olcarboxylic acid* and hydrogenation of the resulting *cyclopentanecarboxylic acid* in presence of nickel at  $170-175^\circ$ . *cyclobutanecarboxylic acid* was obtained by condensing ethyl disodiummalonate with trimethylene bromide, saponifying the ethyl *cyclobutanedicarboxylate*, and distilling the resulting acid.


G. S.

**Spectro-chemistry of Nitrogen. VII.** JULIUS W. BRÜHL (*Zeitsch. physikal. Chem.*, 1912, 79, 1—54. Compare Abstr., 1898 ii, 362, 417).—The author's investigations on the spectro-chemistry of nitrogen compounds are now extended to unsaturated compounds, and to compounds the constitution of which is analogous to that of aromatic compounds. For the numerical data as to the molecular

refractivities for the  $\alpha$ -hydrogen and  $D$ -lines, and the molecular dispersion  $M_\gamma - M_\alpha$  of a large number of compounds, the original paper must be consulted.

The first table contains a summary of the data for homologous series of compounds of the pyrazine, pyridine, piperidine, ketazine, and other groups, and it is shown that the alicyclic compounds, such as the piperidines, the unsaturated homologous compounds of linear structure, and also the cyclic uninuclear compounds, all have approximately the normal value for the increment  $\text{CH}_2$  (about 4.6 for  $M_\alpha$  and 0.11 for the dispersion  $M_\gamma - M_\alpha$ ). Multinuclear nitrogen compounds, such as the quinoxalines, phenyleneamidines, and quinolines, have rather higher refraction increments and higher dispersion increments for the  $\text{CH}_2$  group.

The second table contains the data for thirteen groups of isomeric compounds, and the conclusions which can be drawn as to the constitution of the compounds are discussed in detail. Many of the cases of isomerism have been dealt with in previous papers. The results confirm the previous rule as to the very slight optical effect of ring formation. From a comparison of the refractivities of pyridazine, pyrazine, and ethylene cyanide, the conclusion is drawn that the formula  is the only possible one for pyridazine, and

 is the most probable formula for pyrazine.

The third table contains data which permit of the calculation of the constants for nitrogen doubly bound to carbon (the carbim group  $\text{N}=\text{C}$ ). In general, the nitrogen of this group in open chains, in which it is not conjugated with other unsaturated groups, has smaller refraction and dispersion values than when the carbim group is conjugated. The atomic functions of the nitrogen of unconjugated carbim compounds are approximately equal for the ketoximes, aldioximes, alkylalkylideneamines, and dialkylimines (that is, in the combinations  $\text{O}-\text{N}=\text{C}$  and  $\text{C}-\text{N}=\text{C}$ ), but if the third valency of the carbim C atom is satisfied with hydrogen, as in the imino-ethers, the optical values for the nitrogen are smaller than for the above compounds; when the place of the hydrogen is taken by a halogen the refractivity of the nitrogen, and especially the dispersion, again increase. The magnitude of the refractivity of the nitrogen in the conjugated carbim group also depends on the nature of the group with which it is conjugated.

The last section of the paper deals with the optical effect of ring closing in unsaturated heterocyclic systems. As the optical properties of the nitrogen and of the ethylene linkings cannot easily be determined separately in these compounds, it is necessary to assume that one of these is constant, and ascribe the whole of the variation to the other. Assuming that the value for the nitrogen is constant, the value of the double bond in the heterocyclic compounds is much smaller than the normal value. Similarly, the refractivity of the  $\text{C}=\text{N}$  linking in the heterocyclic compounds is smaller than the

normal value, so that heterocyclic ring-closing has a depressing effect on the refractivity. G. S.

**Investigation of Mercury Lines. Structure. Changes in the Lines and Spectrum on Dilution of the Metal Vapour. Zeeman Effect in Weak and Strong Fields.** G. WENDT (*Ann. Physik*, 1912, [iv], 37, 535—560).—Wave-length difference measurements have been made in the grating and prism spectra of mercury in order to ascertain the relative positions of the chief lines and their satellites. The measurements extend over the visible and ultra-violet region from  $\lambda=2967$  to  $\lambda=5804$ . The changes in the character of the spectrum due to varying pressure of the mercury vapour and the foreign gas present in the discharge tube or mercury lamp and those due to the action of a magnetic field have also been examined.

H. M. D.

**Absorption and Refraction Methods in Relation to Ethyl Acetoacetate.** ARTHUR HANTZSCH (*Ber.*, 1912, 45, 559—567).—A reply to Auwer's criticism (this vol., ii, 4) of the author's previous work (*Abstr.*, 1910, i, 811). The superiority of absorption methods over refractometric measurements in dealing with tautomeric problems is emphasised, and illustrated by reference to the absorption spectra of ethyl dimethylacetoacetate, ethyl diethylacetoacetate, and ethyl  $\beta$ -ethoxycrotonate. F. B.

**Significance of the Absorption Method for the Chemistry of the Terpenes.** ARTHUR HANTZSCH (*Ber.*, 1912, 45, 553—559).—The author shows that the purity of the terpenes is best controlled, and the compounds themselves best characterised, by means of their ultra-violet absorption spectra. When the terpenes are not quite pure, fractions differing in b. p. by only  $0.1^\circ$  often show considerable differences in the form and position of their absorption curves. The absorption curves of the following compounds in alcoholic solution are recorded:  $\alpha$ -pinene, *d*- and *l*-limonene, dipentene, *l*- $\alpha$ -phellandrene,  $\beta$ -phellandrene, sylvestrene, caryophyllene, *m*- and *p*-cymene, *d*- and *l*-camphor, *d*- and *l*-borneol, *d*- and *l*-laurinol.

It is found that all these substances, with the exception of *m*- and *p*-cymene,  $\alpha$ -phellandrene, *d*- and *l*-laurinol, and caryophyllene, show general absorption, and that solutions of the terpenes and camphors do not conform to Beer's law, the absorption of equimolecular solutions increasing slightly with the dilution. Further, the results confirm the conclusion of Crymble, Stewart, Wright, and Rea (*Trans.*, 1911, 99, 1269) that the power of absorption increases as the contiguity of the double linkings becomes more pronounced.

Dipentene, *d*-, *l*-, and *i*-limonene show slight differences in their absorption curves, but these are probably due to the presence of difficultly removable impurities. F. B.

**Photographic Determination of the Intensity Distribution in Blood Spectra.** WOLFGANG HEUBNER and H. ROSENBERG (*Biochem. Zeitsch.*, 1912, 38, 345—384).—A photographic method of estimating

the relative intensity of the absorption of light of different wave-lengths in the blood absorption bands is described, and the results obtained in the examination of normal blood from different sources are recorded. The method depends on the photometric estimation of the light which is transmitted by the negative on which the absorption spectrum has been suitably recorded and developed. When proper precautions are taken, the extinction of the light by the precipitated silver affords a measure of the extent to which the colouring matter of the blood has absorbed light of different wave-lengths.

Normal blood from rabbits, sheep, and pigs was found to have the same intensity distribution within the limits of error of the measurements.

Observations relating to the spectrum of methæmoglobin are also recorded. The absorption maxima are slightly displaced in comparison with those of the oxyhæmoglobin bands. H. M. D.

**Influence of Fluorescence on Ionisation by Collision.** J. FRANCK and W. WESTPHAL (*Ber. Deut. physikal. Ges.*, 1912, 14, 159—166).—Experiments are described which show that the intensity of the glow discharge current through iodine vapour is increased to a considerable extent when the vapour is caused to fluoresce under the influence of light rays. In agreement with previous observations, it is found that the fluorescence is not accompanied by any measurable amount of ionisation, and to explain the variation in the intensity of the current of the glow discharge, it is supposed that the energy of the vibrating electrons is increased by the light energy absorbed in such a way that many more ions are produced by collision when the discharge is passed through the fluorescing vapour as compared with the number produced in the case of the non-illuminated vapour. H. M. D.

**Rotatory Power of Electrolytes. I and II.** CORRADO BONGIOVANNI (*Gazzetta*, 1912, 42, i, 179—185, 194—196).—The ions of optically active electrolytes have not a distinct rotatory power of their own, because the author finds that the rotatory power of a solution of an optically active electrolyte is not altered when it is treated with a second electrolyte having a common ion. The author's experiments were effected with normal potassium tartrate with addition of potassium nitrate or potassium sulphate, potassium sodium tartrate with addition of potassium sulphate, quinine sulphate with addition of potassium sulphate, quinine dihydrochloride with addition of calcium chloride, quinine dihydrochloride with addition of quinine sulphate.

R. V. S.

**Chemical Changes Produced by Different Kinds of Rays.** V. CARL NEUBERG (*Biochem. Zeitsch.*, 1912, 39, 158—166).—As various authors have described changes in chemical substances in the light from quartz lamps which the author has not succeeded in producing in sunlight in the absence of catalysts, it was thought that the differences were due to the differences in the rays from the two sources. Under "physiological conditions," however, the author has also failed to produce such effects with rays from quartz lamps.

In all cases, in the presence of catalysts, especially iron salts, marked changes have been produced. The substances investigated were dextrose, sucrose, and lactic and benzoic acids. S. B. S.

**The Transformation of Energy in Photochemical Changes in Gases.** II. EMIL WARBURG (*Sitzungsber. K. Akad. Wiss. Berlin*, 1912, 216—225. Compare Abstr., 1911, ii, 834).—Under the influence of the silent discharge, ammonia ceases to be decomposed when the proportion of undecomposed gas has fallen to 5.6%. Since nitrogen and hydrogen do not absorb rays of wave-length smaller than  $\lambda = 0.2\mu$ , it was to be expected that this equilibrium condition would not be attained in the action of short-waved rays on ammonia or its mixtures with  $N_2 + 3H_2$ . Experiments made with a mixture containing 4.9% of ammonia show that this is actually the case, and that the photochemical yield is not much smaller for this mixture than for pure ammonia.

The formation of ozone from oxygen under the influence of these rays has also been examined. At a pressure of 100—150 kilograms per square cm., rays of wave-length  $\lambda = 0.2\mu$  are almost completely absorbed by oxygen in passing through a column two cms. long. Of the absorbed radiant energy, 46% is used up in the production of ozone. On the basis of Einstein's theory of energy quanta, the calculated proportion of the absorbed energy which is photochemically effective amounts to 50%. H. M. D.

**A Connexion between Chemical Energy and Optical Frequency.** JOHANNES STARK (*Ber. Deut. physikal. Ges.*, 1912, 14, 119—122).—Polemical against Haber (*ibid.*, 1911, 13, 1117). H. M. D.

**Alloys and Electrolytic Depositions of Radium.** FRÉDÉRIC DE MARE and CHARLES JACOBS (*Bull. Acad. roy. Belg.*, 1912, 53—54).—By heating a mixture of radium sulphate, silver chloride, calcium carbonate, and carbon, in a Fletcher furnace, a yellowish-white, silver-radium alloy was obtained, which exhibited marked radioactivity. On electrolysing a solution of radium acetate, using platinum electrodes, a brown deposit was formed at the cathode, which was very radioactive.

By other experiments the authors show that quartz is traversed by the luminous radiations emitted from a radium salt, but not by the  $\alpha$ -,  $\beta$ -, or  $\gamma$ -rays. W. G.

**Secondary Radiation in Gases for Primary Rays in the Neighbourhood of the Optimum Velocity.** WALTHER KOSSEL (*Ann. Physik*, 1912, [iv], 37, 393—424).—The author has investigated the amount of the secondary radiation which is emitted by air and other gases when acted on by primary cathode rays of 200 to 1000 volts. In the case of a particular gas, the number of secondary electrons which are liberated by a primary ray over a given length of path is proportional to the pressure of the gas. The relationship between the secondary ray production and the absorption of the primary rays of different velocities depends very largely on the speed of the

primary electrons. As the speed diminishes, the absorption increases in a continuous manner, the rate of increase becoming greater and greater as the speed of the primary ray is reduced. On the other hand, although the secondary ray production follows a similar course at first, a maximum is reached at a certain speed of the primary ray, and further reduction of the speed leads to a rapid falling off in the amount of the secondary radiation.

Experiments with different gases (air, carbon monoxide, carbon dioxide, nitrogen, sulphur dioxide, and helium) show that at 1000 volts, the secondary ray production is determined solely by the density of the gas. Hydrogen forms an exception, the number of secondary electrons emitted being four times as large as corresponds with the density. The abnormal behaviour of hydrogen is also exhibited in its compounds, as is shown by the experimental data for methane.

H. M. D.

**Energy of the Electrons Emitted by Glowing Calcium Oxide.** HANS SCHNEIDER (*Ann. Physik*, 1912, [iv], 37, 569—593).—The energy change, which is associated with the emission of electrons by strongly heated calcium oxide, has been measured at a series of temperatures between 1100° and 1350°. The method employed depends on the measurement of the extra electrical energy which must be supplied to a platinum-iridium wire, covered with a thin layer of the oxide, in order to compensate for the loss of energy due to the emission effect. At all temperatures the values obtained for the energy of emission are considerably greater than those calculated from the theory developed by Richardson, and the observed effect increases more rapidly with the temperature than would be anticipated on the basis of theory. A comparison is made between the energy of electron emission and the energy of radiation of a black body at the same temperature, and it is found that the former increases with the temperature much more rapidly than the latter.

H. M. D.

**The Characteristic Homogeneous Röntgen Radiation from Elements of High Atomic Weight.** J. CROSBY CHAPMAN (*Proc. Camb. Phil. Soc.*, 1912, 16, 399—404).—Experiments are described which show that when penetrating X-rays are allowed to fall on lead, it emits a characteristic homogeneous radiation. When the superposed scattered radiation is allowed for, the absorption of these rays by aluminium is in almost perfect agreement with the exponential formula. The percentage absorption of the rays by 0.0067 cm. of aluminium is 26.2 and  $\lambda/\rho = 17.4$ .

A comparison of the absorption of the rays from different secondary radiators by aluminium and lead shows that the homogeneous radiation emitted by lead has the same properties as those of the elements of lower atomic weight. In accordance with this it is found that the rays from selenium ( $\lambda/\rho = 18.9$ ) are unable to excite the characteristic lead rays, whilst the rays from bromine ( $\lambda/\rho = 16.3$ ) possess this property. The curve showing the relation between the absorption in aluminium and the relative absorption in lead commences therefore to rise between selenium and bromine.

From these results it appears that the elements of high atomic weight behave similarly to those of the group which has already been investigated in detail. H. M. D.

**Theory of the Photo-electric Current in Gases.** A. PARTZSCH (*Ber. Deut. physikal. Ges.*, 1912, 14, 60—73).—It is shown that the proportion of the electrons leaving the negative electrode which reach the positive pole is not determined by the distance  $l$  between the parallel plates, but by the reduced distance  $l(1 - V/v)$ , in which  $V$  represents the potential difference required for ionisation, and  $v$  the actual potential difference between the electrodes. The formulæ given by Townsend for the photo-electric current are modified by introduction of this correction factor.

Measurements have been made of  $NV$  and  $V$ , where  $N$  is the number of collisions experienced by an ion in traversing a distance of one centimetre in a gas at a pressure of one millimetre of mercury. According to Stoletow's law,  $NV$  should be the same for different gases. The values obtained for air, nitrogen, hydrogen, oxygen, and carbon dioxide respectively are as follows:  $NV$  340, 346, 153, 268, and 380;  $V$  27.1, 27.9, 27.8, 23.9, and 23.5. The mean ionisation potential is, therefore, very nearly the same for air, nitrogen, and hydrogen, but is distinctly smaller for oxygen and carbon dioxide. The smaller potential in these cases is supposed to be connected with their electro-negative character. From the value of  $N$ , it appears that the free path of an ion is about eleven times as large as the free path of a molecule.

For mixtures of nitrogen and hydrogen,  $NV$  does not vary linearly with the percentage composition of the mixture. H. M. D.

**The Selective Photo-electric Effect of Lithium and Sodium.** ROBERT POHL and P. FRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1912, 14, 46—59. Compare Abstr., 1910, ii, 379, 472, 922; 1911, ii, 787).—A method is described by which a metallic lithium surface has been obtained which shows the existence of a selective photo-electric effect similar to that which has been already observed in the case of sodium, potassium, and rubidium. The method consists in distilling the lithium in a vacuum from an electrically heated iron crucible and condensing the vapour on a water-cooled platinum plate or dish. Sodium surfaces can be obtained in the same way, and for both metals the dependence of the photo-electric current on the wave-length of the incident light has been examined in detail. From the resonance curves, it is found that the maximum for lithium is at about  $\lambda = 280\mu\mu$ , and that for sodium at about  $\lambda = 340\mu\mu$ . The curves obtained in different experiments with metal surfaces produced in slightly different ways are not coincident, and this circumstance leads the authors to the conclusion that the accuracy with which the maxima have been determined up to the present is not greater than about  $\pm 10\mu\mu$ . H. M. D.

**Photo-electric Phenomena with Antimony Sulphide (Antimonite).** J. OLIE, jun., and HUGO R. KRUYT (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 14, 740—743).—According to Jaeger (Abstr., 1907,

ii, 923), Japanese antimonite resembles selenium in regard to the sensitiveness of its electrical conducting power to light.

Other less pure specimens of antimonite do not exhibit this property, and the authors have, therefore, prepared pure antimony sulphide by heating the constituents in exhausted tubes at about  $600^{\circ}$  with the object of testing its conducting properties. Photo-electrically sensitive products are readily obtained in this way, and the maximum degree of sensitiveness is reached when the antimony and sulphur are present in the exact proportion required by the formula,  $\text{Sb}_2\text{S}_3$ . This sensitiveness is of the same order as that exhibited by Japanese antimonite. The rapid change in the photo-electric sensitiveness when the composition deviates slightly from  $\text{Sb}_2\text{S}_3$  is probably due to the formation of mixed crystals. Small quantities of impurities also appear to be of considerable importance, and the authors have observed that the nature of the glass, of which the melting tubes are constructed, has an influence on the sensitiveness of the product to light. This may account for the discrepancy between Jaeger's observation that Japanese antimonite loses its sensitiveness to light when melted and resolidified, whereas the authors find that this operation can be carried out without any appreciable alteration in the effect.

H. M. D.

**Electric Light Accumulator.** CHR. WINTHER (*Zeitsch. Elektrochem.*, 1912, 18, 138—143).—When an aqueous solution of ferrous and mercuric chloride is exposed to ultra-violet light, the system is partly transformed into ferric chloride and calomel. The reverse reaction proceeds spontaneously and completely; it is extremely slow at the ordinary temperature, so that the products can remain in contact without appreciable change, but when arranged to give a current, it goes at a much greater rate, which depends on the temperature.

For purposes of investigation the cell was constructed as follows. In a glass funnel, closed at the lower end, a perforated platinum plate was fixed; the plate was soldered to a platinum wire which passed out through a hole in the funnel. On the plate a layer of platinised asbestos was placed and then the solution which was exposed to the light from a quartz-mercury vapour lamp. After the illumination the differences of potential were measured, a platinum electrode being placed for this purpose in the upper liquid. The *E.M.F.* in some cases was as much as 0.1 volt, and currents of 1 milliamp. were obtained.

The results were complicated by the oxidation of the ferrous salt by the oxygen of the air; the effect of this process on the equilibrium is discussed in detail. Another uncertainty arose from the fact that owing to insufficient stirring the concentration of ferric chloride was not the same in the upper and lower layers.

The apparatus was also exposed to sunlight, and gave *E.M.F.*'s of 20—30 millivolts, but owing to the slowness of the action the results were greatly complicated by direct oxidation.

G. S.

**The Dielectric Constant for Carbon Dioxide in the Neighbourhood of the Critical Point.** L. VERAÏN (*Compt. rend.*, 1912, 154, 345—347).—The second method described by Drude

(Abstr., 1897, ii, 438) has been employed to determine the dielectric constant for carbon dioxide at different temperatures between  $-4$  and  $30^{\circ}$ . The results are plotted in the form of a curve. It is found that the two constants for the gas and liquid approach one another as the temperature rises, and coincide at about  $31.4^{\circ}$ ; at this temperature the constant has the value 1.25. W. O. W.

**Experiments with Liquid Helium. Electrical Resistance of Pure Metals, etc. VI. The Sudden Change in the Rate at which the Resistance of Mercury Disappears.** H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 14, 818—821. Compare Abstr., 1911, ii, 575, 687).—Further measurements have been made of the electrical conductivity of pure mercury at liquid helium temperatures. The mercury was contained in a series of seven glass U-tubes of about 0.005 square mm. cross section, the tubes being joined together at their upper ends by inverted Y-pieces which allow of freezing without danger to the tubes, and without breaking the continuity of the thread of mercury. Between  $4.29^{\circ}$  and  $4.21^{\circ}$  (absolute) the resistance falls gradually, but between  $4.21^{\circ}$  and  $4.19^{\circ}$  it diminishes very rapidly, and apparently disappears at the latter temperature. (Temperature measurements are referred to  $4.25^{\circ}$  as the boiling point of helium.) H. M. D.

**Electrical and Thermal Conducting Power and the Wiedemann-Franz Ratio for Antimony-Cadmium Alloys between  $0^{\circ}$  and  $-190^{\circ}$ .** ARNOLD EUCKEN and GEORG GEHLHOFF (*Ber. Deut. physikal. Ges.*, 1912, 14, 169—182).—The high thermoelectric potential differences which are exhibited by antimony-cadmium alloys when combined with copper have led the authors to examine the thermal and electrical properties of these alloys in detail. The thermal and electric conductivities of various alloys were measured at  $0^{\circ}$ ,  $-79^{\circ}$ , and  $-190^{\circ}$ , and the variation with the composition is exhibited in the form of curves.

The thermal conductivity ( $\Lambda$ ) varies very rapidly with change in composition, and at all three temperatures the minimum appears to be reached in the neighbourhood of the compound SbCd. At this point the ratio  $\Lambda_{-190^{\circ}}/\Lambda_{0^{\circ}}$  shows a very sharp maximum.

The electrical conductivity ( $K$ ) varies with the composition to a still greater extent, and the compound SbCd again corresponds with a minimum conducting power at all three temperatures. The extent of the change in electrical conductivity with the composition is seen from a comparison of the following values for  $K$  at  $0^{\circ}$ : Cd  $1.289 \times 10^5$ , SbCd  $1.99 \times 10^1$ , Sb  $2.565 \times 10^4$ . The ratio  $K_{-190^{\circ}}/K_{0^{\circ}}$  also exhibits a sharp maximum for the composition SbCd, the ratio having minimum values for alloys which do not differ greatly in composition from the definite compound.

If curves are plotted which show the variation of  $\Lambda/K$  with the composition, these are also found to have a very sharply defined maximum at the composition SbCd. For cadmium the value of the ratio at  $0^{\circ}$  is 1.883, for antimony 1.485, and for SbCd 158. The curves for the ratio  $\Lambda/K$  are very similar in form to those which show

the variation of the thermo-electric force and of the Hall effect with the composition.

In reference to the thermal conductivity it is pointed out that the alloy of the composition SbCd has approximately the same conductivity as ordinary soda glass, and it is suggested that this is probably not due to electrons, but to the same cause as that which determines the conductivity of so-called non-conducting crystals. H. M. D.

**Electrical Conductivity of Copper-Arsenic Alloys.** NICOLAI A. PUSHIN and E. G. DISHLER (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 125—132).—The addition of arsenic to copper causes a rapid increase in the specific resistance (in ohms) from  $1.708.10^{-6}$  at  $25^{\circ}$  (or  $1.538.10^{-6}$  at  $0^{\circ}$ ) to  $35.0.10^{-6}$  at  $25^{\circ}$  ( $34.8.10^{-6}$  at  $0^{\circ}$ ) for a content of 6% of arsenic. At this point, the curve of resistance suddenly changes its direction, the resistance continuing to increase, but more slowly, to  $63.0.10^{-6}$  at  $25^{\circ}$  ( $59.0.10^{-6}$  at  $0^{\circ}$ ) for 28.5% of arsenic. With higher proportions of arsenic, the specific resistance gradually diminishes to the value  $52.6.10^{-6}$  at  $25^{\circ}$  ( $49.3.10^{-6}$  at  $0^{\circ}$ ) for 42% of arsenic. Attempts to prepare copper-arsenic alloys containing more than about 44—45% As resulted in volatilisation of the excess of arsenic. These results are not in agreement with those of Friedrich (*Metallurgie*, 1908, 5, 529).

It has been shown by various authors that: (1) for mechanical mixtures, the electrical conductivities of alloys and their temperature-coefficients are additive in character; (2) when solid solutions are formed, the conductivity and its temperature-coefficient diminish as the concentration of the solid solution increases; (3) an intermetallic compound possesses a characteristic conductivity, peculiar to it; (4) the temperature-coefficient of the conductivity of such a chemical compound differs little from that of pure metals

Consideration of the melting-point diagram of the system copper-arsenic given by Friedrich (*loc. cit.*) and of the resistance curve obtained by the author, shows that these two metals form a solid solution with a maximum concentration of 6% of arsenic. The proportion 28.2% of arsenic corresponds with the compound  $\text{Cu}_3\text{As}$ , which also occurs naturally as domeykite. No indication is given by the curves of the existence of a compound,  $\text{Cu}_5\text{As}_3$ , and the constancy of the temperature-coefficient of conductivity in the region 28.5—42% As indicates the absence of any solid solution.

Tempering causes little change in the resistance of copper-arsenic alloys poor in arsenic, but is accompanied by an increase of 60—70% in the resistance of those containing 32% and upwards of arsenic; this phenomenon is probably due to a profound change in the chemical nature of the alloys. T. H. P.

**The Electrical Conductivity of Solutions of Alkali Acetates in Acetic Acid.** KARL HOPFGARTNER (*Monatsh.*, 1912, 33, 123—139).—In the investigation of the conductivity of sodium and potassium acetates in acetic acid solution (Abstr., 1911, ii, 849) some surprising values were obtained. It is now discovered that the conductivities of solutions of the acetates of sodium, potassium, and lithium in acetic

acid are much lower than those of the corresponding aqueous solutions ; also starting with a gradually increasing concentration from very weak solutions, the molecular conductivity for all three acetates first shows a fall to a minimum, followed by a rise to a maximum with again a subsequent decrease. The minimum occurs at a concentration of  $N/30$  for potassium and lithium acetates, and approx.  $N/20$  for sodium acetate ; the maximum occurs at concentrations a little over normal. Near the concentrations of maximum conductivity, the temperature-coefficient reaches a minimum.

The values obtained by Konowaloff (Abstr., 1893, ii, 356) for the molecular conductivity of aniline and dimethylaniline acetates in acetic acid show similar characteristics.

D. F. T.

**Conductivity and Ionic Concentration in Mixtures of Molybdic Acid with Organic Acids.** ROBERT WINTGEN (*Zeitsch. anorg. Chem.*, 1912, 74, 281—290. Compare Rimbach and Neitzert, Abstr., 1907, ii, 269).—The high conductivity of the complex acids containing molybdenum might be due either to the increased strength of the acid or to the increased velocity of transport of the anion. It is now shown, by measurements of the velocity of hydrolysis of methyl acetate, that the complexes with organic acids containing hydroxyl groups are much stronger acids than their components.

C. H. D.

**Electric Deposition of Carbon from Flames.** BRUNO THIEME (*Zeitsch. Elektrochem.*, 1912, 18, 131. Compare this vol., ii, 122).—When a thin wire as anode and a wire net as cathode are placed near one another in a flame rich in carbon and the poles are connected with a source of potential of 110 volts, soot is deposited on the cathode. When the growths of carbon reach from cathode to anode a fairly large current passes between the poles, an electro-magnet is thereby brought into action and attracts the cathode so strongly that the soot is shaken off, and by interruption of the current the cathode returns to its original position. The soot thus obtained is in a very finely divided condition.

G. S.

**Concentration Cells with Ternary Electrolytes.** J. E. A. GEISSLER (*Zeitsch. Elektrochem.*, 1912, 18, 131—137).—A complicated formula is obtained which admits of the calculation of differences of potential between solutions containing ternary electrolytes, and it is shown that on the basis of certain assumptions the formula can be simplified. It has been tested by means of measurements on concentration cells containing solutions of magnesium chloride of different concentrations associated with the calomel electrode, and the agreement between observed and calculated values is fairly satisfactory (compare Kümmell, Abstr., 1905, ii, 226).

G. S.

**Anodic Behaviour of Uranium.** UMBERTO SBORGÌ (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 135—140).—The author has investigated the behaviour of uranium as anode in the electrolysis of a number of different solutions. The uranium employed contained impurities,

especially carbon, but reasons are adduced for the belief that these do not greatly effect the results obtained. In many cases an evolution of gas was noticed; it consisted chiefly of carbon dioxide, but the amount was usually negligible. The anode dissolved in sulphuric acid and sulphates, nitric acid and nitrates, hydrochloric acid and chlorides, bromides, acetates and chlorate. In iodides, separation of the halogen was also observed. In all the experiments except three, the metal dissolved as though it had the valency four, but in some cases allowance has to be made for the evolved gas. In two experiments with sulphates and in one with nitrates, the results indicated a valency of six. In phosphates and in alkalis the electrode was covered with a yellow deposit, and the current fell to a minimum; when the deposit was mechanically removed at frequent intervals, the result agreed with the valency four. These experiments and also experiments on the anodic polarisation in nitrates, sulphates, and chlorides indicate that uranium is not capable of becoming passive.

R. V. S.

**Function of Interatomic Electrons in Electrolysis.** PIERRE ACHALME (*Compt. rend.*, 1912, 154, 647—649).—An extension of the hypothesis previously advanced, electrolysis being regarded as accompanied by absorption of electrons by the liquid in the neighbourhood of the negative pole, and to an equal extent by the positive electrode.

W. O. W.

**Free Energy of Dilution of Hydrochloric Acid.** RICHARD C. TOLMAN and ALFRED L. FERGUSON (*J. Amer. Chem. Soc.*, 1912, 34, 232—246).—The *E.M.F.* has been measured at 18° between calomel and hydrogen electrodes of cells containing hydrochloric acid of known concentration *C*, and the free energy change  $\Delta F_{18}$  has been determined of the reaction  $\frac{1}{2}\text{H}_2(1 \text{ atm.}) + \text{HgCl}(s) = \text{Hg} + \text{HCl}(\text{concentration } C)$ . Determinations have been made at concentrations of 0.1*N*, 0.02*N*, 0.01*N*, and 0.002*N*, and the free energy of dilution calculated. The averages of the differences between the *E.M.F.* in 0.1*N* and the more dilute solutions were as follows: 0.02*N*—0.1*N*, 0.07617 ± 0.0009; 0.01*N*—0.1*N*, 0.10913 ± 0.00018; 0.002*N*—0.1*N*, 0.18711 ± 0.00127. The values in joules of the free energy of dilution,  $-\Delta F$ , obtained by multiplying the average differences in *E.M.F.* by the value of Faraday's equivalent, 96,580 coulombs, are: 0.02*N*, 7356.5; 0.01*N*, 1054.0; 0.002*N*, 1807.1.

In view of the fact that it has been found, in general, for solutions of non-electrolytes and weak electrolytes that the "active mass" or "fugacity" of the substances present is proportional to the concentration (Lewis, *Abstr.*, 1908, ii, 465), calculations have been made from the conductivity measurements of the ratios of the concentration of non-dissociated hydrochloric acid in 0.1*N*-solution to that in the more dilute solutions, and also of the corresponding ratios of the concentration of the hydrogen ions. The results show wide discrepancies between the "fugacity" ratios and the concentration ratios of the non-dissociated acid, and smaller but real discrepancies between these ratios for the ions. The conclusion is drawn that for strong electrolytes, even in dilute solutions, the "fugacity" of the ions is not strictly proportional

to the concentration, whilst the "fugacity" of the non-dissociated electrolyte is very far from proportional to the concentration. E. G.

**Influence of Electrolytes on the Dissociation Constant of Water.** G. POMA and B. TANZI (*Zeitsch. physikal. Chem.*, 1912, 79, 55—62).—As it has been suggested that water is more highly dissociated in the presence of neutral salts than in the pure condition, the authors have investigated the question by the electrometric method. The *E.M.F.* of a cell containing dilute acid on one side and alkali on the other was measured with and without the addition of a salt, and the dissociation constant for water calculated in the usual way. The results show that neutral salts diminish the dissociation of water. With *N/20*-acid and alkali at 25°, the dissociation constant was  $1.247 \times 10^{-14}$ ; when the solutions were 2.55*N* with reference to potassium chloride, the constant fell to  $0.255 \times 10^{-14}$ . Further, as would be anticipated, the constant is less with strong acid and alkali without neutral salt than with weak acid and alkali under the same conditions. G. S.

**Theory of Electrolytic Ions. V. The Dissociation of Fused Salts.** RICHARD LORENZ (*Zeitsch. physikal. Chem.*, 1912, 79, 63—70. Compare Abstr., 1910, ii, 577).—The dissociation of fused salts cannot be determined from the results of conductivity data alone, and the author suggests a rather complicated indirect method which admits of an approximate estimate of the dissociation.

There are two kinds of electrolytic conductivity, according as the ions are derived from the solvent (for example, pure water) or are not related to the solvent, as for most electrolytes in aqueous solution. Fused salts belong to the former type, which is termed Grotthus conductivity, in contrast to the ordinary Hittorf conductivity. The speed of the ions in the case of Grotthus conductivity is two to three times greater than that calculated from the atomic radii, and this is ascribed to exchange between the ions and the ionised molecules of the solvent (*loc. cit.*). That this is valid for fused salts is shown by diffusion experiments in which salts diffuse into solvents with a common ion, for example, silver nitrate dissolved in fused potassium nitrate diffused into pure fused potassium nitrate. Therefore to obtain the Hittorf conductivity necessary for calculating the degree of dissociation, the observed electrical conductivity has to be divided by two. The limiting value of the electrical conductivity is calculated by Einstein's formula, making use of the viscosities and the radii of the ions in the two solvents, water and fused salt. From the Hittorf conductivity and the limiting conductivity it is found that at 388° fused sodium nitrate is dissociated to the extent of 31.5%. No great accuracy is claimed for the results, as the diffusion data are very uncertain. G. S.

**The Action of the Electric Discharge on Liquids and Gases.** ALEXANDRE DE HEMPTINNE (*Bull. Soc. chim. Belg.*, 1912, 26, 55—63).—When a thin layer of oleic acid is submitted to the action of an electrical discharge in an atmosphere of hydrogen, gas is absorbed with the formation, at first, of stearic acid; under prolonged action of

the discharge polymeric products are formed. As the result of experiments with different kinds of apparatus, using commercial olein, the following conclusions are drawn: (1) The quantity of substance transformed per unit of electrical energy increases to a certain limit as the pressure decreases, the limit varying with the nature of the discharge and with the apparatus used. (2) Proportionality does not always exist between the quantity of substance transformed and the effective intensity of the current. (3) With a fixed intensity of current there is a maximum amount of transformation depending on the density of the discharge, which maximum varies with the pressure. (4) For transformation to take place it is necessary for the discharge to act both on the liquid and on the gas. (5) There is no evidence to show that the sign of the discharge plays any part.

The apparatus described by the author can be used for deodorising fish oils, or for polymerising mineral oils or mixtures of mineral with vegetable or animal oils. The viscosity of such polymerised oils varies much less with the temperature than does that of the pure mineral oils.

T. S. P.

**The Potential Gradient in the Non-striated Positive Column of the Glow or Arc Discharge in Nitrogen and Hydrogen for Large Current and Gas Densities.** W. MATTHIES and H. STRUCK (*Ber. Deut. physikal. Ges.*, 1912, 14, 83—103).—In place of the ordinary method of measuring the potential gradient in the discharge column, the authors have made use of the "ring" method recently described (*ibid.*, 1911, 13, 552). This can be used when the ordinary method fails to give results because of the high temperature in the path of the discharge.

The dependence of the potential gradient on the gas pressure, the current density, and the cross section of the tube was examined in detail, these factors being varied between wider limits than in previous work on the subject. In the case of nitrogen, for example, the pressure was varied from 5 to 160 mm. of mercury, and the current density from 0.02 to 40 amperes per square cm. Curves are plotted to show the connexion between the potential gradient and the other factors involved, and the behaviour of the two gases is compared. As a result of these measurements, it appears that the potential gradient in the positive column of the glow or arc discharge at higher pressures is a linear function of the gas pressure.

H. M. D.

**Relation between Current, Voltage, Pressure, and the Length of the Dark Space in Different Gases.** FRANCIS W. ASTON and HUBERT E. WATSON (*Proc. Roy. Soc.*, 1912, A, 86, 168—180).—Previous experiments with hydrogen, nitrogen, oxygen, and air (compare *ibid.*, 1907, A, 79, 80) have been extended to carbon monoxide, argon, and helium. When the argon and helium are impure, their behaviour closely resembles that of the other gases, in that it agrees approximately with the empirical equations:  $D = A/P + B/\sqrt{c}$  (1) and  $V = E + F\sqrt{c}/P$  (2), in which  $D$  is the length of the dark space,  $V$  the potential difference between the electrodes,  $P$  the pressure of the gas,  $c$  the current density, and  $A$ ,  $B$ ,  $E$ , and  $F$  are constants.

Similar experiments were also made with carefully purified argon, helium, neon, krypton, and xenon. Apart from small individual peculiarities the behaviour of these five gases is very much the same, provided the measurements are made at constant pressure; thus, the curves obtained by plotting  $D$  against  $1/\sqrt{c}$  and  $V$  against  $\sqrt{c}$  are very similar to one another. The range of pressures over which the similarity holds varies, however, from 1.5—0.2 mm. in the case of helium to 0.3—0.06 mm. for xenon.

Of the equations (1) and (2), the former holds good only at high current densities in the case of the pure inert gases; and instead of (2), it is found that the connexion between voltage and current density can be much more satisfactorily represented by the equation  $V = G + KD\sqrt{c}$ , where  $G$  and  $K$  are constants. H. M. D.

**Magnetic Examination of the Function of the Water Molecule in Certain Dilute Solutions.** A. E. OXLEY (*Proc. Camb. Phil. Soc.*, 1912, 16, 421—427).—The magnetic susceptibilities of dilute solutions of nickel sulphate, nitrate and chloride and of cobalt chloride have been investigated in order to ascertain whether the varying hydration of the molecules of the dissolved salt has any influence on the paramagnetic properties. In all cases the susceptibility is accurately proportional to the concentration, and any alteration in the degree of hydration is therefore without influence on the magnetic properties. This result would be expected if it is assumed that the magnetic salt nuclei can undergo orientation independently of the surrounding envelope of water molecules. H. M. D.

**Magneto-optical Effects in Chlorine and Iodine.** ROBERT W. WOOD (*Ann. Physik*, 1912, [iv], 37, 594—596).—A claim of priority and polemical against Heurung (*Abstr.*, 1911, ii, 963). H. M. D.

**Refraction and Magnetic Rotation of Mixtures.** PAUL T. MULLER and (Mlle.) V. GUERDJIKOFF (*Compt. rend.*, 1912, 154, 507—510).—Becquerel (*Ann. Chim. Phys.*, 1877, [v], 12, 5) gave the expression  $R/n^2(n-1) = B$  for the relation between  $n$ , the index of refraction for a substance, and  $R$ , the ratio of the angle of magnetic rotation to that of carbon disulphide.  $B$  is fairly constant for compounds of the same type, but is variable for aqueous solutions. The author extends Becquerel's observations to a number of diamagnetic substances, such as ammonium nitrate, acetic and sulphuric acids, in aqueous solutions of greater concentration. In these cases the above formula is only very approximately correct.

For aqueous solutions of lithium chloride, the relation between  $n$  and concentration,  $c$ , is linear up to  $c = 36\%$ ; above this point a sudden increase occurs, and then the relation again becomes linear until saturation is reached. Ammonium nitrate solutions give a similar result. With mixtures of aniline and alcohol, a sudden increase in the refractive index occurs when the proportion of the former reaches 20.5—29.7%.

W. O. W.

**Use of the Magnetic Field in Determining Constitution.**  
**XIII.** PAUL PASCAL (*Bull. Soc. chim.*, 1912, [iv], 11, 159—163).—In this part the discussion of halogenated compounds is continued (compare this vol., ii, 229). In polyhalogenated substances the depreciation of molecular magnetic susceptibility shown by monohalogenated compounds is accentuated, and is about  $58 \times 10^{-7}$  for di-iodo-derivatives,  $60 \times 10^{-7}$  for dibromo-compounds, and  $45 \times 10^{-7}$  for dichloro-derivatives. These depreciations are possibly due to mutual saturation of residual valencies between the halogen atoms in the molecules. When the relations between halogen and hydrogen atoms are such that hydracid is not easily eliminated, the fall in magnetic susceptibility is much less, for example, in dichloroacetylene it is only  $22 \times 10^{-7}$ . The fall is still more marked when more than one halogen atom is attached to the same carbon atom, and in such cases the fall increases with the number of halogen atoms so attached, and with their atomic weight; thus for tetrachloroethane it is  $32 \times 10^{-7}$ , for tetrabromoethane it is  $119 \times 10^{-7}$ , and for tetrachlorodibromoethane it is  $287.5 \times 10^{-7}$ . Fluorine compounds, on the contrary, show little magnetic susceptibility depreciation, unless disturbing influences are introduced by some other atom or group; thus difluoroethyl alcohol shows  $-4 \times 10^{-7}$ , but bromofluoroacetic acid exhibits a fall of  $37 \times 10^{-7}$ . In general these results support the view that the halogens exert supplementary valencies, giving rise to multiple linkings, and that these cause the abnormalities observed in various physical properties of halogenated substances.  
T. A. H.

**Use of the Magnetic Field in Determining Constitution.**  
**XV.** PAUL PASCAL (*Bull. Soc. chim.*, 1912, [iv], 11, 201—206. Compare preceding abstract).—In this part inorganic haloids are considered, and tables of the molecular magnetic susceptibilities of halogen compounds of phosphorus, antimony, silicon, tin, and boron are given. These are all much below the calculated values, and there is no obvious regularity in the values of the depreciation. If, however, the sums of the atomic weights of the halogen groups of the compounds are used as abscissæ and the corresponding depreciations,  $D$ , of magnetic susceptibility as ordinates, a number of points are obtained, which group themselves about a series of lines coming from the origin, and which make with the axes, angles which are simple multiples of the smallest, which is equal to  $-0.2468 \times 10^{-7}$ , so that, in general,  $D = 0.2468N.10^{-7}\Sigma a$ , where  $N$  is an integer and  $\Sigma a$  is the sum of the atomic weights of the halogens in the compound; but since  $D = \Sigma ad$ , where  $d$  is the lowering of magnetic susceptibility due to one halogen, the expression simplifies to  $d = 0.2468N.10^{-7}$ . It is then shown that the specific susceptibility of many elements can be expressed in the form:— $(24 \times 0.2468 - 0.0132)10^{-7}$ , which is that of chlorine, the first and third figures varying for each element; this implies that the specific susceptibility of an element is the sum of those of its aliquot parts, and the lowering never reaches this sum; thus, for chlorine the maximal fall is  $19 \times 0.2468.10^{-7}$ . In a homologous series of elements, leaving out the first, which is always abnormal, the number of aliquot parts decreases with increasing atomic weight; thus,

for chlorine it is 24, bromine 16, iodine 15. If the views of Langevin (*Ann. Chim. Phys.*, 1905, [viii], 5, 70) and of Drude (*Ann. Physik*, 1904, [iv], 14, 677) be accepted, these numbers would represent subdivisions of the elements of which only a portion, 19 in the case of chlorine, would be effective in chemical compounds containing that element. A number of instances are quoted in which calculated values of magnetic susceptibilities have been verified experimentally by independent investigators.

T. A. H.

**Thermal Constants of Tungsten at High Temperatures.** O. M. CORBINO (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 188—194).—The author has recently (*ibid.*, 1912, [v], 21, i, 181) described a method for obtaining in the case of a thin conducting filament the value of the ratio  $c/a$ , where  $c$  is the thermal capacity of the filament, and  $a$  is the true coefficient of variation of its resistance with the temperature. In the present paper are recorded the results with experiments with a tungsten filament (a 50 c.p., 105 volt lamp). Taking the temperatures as known, and this is the case only as far as  $1500^{\circ}$ , the thermal capacity of the filament remains constant. Above this temperature the value of  $c/a$  may be used to give the thermal capacity, making the most probable suppositions as to the temperature, or on the assumption that the thermal capacity remains constant above  $1500^{\circ}$  also, they may be employed to deduce the temperature of the filament. The specific heat of tungsten at temperatures from  $800$  to  $1500^{\circ}$  is  $0.0334$ , corresponding with an atomic heat of  $6.09$ , a value which agrees well with Einstein's theory that the atomic heats of all the elements reach the limiting value  $6$ , and so furnishes an argument in favour of the validity of the method for the determination of high temperatures used above.

R. V. S.

**Specific Heat of Binary Mixtures.** I. ALFRED SCHULZE (*Ber. Deut. physikal. Ges.*, 1912, 14, 189—210).—The specific heats of various binary mixtures have been measured at different temperatures by an electrical heating method. The experimental results are shown in the form of curves obtained by plotting the molecular heat as a function of the molecular composition of the mixtures.

For mixtures of benzene and ethylene chloride at  $20^{\circ}$ ,  $35^{\circ}$ , and  $50^{\circ}$ , the observed molecular heats are nearly in agreement with those calculated from the mixture rule. At the two lower temperatures there are, however, distinct deviations at the ethylene chloride end of the series, and the lower values obtained experimentally are attributed to a slight association of the ethylene chloride.

Mixtures of ethyl ether and chloroform have much larger molecular heats than those which correspond with the mixture rule. The data for  $20^{\circ}$ ,  $0^{\circ}$ ,  $-30^{\circ}$ , and  $-50^{\circ}$  show that the deviation from the simple additive behaviour increases rapidly as the temperature falls. It is supposed that this is due to the formation of a compound, the stability of which increases as the temperature decreases, and reference is made to the similarity between the molecular heat curves and the curves representing the variation of the vapour pressure and the refractive power for long-waved rays with the composition of the

mixture. Mixtures of acetone and chloroform at 35°, 20°, and -10°, of benzene and chloroform at 55°, 20°, and 6°, and of benzene and ethyl ether at 20° and 6° exhibit behaviour similar to that of mixtures of ethyl ether and chloroform, and in these cases it is also assumed that the high molecular heat value of mixtures is due to the formation of a compound.

H. M. D.

**Nernst's Theorem of Heat and Chemical Facts.** PHILIP KOHNSTAMM and L. S. ORNSTEIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 14, 802—818).—A criticism of Nernst's heat theorem as applied to chemical changes. The integration constant in the equation of equilibrium should be equal to the algebraic sum of the constants in the vapour pressure formulæ for each of the substances participating in the equilibrium. These constants depend, however, to a large extent on the assumptions which are made in reference to the variation of the specific and latent heats with the temperature. If, on the other hand, it is assumed that the constants of integration for chemical equilibria can be determined directly from the experimental data relating to the equilibrium, it is yet necessary to show that the values obtained in this way can be represented as the summation of a series of constants relating to each of the substances concerned, and these constants should have the same value whatever the particular chemical equilibrium from which they are derived. As yet this has not been demonstrated, and on that account the validity of the heat theorem in its application to chemical changes is devoid of experimental verification.

H. M. D.

**Gas Equilibria.** F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 14, 743—758. Compare Kohnstamm and Ornstein, preceding abstract).—From the experimental data relating to the equilibrium  $2\text{CO} + \text{O}_2 \rightleftharpoons 2\text{CO}_2$  at different temperatures, the author has calculated the energy and entropy constants on different assumptions as to the dependence of the specific heats of the substances concerned on the temperature. The values thus obtained for the energy constants are in moderately good agreement, but the entropy constants vary considerably according to the assumption which is made in extrapolating the specific heats to low temperatures.

The most probable values are considered to be those which are derived from the relationship between the specific heats and the oscillation frequencies of the atoms in the gas molecules deduced by Bjerrum (*Zeitsch. Elektrochem.*, 1911, 17, 731). Bjerrum's data are also applied to the calculation of the constants characteristic of the dissociation of water, and by means of these constants the water-gas equilibrium is also submitted to examination.

H. M. D.

**Characteristic Vibration Frequencies of Elements in Compounds.** F. KOREF (*Physikal. Zeitsch.*, 1912, 13, 183—188).—An attempt is made to calculate the changes in the characteristic vibration frequencies of the elements when these enter into chemical combination with other elements. The frequency of an element in the free state has been shown by Lindemann (*Physikal. Zeitsch.*, 1910, 11, 609) to be

related to its atomic weight, atomic volume, and its melting point, and the formula expressing the connexion between these quantities is now applied to compounds. Since the atomic volume is an additive property, the relationship between the vibration frequency of the free element ( $\nu$ ) and that of the element in combination ( $\nu'$ ) can be reduced to the form  $\nu'/\nu = \sqrt{T_s'/T_s}$ , where  $T_s$  and  $T_s'$  are the melting points of the element and compound respectively. In the derivation of this formula, it is assumed that the melting point of the compound represents the temperature at which the amplitudes of the atomic vibrations become sufficiently great to bring the atoms of neighbouring molecules into contact. The atomic frequencies for the constituents of a number of compounds are calculated from the above formula, and it is shown that the molecular heat values derived from these are in satisfactory agreement with the observed values at a series of different temperatures.

The calculated atomic frequencies are also shown to agree with those yielded by the residual ray measurements of Rubens in the case of potassium chloride, bromide and iodide, and of sodium chloride. For calcium fluoride the observed wave-lengths of the residual rays are, however, appreciably different from those indicated by the atomic frequencies calculated from the formula.

According to Nernst's heat theorem, the affinity of a chemical change can be calculated from the thermal data and the specific heats of the reacting substances. Since the specific heats are determined by the vibration frequencies of the atoms, it follows that the affinity can be evaluated on the basis of a knowledge of the thermal change accompanying the reaction and of the melting points and densities of the reacting substances and final products. The affinity diminishes with rising temperature if the sum of the values of  $nT_s$  (where  $T_s$  is the melting point of one of the substances concerned in the reaction and  $n$  the number of atoms in the molecule) is much greater for the products of the reaction than it is for the original substances.

H. M. D.

**Fusibility Curves of Certain Binary Systems Volatile at Very Low Temperatures.** GEORGES BAUME and NÉOPTOLÈME GEORGITSES (*Compt. rend.*, 1912, 154, 650—652. Compare Abstr., 1911, i, 414, 696, 830).—The fusibility curves for the systems hydrogen chloride with hydrogen sulphide, ethane, and propionic acid are reproduced, together with Bagster's curves for the systems hydrogen sulphide with hydrogen bromide and iodide. The systems containing hydrogen sulphide show minima indicating the identical composition of two phases at the same temperature. The system hydrogen chloride–propionic acid tends to form glasses, and could not be completely studied, but evidence was obtained for the existence of a compound,  $C_2H_5 \cdot CO_2H, HCl$  or  $CEt \cdot C(OH)_2Cl$ . W. O. W.

**Apparatus for Determining the Melting Point and Molecular Weight of Organic Compounds.** RUDOLF FABINYI (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [i], 210—213).—Three platinum wires dip below the surface of mercury in a vessel contained in a large

double air-bath. One of the wires is bare, one is coated with urethane or naphthalene by immersion in the molten substance and cooling, and the third is coated with a solution of the substance to be examined in urethane or naphthalene. A Beckmann thermometer is placed in the mercury, and electrical circuits are arranged so that two different electric bells are rung by the melting of the coatings. The difference between the readings of the thermometer at the ringing of the first and second bell gives the depression.

The coating should be performed only a few tenths of a degree above the freezing point, and the thickness should not exceed 0.5 mm.

C. H. D.

**Lowering of the Melting Point by One-sided Pull or Pressure.** EDUARD RIECKE (*Centr. Min.*, 1912, 97—104).—The one-sided pressure under consideration may be illustrated by placing a weight on the top of a block of ice immersed in water; the pressure on top and bottom is then greater than on the sides. The effect of the one-sided pressure is to lower the melting point of ice according to the formula  $\theta = aZ_t^2$ , where  $a$  is 0.00036 when the pressure is expressed in kilog./cm<sup>2</sup>. The value of  $Z_t$  is not, however, the original pressure exerted. Since some ice melted owing to the increase of pressure, the diameter of the block of ice became smaller, and therefore the pressure per sq. cm. is slightly greater. Calling  $Z_c$  the original pressure, a formula is deduced connecting  $Z_c$ ,  $Z_t$ , and the lowering of the melting point due to the pressure. If the pressure is released, the original conditions should be restored, and the conditions under which this takes place reversibly are considered.

G. S.

**Application of the Pyrometric Method to the Investigation of Equilibria at High Pressures.** NICOLAI A. PUSHIN and I. V. GREBENTSCHIKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 112—125).—The authors describe the apparatus and method they have employed to determine the relation between temperature of crystallisation and pressure at high pressures. The substances investigated were diphenylamine, urethane, and *p*-nitroanisole, the crystallising point being determined by the pyrometric method, that is, by means of the cooling curve at constant pressure. This method is found to be considerably more accurate and rapid than the manometric method, and requires only 1—2 grams instead of about 40 grams.

If  $p$  represents the pressure in kilograms per sq. cm., and  $t$  the temperature of crystallisation in degrees Centigrade, the relation for diphenylamine is given by:  $t = 53.2 + 0.02789p - 0.00000165p^2$ . According to this expression, the maximum temperature of crystallisation is 170°, corresponding with a pressure of 8450 kilograms per sq. cm.; increase of the pressure above this value results in lowering of the crystallising point. Tammann (*Krystallisiren und Schmelzen*), using the manometric method in which the variation of pressure at constant temperature is observed, obtained the relation:  $t = 53.4 + 0.0245p - 0.00000100p^2$ , the maximum divergence of the calculated from the observed temperature being 0.5°, whereas in the authors' measurements it was 0.0°. Tammann gave  $t_{\max.}$  as 200°, and the corresponding  $p_{\max.}$  as 10200.

For urethane,  $t = 48.3 + 0.01016p - 0.00000106p^2$ ;  $t_{\max.} = 73^\circ$  and  $p_{\max.} = 4800$  kilograms per sq. cm.

For *p*-nitroanisole,  $t = 52.5 + 0.02365p - 0.00000113p^2$ ;  $t_{\max.} = 182^\circ$  and  $p_{\max.} = 10460$ . T. H. P.

**Influence of Pressure on Equilibria in Binary Systems.** NICOLAI A. PUSHIN and I. V. GREBENTSHIKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 244—263).—By means of the pyrometric method previously described (compare preceding abstract), the authors have investigated the cooling curves at various pressures of eutectic mixtures of sodium (85 atom. %) and mercury, urethane (61 mol. %) and *p*-nitroanisole, and urethane (61 mol. %) and diphenylamine, and also of a mixture of 85 mol. % of urethane with diphenylamine.

The results show that the relation between the temperature of crystallisation of eutectic mixtures and the pressure is expressed by an equation of the same type as for chemically individual substances. Increase of the pressure is accompanied by change in the composition of the eutectic mixture, which becomes enriched in that component for which  $dT/dp$  has the lower value. Starting from the curve of solubility of the latter component, either component alone or both together may be caused to crystallise out by suitable alteration of the pressure. With continual increase of the pressure, the solubility curve of one and the same substance shows increasing divergence from parallelism to its original position. T. H. P.

**Acetic Acid as an Ebullioscopic Solvent.** ERNST BECKMANN [with K. HARING, R. HANSLIAN, and J. VON BOSSE] (*Zeitsch. anorg. Chem.*, 1912, 74, 291—296).—Various values are given for the ebullioscopic constant of acetic acid. Experiments have now been made, using electrical heating (Abstr., 1908, ii, 1014). The value obtained, using acetic acid of m. p.  $16.2^\circ$ , is  $30.75^\circ$  under 760 mm. pressure, which gives a heat of evaporation of 99.3 cal. Even minute quantities of water lower the constant, and it is advisable before making an estimation to make a control experiment with benzil, acetanilide, or diphenylamine. C. H. D.

**A General Law of Dissolution.** EMILE BAUD (*Compt. rend.*, 1912, 154, 351—352. Compare this vol., ii, 233).—The formula given in a previous communication, connecting absolute temperature of fusion, molecular heat of fusion, and heat of dilution, has been tested by applying it to mixtures of acetic acid with benzene or ethylene dibromide, the heats of dilution of these substances having been found experimentally. The results are given in tabular form, and show fair agreement between observed and calculated values for the temperatures of fusion. W. O. W.

**Compressibility of Certain Liquids.** EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 65—111. Compare Abstr., 1910, ii, 393, 394).—Starting with van der Waals' equation of state,  $(p + a/v^2)(v - b) = RT$ , and taking the volume of a liquid at  $0^\circ$  and 1 atmosphere pressure as unity, the author derives the following

equation for the variation of the volume of a liquid with the pressure at constant temperature:  $(p + a/v^2)(v - b) = (1 + a)(1 - b)(1 + at)$ . This equation simplifies to:  $v = b + (1 + a)(1 - b)(1 + at)/(a/v^2 + p)$  or  $v = A + B/(C + p)$ . This isothermal equation for liquids is shown to correspond well with Amagat's results (Abstr., 1893, ii, 152). The coefficient of compressibility,  $\beta$ , at pressure  $p$  is given by:  $\beta = 1/v \cdot dv/dp = -B/[A(C + p)^2 + B(C + p)]$ . Expressions are also given for the true coefficient (at zero pressure) and for the mean coefficient between two pressures  $p_1$  and  $p_2$ .

The results of the author's measurements are as follows,  $v$  being the volume at pressure  $p$  (in atmos.) referred to the volume at zero pressure as unity, and  $\delta$  the difference between the observed volume and that calculated from the formula.

Carbon tetrachloride: Below 300 atmos.,  $v = 0.80365 + 444.54/(2264 + p)$ ;  $\delta = \pm 0.000017$ ;  $\beta_0 = 0.0000867$ . From 300 to 600 atmos.,  $v = 0.76862 + 631.10/(2728.3 + p)$ ;  $\delta = \pm 0.00006$ ;  $\beta_0 = 0.0000848$ .

Chlorobenzene:  $v = 0.76671 + 845.78/(3625.5 + p)$ ;  $\delta = \pm 0.00008$ ;  $\beta_0 = 0.0000643$ .

Bromobenzene:  $v = 0.84855 + 377.72/(2494.0 + p)$ ;  $\delta = \pm 0.00007$ ;  $\beta_0 = 0.0000607$ .

Toluene:  $v = 0.81944 + 409.51/(2268.7 + p)$ ;  $\delta = \pm 0.00003$ ;  $\beta_0 = 0.0000796$ .

Ethylbenzene:  $v = 0.85745 + 250.18/(1755.0 + p)$ ;  $\delta = \pm 0.00005$ ;  $\beta_0 = 0.0000812$ .

1 : 2 : 4-Trimethylbenzene ( $\psi$ -cumene):  $v = 0.83295 + 402.50/(2408.0 + p)$ ;  $\delta = \pm 0.00010$ ;  $\beta_0 = 0.0000694$ .

Descriptions are given of the manometer and piezometer employed, which were of special construction. T. H. P.

**Viscosities of Gaseous Chlorine and Bromine.** ALEXANDER O. RANKINE (*Proc. Roy. Soc.*, 1912, A, 86, 162—168).—By means of a modified form of the apparatus described previously (Abstr., 1910, ii, 188), the author has compared the viscosities of chlorine and bromine with that of air under similar conditions of pressure and temperature. From these data, the coefficient of viscosity of chlorine is found to be  $1.297 \times 10^{-4}$  at  $12.7^\circ$  and  $1.688 \times 10^{-4}$  at  $99.1^\circ$ , and that of bromine,  $1.869 \times 10^{-4}$  at  $98.7^\circ$ . From the two values for chlorine, the constant  $C$  in Sutherland's formula  $\eta = K.T^{3/2}/(1 + C/T)$  is calculated = 325. This gives  $T_c/C = 1.28$ , where  $T_c$  is the critical temperature, whereas for most gases for which data are available this ratio is equal to 1.14.

If the viscosities of chlorine and bromine at the corresponding temperature = 0.6466 are used in the evaluation of  $\eta^2/A$ , where  $A$  is the atomic weight of the element,  $4.19 \times 10^{-10}$  is obtained for chlorine and  $4.37 \times 10^{-10}$  for bromine. This approximate agreement of the two values suggests that  $\eta_c^2/A$  (where  $\eta_c$  is the viscosity at the critical temperature) is constant for the halogen group of elements, just as it is for the inert gases. The value of the constant is, however, different for the two groups. H. M. D.

**Viscosity of Liquid Mixtures, their Dependence on the Temperature and the Relationship between the Vapour Pressure and the Viscosity of Liquids.** OTTO FAUST (*Zeitsch. physikal. Chem.*, 1912, 79, 97—123).—The viscosities of the following binary mixtures have been measured at a series of temperatures in each case, and the results are given in tabular form: benzene–ethylene chloride, chloroform–acetone, pyridine–acetic acid, pyridine–water, acetic anhydride–water, acetic acid–aniline, acetone–carbon disulphide, acetone–ethyl ether, pyridine–aniline, acetic acid–acetone, aniline–acetone. The significance of the occurrence of maxima and minima on the viscosity concentration curves is discussed. With increase of temperature, maxima are displaced towards the substance with the higher viscosity.

The main object of the paper is a comparison of the viscosities of binary mixtures with their vapour pressures. If viscosity is due mainly to attraction between molecules, which attraction has to be overcome when vapour pressure is exerted, it is to be anticipated that a maximum of viscosity will correspond with a minimum of vapour pressure. It is shown that this rule holds for the binary mixtures in question with some exceptions. The exceptions are pyridine–acetic acid, aniline–acetic acid, acetic anhydride–water, and chloroform–acetone, and their behaviour is ascribed to chemical combination.

The relationship between viscosity and vapour pressure also holds to some extent for pure liquids. For 22 non-associated liquids for which the data are available, the rule holds approximately that the greater the vapour pressure, the smaller is the viscosity; this regularity does not apply to associated liquids.

A bibliography of the literature on viscosity is given in the paper.

G. S.

**Fluidity and Vapour Pressure.** EUGENE C. BINGHAM (*Amer. Chem. J.*, 1912, 47, 185—196).—In an earlier paper (Abstr., 1910, ii, 395) it has been pointed out that the fluidities of the aliphatic hydrocarbons are nearly identical at the b. p., that the same is true of the ethers, and that, in general, for each of these classes of compounds, the fluidity is a linear function of the vapour pressure.

It is now shown that if the fluidities of non-associated compounds at their b. p. are multiplied by such factors that these compounds at the b. p. may have the same fluidity value (which has been arbitrarily selected as 500), then any fluidity whatever when multiplied by the particular factor for the compound and plotted against the vapour pressure observed at the same temperature will fall on a single curve for all such substances. Hence it follows that the vapour pressures of non-associated liquids can be calculated if their fluidities and b. p.'s are known. A comparison of seventeen substances has been made over a certain range of temperature and for vapour pressures of more than 100 mm., and it has been found that the average percentage difference between the observed and the calculated vapour pressures is but little more than 3%. The relation does not hold, however, for highly associated compounds, and this seems to be due to the vapour pressure of such substances increasing more slowly than would be anticipated from a

study of the fluidity-vapour pressure curves of non-associated compounds. E. G.

**Rate of Absorption of Gases by Charcoal.** F. BERGTER (*Ann. Physik*, 1912, [iv], 37, 472—510).—The rate at which air, oxygen, and nitrogen are absorbed by cocoa-nut charcoal has been measured at 0°. The experimental data have reference to the slow absorption process which succeeds the very rapid and relatively large initial effect.

In order to obtain consistent results in successive experiments it is necessary that the charcoal should be heated at a temperature not less than 550°. The fineness of subdivision of the charcoal has no appreciable influence on the rate of absorption after the first few minutes.

The data for air at pressures between 735·6 and 4·52 mm. indicate that the volume  $m$  (reduced to 760 mm. and 18°) absorbed by 1 gram of charcoal after time  $t$  can be represented by  $m = m_1.t/(a + t) + m_2.t/(b + t)$ , where  $m_1$ ,  $m_2$ ,  $a$  and  $b$  are constants, provided that the pressure is greater than about 20 mm.

For nitrogen between 9·6 and 0·38 mm. the rate of absorption can be expressed by  $m = m_0(1 - 0·95e^{-3·5t} - 0·05e^{-0·15t})$ , where  $m_0$  is a constant.

The ratio in which two gases are absorbed is dependent on the pressure. Between 0·5 and 10 mm. pure oxygen is absorbed from thirty to forty times as strongly as nitrogen.

In presence of oxygen, the absorption capacity of the charcoal for nitrogen appears to be increased. H. M. D.

**Procedure in Observing the Dissociation of Nitrogen Peroxide.** ALBERT COLSON (*Compt. rend.*, 1912, 154, 428—431. Compare this vol., ii, 238; Scheffer and Treub, *ibid.*, ii, 132).—One method employed in studying the equilibrium in gaseous nitrogen peroxide consisted in breaking a bulb of the liquid at the bottom of a flask, and measuring the volume of gas evolved over water. The values for the partial pressures,  $p$  and  $p'$ , so obtained pointed to the existence of a minimum value for  $K$  in the expression  $p^2/p' = K$ , but this is due to an insufficiently rapid diffusion of gas, and was not observed in the second method used, in which the bulb was broken at the centre of the flask and the gas pressure measured by a sulphuric acid manometer. It was thus found that  $K$  is fairly constant under variable pressures. The same ratio for the dissolved substances, however, varies in a different manner, as pointed out in a previous communication. It follows, therefore, that the dissolved molecule is different from the gaseous molecule, a conclusion in harmony with observations on the equilibrium between the two allotropic modifications of phosphorus (*Abstr.*, 1908, ii, 176). W. O. W.

**Comparison of the Gaseous and Dissolved Molecules.** P. LANGEVIN (*Compt. rend.*, 1912, 154, 594—596).—A reply to recent criticisms of Colson (this vol., ii, 238) on the application of the law of mass action to the dissociation of nitric peroxide in the gaseous state and in chloroform solution. It is shown that in concentrations sufficiently dilute, the dissociation constant for chloroform solutions is

in good agreement with the law of mass action, allowance being made for the known difficulties of calorimetric estimation. The nitric peroxide in concentrated solution is not comparable with that in the gaseous condition, and hence there is no basis for Colson's deductions from the data given by Cundall.

W. O. W.

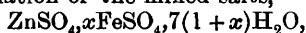
**Thermal Dissociation of Barium Peroxide.** JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1912, 34, 246—258).—This investigation was carried out in view of the discrepancies between the results of Le Chatelier (Abstr., 1893, ii, 71) on the thermal dissociation of barium peroxide and those obtained in more recent work.

The method employed in determining the equilibrium pressures is fully described. The phase relations were studied by determining the effect of removing successive portions of oxygen, the temperature being kept constant. The results show that solid solutions of the oxide and peroxide in each other are formed, and that the usual temperature-pressure curve has a definite significance only in the region in which these two solid solutions are saturated and co-existent. Equilibrium is reached very rapidly in the univariant system, that is, where saturated solutions of the oxides are present, but more slowly in the divariant system, since diffusion must take place in the solid until a new concentration is attained. The limits are indicated between which the system is univariant. The effect that the moisture present has on the equilibrium is demonstrated. On the basis of the results obtained, an explanation is given of the conditions necessary for the production of a quantitative yield of barium peroxide from the oxide, and also of those required for a complete reversal of the equilibrium.

The dissociation pressures in the interval in which the system is univariant are given by the equation:  $\log p = -6850/T + 1.75 \log T + 3.807$ . The heat of the reaction at constant pressure and an average temperature of 775° has been calculated and found to be 35370 cals. The partial pressure of the oxygen has been calculated on the assumption that the partial pressure of the steam present is the same as that given by barium hydroxide alone as measured by Johnston (Abstr., 1908, ii, 358), and from these values the heat of dissociation of the solid solutions is found to be 37420 cals.

E. G.

**Dissociation of Mixed Hydrated Salts.** LUIGI ROLLA and GIOVANNI ANSALDO (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 272—277. Compare Rolla, Abstr., 1911, ii, 375).—The equilibrium temperature for  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  determined with the tensimeter is 16.4°. Mixtures of the two salts containing various proportions of the constituents are in equilibrium with zinc sulphate heptahydrate (or with ferrous sulphate heptahydrate) at this temperature, and this shows that the dissociation of the mixed salts,



is normal, each constituent dissociating as though it were isolated. Further experiments are quoted which show that the relative quantities of the two sulphates in the mixed salt influence the degree of hydration of the solid solution which is formed by the dissociation.

R. V. S.

**The Permeability of Iron to Hydrogen.** GEORGES CHARPY and S. BONNEROT (*Compt. rend.*, 1912, 154, 592—594).—That iron is permeable to hydrogen has been known since the work of Saint Claire Deville and Troost, but no quantitative measurements have yet been made. The authors have measured the rate of diffusion of hydrogen into thin-walled, steel cylinders at different temperatures, and have shown that whilst practically no diffusion occurs under atmospheric pressure below 325°, osmosis is perceptible at 350° and is about 40 times as rapid at 850°.

Nascent hydrogen diffuses through iron or steel at the ordinary temperature, and in doing so acquires special chemical activity. A steel cylinder was placed in acid, or made the cathode in a solution of sodium hydroxide. Under these conditions, hydrogen diffused into the interior of the cylinder, but failed to do so if the surface from which it was liberated was placed a few millimetres from the cylinder. The rate of diffusion varied with the thickness of the walls and the nature of the metal, and also in a somewhat indefinite way with the interior pressure. Preliminary experiments show that diffusion is not inhibited by a pressure of 14 atmospheres. W. O. W.

**Velocity of Crystallisation and Dissolution.** ROBERT MARC (*Zeitsch. Elektrochem.*, 1912, 18, 161—162).—Polemical against Wagner (compare this vol., ii, 29). G. S.

**Crystallisation from Aqueous Solutions. VI.** ROBERT MARC (*Zeitsch. physikal. Chem.*, 1912, 79, 71—96. Compare Abstr., 1910, ii, 834).—It is shown that in the case of potassium nitrate, chloride and chlorate, mercuric chloride and oxalic acid the rates of solution in, and of crystallisation from, water at 0° are equal, even when the solutions are vigorously stirred. As in the previous experiments, the crystallisation is retarded by the addition of dyes, and finally stopped before equilibrium is reached, whereas dyes have very little influence on the rate of solution. An exception to the last statement has been found in mercuric chloride; in this case the addition of a dye stops the dissolution before the true equilibrium is reached. This is probably due to a chemical change at the surface of the crystals.

Above a certain point, a further increase in the rate of stirring has no influence on the rate of dissolution and crystallisation. This is readily explained on the assumption that the crystals are surrounded by a very thin layer of solution, the thickness of which is not affected by increasing the rate of stirring above a certain point; this unaltered layer is adsorbed by the crystal, and the rate of dissolution and crystallisation depends only on the rate of establishment of the adsorption equilibrium.

The effect of dyes in retarding crystallisation is a diffusion phenomenon, being connected with the slow diffusion of the dye in the crystal. G. S.

**Optical Observations on a Liquid-crystalline Active Substance.** FELIX STUMPF (*Ann. Physik*, 1912, [iv], 37, 351—379).—The optical properties of active amyl *p*-cyanobenzylideneamino-

cinnamate have been examined. Above  $105^{\circ}$  the ester forms an isotropic liquid, which can be supercooled to  $96^{\circ}$ . Between  $102^{\circ}$  and  $105^{\circ}$  it forms a turbid, crystalline liquid, and between  $92^{\circ}$  and  $102^{\circ}$  a second modification, which is relatively very transparent. The second form can be cooled to  $75^{\circ}$  without solidifying, and the optical measurements have reference to this liquid crystalline phase.

The refractive index, perpendicular to the optical axis, was determined for different wave-lengths at various temperatures, and the results are exhibited in the form of curves. The rotation of the plane of polarisation parallel to the optical axis was also measured. The curves showing the variation of the rotation with the wave-length of the incident light are convex to the wave-length axis. The convexity of these curves becomes more pronounced as the temperature falls, and at the same time the wave-length corresponding with the minimum rotation diminishes appreciably. Mixtures of the ester and cyanoanisidine, which can be examined at lower temperatures, exhibit similar relationships.

H. M. D.

**Crystalloids and Colloids or Molecular and Micellary States.** GIOVANNI MALFITANO (*Ann. Chim. Phys.*, 1912, [viii], 25, 159—253).—The first part of this paper has been abstracted already (this vol., ii, 240). In this portion a connected account is given of researches by the author and his collaborators on the changes which occur in the interaction of ferric chloride and water, and which result in the building up of complex colloidal compounds containing hydrogen, oxygen, iron, and chlorine, and the influence on the formation of such substances of changes in physical conditions, presence of electrolytes, etc. The experimental details and views now advanced have for the most part been given already in the following abstracts: 1905, ii, 14, 72, 459; 1906, ii, 33, 450, 526, 647; 1907, ii, 94, 692; 1908, ii, 111, 288, 1042; 1909, ii, 473; 1911, ii, 102, 377; Michel, 1909, ii, 48, 146.

T. A. H.

**A More Exact Definition of Colloidal Systems and the Classification of Colloids.** FILIPPO BOTTAZZI (*Koll. Chem. Beihefte*, 1912, 3, 161—184).—The author considers that there are not sufficient grounds for the subdivision of colloidal systems into a number of different groups (suspensoids, emulsoids, solutoids, dispersoids, etc.). The most satisfactory basis for distinguishing between different disperse systems is that which has reference to the physico-chemical properties. On this basis the author would distinguish between suspensions and solutions and subdivide solutions into colloidal solutions or hydrosols and crystalloidal solutions.

H. M. D.

**[Classification of Colloids.]** WOLFGANG OSTWALD (*Koll. Chem. Beihefte*, 1912, 3, 185—190).—A criticism of the views expressed by Bottazzi (compare preceding abstract).

H. M. D.

**Coagulation of Colloidal Copper. Rate of Coagulation.** H. H. PAINE (*Proc. Camb. Phil. Soc.*, 1912, 16, 430—455).—On the assumption that the part of the colloidal substance which is easily separated from the solution may be regarded as the coagulated

portion, the rate of coagulation of colloidal solutions of copper, prepared by the electrical method, has been investigated, and it is shown that the coagulation is a definite time-process. The colloidal copper is dissolved by nitric and sulphuric acids without coagulation. Two mols. of nitric acid are required for the solution of one gram-atom of copper, and since no hydrogen is liberated in the process, it appears that the colloidal particles consist of copper oxide (or hydroxide) which are dissolved according to  $\text{CuO} + 2\text{HNO}_3 = \text{Cu}(\text{NO}_3)_2 + \text{H}_2\text{O}$ . The formation of the oxide probably occurs subsequently to the disintegration, and may be partially responsible for the observed darkening of the colour of the solution.

On addition of an electrolyte, there is an initial period in which the solution remains quite clear; when coagulation commences at the end of this period, the speed at which it occurs diminishes in a continuous manner. For colloidal solutions of different concentrations, the rate of coagulation is proportional to the square of the initial concentration. This is in accordance with the mass action law, and indicates that coagulation is brought about directly by the mutual attraction of the particles. It is inconsistent with the assumption that the condensation of the particles takes place on other nuclei, such as the ions.

When the concentration of the electrolyte is varied, the rate of coagulation is proportional to some power of the concentration of the anion in the solution, that is,  $R \propto c^p$ . Within the limits of experimental error the value of the index  $p$  is the same as the index  $n$  in the adsorption formula  $y = a \cdot c^{1/n}$ . The fact that  $p$  has the same value for coagulation with ions of different valency agrees with Fröndlich's view of the mode of action of the ions. When equivalent quantities of the ions have been absorbed, the colloidal particles behave quite similarly in reference to the process of approximation which determines the coagulation.

H. M. D.

**Miscibility in the Solid Condition between Aromatic Nitro- and Nitroso-compounds.** FRANS M. JAEGER and J. R. N. VAN KREGTEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 14, 729—740).—The miscibility of nitro- and the corresponding nitroso-compounds in the solid state has been examined by measurements of the freezing points of liquid binary mixtures. Nitrobenzene and nitrosobenzene show no evidence of the formation of mixed crystals. *p*-Nitroaniline and *p*-nitrosoaniline form mixed crystals on the side of the nitro-compound, the miscibility extending to 35 or 40% of the nitroso-compound. *p*-Nitroethylaniline and *p*-nitrosoethylaniline appear to form a continuous series of mixed crystals, the continuous freezing-point curve having a minimum temperature at 54° and the corresponding binary mixture containing about 30% of the nitroso-compound. In consequence of supercooling and the incomplete attainment of equilibrium, the solidus curve for this mixture presents approximately the form of a eutectic horizontal line. *p*-Nitropropylaniline and *p*-nitrosopropylaniline also form a complete series of mixed crystals, the freezing-point curve showing a minimum at 40·5° and at a concentration of 80% of the nitroso-compound.

From the above results it follows that miscibility in the solid state cannot be regarded as a general property of aromatic nitro-compounds and the corresponding nitroso-compounds. The mutual behaviour is sometimes complicated by the formation of polymorphous modifications  
H. M. D.

**The Law of Transformation in Stages in the Light of the Theory of Allotropy.** ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 14, 788—801).—On the assumption that the molecules of a substance in a given condition are not all alike, but that molecular groups or quasi-associations are present, and that the various phases (solid, liquid, and gaseous) assumed by a substance are characterised by variations in the relative quantities of the different molecular species, it is shown that the order in which the successive phases appear is not solely determined by the changes in free energy. The quasi-molecular groups are supposed to act as nuclei in the change from one form of a substance to another, and the result of the transformation in any given case will depend on the velocity with which the various possible forms are produced under the given conditions of temperature and pressure.  
H. M. D.

**Chemical Equilibria in Solution.** RENÉ DUBRISAY (*Compt. rend.*, 1912, 154, 431—434. Compare this vol., ii, 32).—On adding barium acetate to a solution of succinic acid in water, an equilibrium mixture is formed and barium succinate incompletely precipitated. Sodium chloride diminishes the solubility of succinic acid, and it increases the partition coefficient of acetic acid between water and chloroform. The addition of sodium chloride, therefore, would act in opposite ways in displacing equilibrium, but from Dawson's data (*Trans.*, 1902, 81, 514) and those of Herz (*Abstr.*, 1910, ii, 192), it follows that the salt should have a greater effect on the succinic than on the acetic acid. This has been verified experimentally by mixing saturated solutions of succinic acid and barium acetate, filtering, and adding sodium chloride, when the concentration of barium in the solution was diminished.  
W. O. W.

**Partition of Sodium Oxide between Boric Acid and Carbonic Acid.** FERNANDO AGENO (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 121—123).—In investigating this partition, the author measures the quantity of carbon dioxide dissolved by a known volume of a solution of boric acid and borax of known concentration. If  $a$  be the total sodium oxide,  $x$  that required by the combined carbonic acid, and  $c$  the total concentration of carbonic acid, and if the solution is kept saturated with boric acid (0.90 gram-molecule per litre), the following equation should be satisfied:  $k = 0.90x/(a - x)(c - x)$ . The values obtained for  $k$  at 25° decrease from 2.37 to 0.827 as the amount of sodium oxide is increased, besides being much lower than the value (178) calculated from the dissociation constants of the acids. Among the reasons for this discrepancy are the variation in the solubility of carbon dioxide in the presence of borate and bicarbonate, and the increase in the concentration of the polyborates with increase in the total concen-

tration of the sodium oxide. In this connexion it was found that when a saturated solution of borax, no solid borax being present, was saturated with carbon dioxide at 25° and 763 mm., the ratio  $\text{HCO}_3'/\text{BO}'_2$  was 2.27, whilst when the same solution was treated in the same way in the presence of solid borax, the ratio was 1.7. The partition coefficient varies greatly with the temperature. R. V. S.

**Kinetic Theory of a Gas Constituted of Spherically Symmetrical Molecules.** S. CHAPMAN (*Phil. Trans.*, 1912, A, 211, 433—483).—A mathematical paper in which a kinetic theory of the gaseous state has been developed by the methods adopted by Maxwell and Boltzmann. The analysis is extended to the elastic sphere theory, and expressions are obtained for the viscosity, diffusivity, and thermal conductivity of a gas without assuming any other properties of the molecules beyond that they are spherically symmetrical. Supplementary calculations have also been made for three special cases in which it is assumed (1) that the molecules are rigid elastic spheres, (2) that the molecules are centres of attractive or repulsive force varying inversely as the  $n$ th power of the distance, and (3) that the molecules are rigid elastic spheres surrounded by fields of attractive force. The results obtained are finally examined in their relation to experiment and the results of former theories. H. M. D.

**The Hypohalogenous Acids and the Hypohalogenites.** VI. The Temperature-coefficients of the Reactions between Iodine and Alkali. ANTON SKRABAL (*Monatsh.*, 1912, 33, 99—121. Compare Abstr., 1907, ii, 448; 1909, ii, 224; 1911, ii, 382; this vol., ii, 33).—In the last communication it was demonstrated how from the temperature-coefficients of the reactions between iodine and alkali hydroxide, the corresponding heat of reaction could be calculated. The calculated values for the heats of reaction accorded well with the calorimetric results, but indicated that the temperature-coefficients, contrary to the usual acceptance, may for even the same reaction with varying conditions be of quite different magnitude.

This result called for further experimental confirmation; consequently the reaction:  $3\text{I}'_3 + 6\text{OH}' = 8\text{I}' + \text{IO}'_3 + 3\text{H}_2\text{O}$ , previously investigated in a solution containing sodium carbonate and sodium hydrogen carbonate, has now been examined in a solution containing potassium hydroxide. The experimental temperature-coefficients are found to stand in good agreement with those calculated from the theory. The new temperature-coefficients are applied to the calculation of the corresponding heats of reaction. D. F. T.

**The Rôle of Intra-atomic Electrons in Catalysis.** PIERRE ACHALME (*Compt. rend.*, 1912, 154, 352—355).—The author advances the suggestion that the effect of catalysts in chemical reactions may be explained by their action in diminishing, increasing, or effecting redistribution of the electrons within the molecules of the reacting substances. W. O. W.

**The Conversion of Percentages by Weight into Atomic or Molecular Percentages in Ternary and Quaternary Systems.** FRITZ HOFFMANN (*Metallurgie*, 1912, 9, 133—142).—The

tedious calculations involved in the conversion of percentages by weight into atomic or molecular percentages may be simplified by the use of graphical methods. A method of constructing a triangular scale for each ternary system is described, the triangle being drawn on tracing paper and laid upon the main diagram. A generalised method of projection is also described, which is applicable to quaternary and more complex systems, and may be used for the conversion even when a diagram has not been constructed.

C. H. D.

**Bicentenary Anniversary of M. V. Lomonosoff's Birthday.** BORIS N. MENSCHUTKIN (*Chem. News*, 1912, 105, 73—75, 85—87).—A biographical sketch and an account of the chemical and physical work of Lomonosoff (1711–1765).

H. M. D.

**A Laboratory Balance with Electromagnetic Compensation for the Study of Systems Liberating Gases at an Appreciable Rate.** GEORGES URBAIN (*Compt. rend.*, 1912, 154, 347—349).—A description of a balance designed to effect successive rapid weighings of substances, such as efflorescing salts, undergoing continuous variation in weight. A magnetised needle takes the place of the weights, variation being effected by altering the current passing through a solenoid. The pan at the other end of the beam is suspended in the centre of an electrical resistance, by means of which any desired temperature may be maintained. The balance case is capable of being evacuated. The apparatus described is sensitive to 0.01 mg. with a load of 0.1 gram.

W. O. W.

**Aluminium Tube Furnace.** ALFRED STOCK (*Zeitsch. Elektrochem.*, 1912, 18, 153—154).—The construction of the furnace is fully illustrated in external appearance and in section, the dimensions being also given. The sealed tubes are placed in holes bored in a massive aluminium block, which rests loosely in a stand mainly composed of aluminium bronze. The heating is effected by gas conveyed by copper tubes. The advantages of the aluminium furnace are: (1) it can be used up to 500°, and rapidly reaches the desired temperature; (2) owing to the high conductivity of the metal it has practically the same temperature in all parts; (3) it radiates less heat at 500° than most furnaces do at 300°.

G. S.

**Prevention of "Bumping" of Boiling Liquids.** ERNST PIESZCZEK (*Chem. Zeit.*, 1912, 36, 198).—For this purpose the author recommends the use of a piece of glass tubing about 6—8 cms. long and 3—5 mm. wide. One end is cut off sharply. Into the other end a piece of platinum wire is fused, the upper end of which is bent so as to form a hook which provides a suitable means for introducing or removing the tube. The latter is placed in the liquid with the open end downwards. It is claimed that this device prevents bumping in all liquids, even in such as contain finely-divided solids or are covered with a layer of oily matter.

H. W.

**Extraction Apparatus.** LEONARD P. WILSON (*J. Soc. Chem. Ind.*, 1912, 31, 97—98).—The apparatus described is particularly suitable for extracting substances with non-volatile solvents. It consists of

two wide-mouthed bottles, one being placed in an inverted position over the other, and connected with it by two glass tubes which pass through the rubber stoppers with which both vessels are fitted. One of these tubes passes from the bottom of the lower bottle into the lower portion of the upper one, and is provided with a stopcock between the two; the other tube extends from about two-thirds of the height of the upper bottle to the bottom of the lower bottle, the portion of the tube in the lower bottle being surrounded by a wider tube, which reaches just above the stopper and the upper end of which is open to the air. Another tube leading from the top of the upper bottle is connected with a pump. The material to be extracted is placed in the lower bottle together with the solvent, a portion of the latter being also placed in the upper bottle; when the pump is operated, air is drawn into the lower bottle through the wide tube, causing the solvent to pass upwards into the upper bottle and to circulate through the apparatus.

W. P. S.

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## Inorganic Chemistry.

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**Avoidance of Losses of Cold in the Liquefaction of Hydrogen.** KARL OLSZEWSKI (*Bull. Acad. Sci. Cracow*, 1912, *A*, 1—27).—Apparatus for the liquefaction of hydrogen are figured and described in detail, in particular, a new form in which losses of cold are completely avoided. A thermostat for low temperatures and the liquefaction installation of the Cracow Chemical Laboratory are also fully described. Precise instructions are given of the operations necessary for the liquefaction of hydrogen. E. F. A.

**Decomposition of Water by Solar Radiations.** MIROSLAW KERNBAUM (*Bull. Acad. Sci. Cracow*, 1911, *A*, 583—586).—It was possible to demonstrate the decomposition into hydrogen peroxide and hydrogen of water exposed in quartz vessels to the solar radiations during the first days of July in Paris. The quantity formed is largest when air is present; it is demonstrated by the blue coloration produced with Schönbein's reagent (potassium iodide and ferrous sulphate). E. F. A.

**Solid Solutions of Iodine in Some Cyclic Hydrocarbons.** GIUSEPPE BRUNI and MARIO AMADORI (*Gazzetta*, 1912, *42*, i, 121—126).—It is known that iodine shows an abnormal molecular weight in freezing benzene, because it forms a solid solution with the separated solvent. The authors have determined the molecular weight of iodine cryoscopically in bromoform, diphenyl and dibenzyl, and find it to be normal. In cyclohexane, however (compare Mascarelli, *Abstr.*, 1907, ii, 602), the molecular weight of iodine was found to be 310—320. When dilute solutions of iodine in ethylene bromide and bromoform

are solidified, the colour of the solution is found to have disappeared and the solid is merely grey from disseminated iodine. Dilute solutions of iodine in benzene or *cyclohexane* retain their colour on solidification. Hence the solid solutions of iodine in these two substances have the same colour as the liquid solutions. The solubility of iodine in solid *cyclohexane* is less than its solubility in benzene, the partition coefficient between the solid and liquid phases being 0.20, as compared with about 0.3 in the case of benzene.

R. V. S.

#### Behaviour of Ozone towards Concentrated Sulphuric Acid.

CARL D. HARRIES (*Zeitsch. Elektrochem.*, 1912, 18, 129—130).—Moderately dry ozone is not affected by being passed through concentrated sulphuric acid, but under the same circumstances ozone dried over phosphoric oxide is decomposed to the extent of 1 per cent.

When ozone is passed through a solution of sodium hydroxide about 3—4 per cent. of it is decomposed, and if the gas which has passed through the alkali solution is brought in contact with concentrated sulphuric acid a further fall in concentration of 2—3 per cent. occurs. The author suggests that these results are connected with the presence of "oxozone,"  $O_4$ , in the mixture.

G. S.

**The Catalytic Change of Sulphur Dioxide into Sulphuric Acid.** HEINRICH WIELAND (*Ber.*, 1912, 45, 685—687).—The observations described in a previous paper (this vol., ii, 347) led the author to investigate what happens when moist sulphur dioxide is passed over palladium black, oxygen being rigidly excluded. A reaction takes place, with considerable development of heat, and after expelling the excess of sulphur dioxide with carbon dioxide and extracting the palladium-black with water, considerable quantities of sulphuric acid are found in solution. This sulphuric acid is formed according to the equations:  $H_2SO_3 \rightarrow SO_3 + H_2$ ;  $SO_3 + H_2O \rightarrow H_2SO_4$ . The hydrogen which should result according to the first equation was not detected, in its place sulphur being deposited. This sulphur is formed by the acid of palladium hydride on sulphur dioxide, according to the equation:  $SO_2 + 2H_2 \rightarrow 2H_2O + S$ , as was shown by shaking a solution of sulphurous acid with palladium hydride. Also, if a black which is initially free from hydrogen is used, more sulphuric acid and less sulphur is formed.

In the contact process for making sulphuric acid, it is known that if the sulphur dioxide and oxygen are quite dry, the platinum has no catalytic effect; water must be present. It is possible, therefore, that the reaction by which sulphur trioxide is formed is the one given above, and not the usually accepted one, the hydrogen formed in the first reaction being oxidised to water by the oxygen of the mixed gases.

T. S. P.

**Hexabromoselenates [Selenibromides].** ALEXANDER GUTBIER and W. GRÜNEWALD (*J. pr. Chem.*, 1912, 85, 321—330).—See this vol., i, 241.

**The Supposed Complexity of Tellurium.** GIOVANNI PELLINI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 218—225).—The author has

repeated the fractionations of Flint (Abstr., 1910, ii, 845) and Browning and Flint (Abstr., 1909, ii, 996), and his results agree with those of Harcourt and Baker (Trans., 1911, 99, 1311) in failing to show any complexity. Attempts to fractionate tellurium electrolytically also gave negative results.

The tellurium dioxide from 200 grams of the metal was subjected to an elaborate system of fractionation by Flint's method, and of the large number of fractions obtained those termed "beginning fraction," "end fraction," and "end fraction but one" were analysed by two methods, namely, the conversion of basic nitrate into oxide, and the conversion of tellurium into dioxide. The "beginning fraction" was found to give  $\text{Te} = 127.49$  (mean of determinations by one method),  $\text{Te} = 127.55$  (mean of determinations by the other method), and these values accord well with the accepted atomic weight. The "end" and "end but one" fractions gave higher values (from 127.81 to 129.60), but on further purification gave normal values. The high results are therefore to be ascribed to traces of impurities accumulated during the fractionation.

In the fractionation the author did not observe the same ratio between the quantities of hydrolysed and non-hydrolysed tellurous anhydride as are given by Browning and Flint, for whereas they give 33.3% as unprecipitated, he finds 9.5%, and the divergence from Flint's data is even greater. It is necessary to establish a true equilibrium between the precipitate and the solution by prolonged digestion on a water-bath.

The author's electrolytic fractionation was effected with a portion of the above "beginning fraction" dissolved in sulphuric acid and ammonium hydrogen tartrate and electrolysed at  $50-60^\circ$  with a rotating cathode and a current density 0.38. On each electrolysis a large middle fraction was collected and again dissolved and electrolysed, this process being repeated ten times.

R. V. S.

**Tellurium. II. Compounds of Tellurium and Iodine.**  
FRANS M. JAEGER and J. B. MENKE (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 14, 724-729).—The freezing- and melting-point curves of binary mixtures of tellurium and iodine have been examined. From the thermal behaviour, it appears that  $\text{TeI}_4$  is the only compound which separates from fused mixtures. This compound melts at  $259^\circ$ , and the molten substance appears to be dissociated to a considerable extent. The eutectic on the tellurium side corresponds with  $165^\circ$  and about 41% of tellurium, and this eutectic is nearly identical in composition with the assumed compound  $\text{TeI}_2$ . On the iodine side, the eutectic lies very close to the iodine axis, and corresponds with a temperature of  $108^\circ$ . Solid solutions are not formed to any appreciable extent, and no evidence has been obtained of the formation of the assumed compound  $\text{TeI}_6$ .

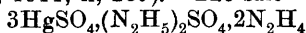
H. M. D.

**Catalytic Oxidation of Ammonia. I.** D. MENEGHINI (*Gazzetta*, 1912, 42, i, 126-134. Compare Schmidt and Böcker, Abstr., 1906, ii, 349).—A mixture of ammonia and air passes unchanged over a heated platinum spiral below about  $350^\circ$ . Above  $400-450^\circ$  the

reaction proceeds with greater vigour, and even a small variation of temperature makes a considerable difference in the consumption of oxygen. The action is complicated by the circumstance that at a certain temperature (depending on the pressure and velocity of the gas, but lying above  $550^{\circ}$ ) dissociation of ammonia into nitrogen and hydrogen takes place. Similar results were obtained when roasted pyrites (ferric oxide with traces of copper) was used as catalyst.

R. V. S.

**Double Salts of Hydrazine.** ADOLFO FERRATINI (*Gazzetta*, 1912, 42, i, 138—178. Compare Ranfaldi, *Abstr.*, 1906, ii, 664; Franzen and Lucking, *Abstr.*, 1911, ii, 285).—The salt



is a white powder obtained by treating with yellow mercuric oxide a solution of hydrazine sulphate containing excess of sulphuric acid.

Cuprous chloride and hydrazine hydrochloride yield the unstable salts  $3\text{CuCl} \cdot \text{N}_2\text{H}_5\text{Cl}$  (which forms thin, hexagonal, colourless tablets, m. p.  $170$ — $172^{\circ}$ ) and  $\text{CuCl} \cdot \text{N}_2\text{H}_5\text{Cl}$  (which crystallises in stellar aggregates of colourless tablets, m. p.  $129$ — $130^{\circ}$ ). From the solution subsequently the two cupric salts investigated by Ranfaldi can be isolated; the second of these has the formula  $\text{CuCl}_2 \cdot \text{N}_2\text{H}_5\text{Cl} \cdot \frac{1}{2}\text{H}_2\text{O}$ . The salt  $3\text{CuBr} \cdot 2\text{N}_2\text{H}_5\text{Cl}$  forms rectangular, iridescent tablets, m. p.  $130$ — $132^{\circ}$  (forming a pasty liquid). Cuprous bromide and hydrazine hydrochloride also yield a compound, m. p.  $145$ — $147^{\circ}$  (forming a pasty liquid), the composition of which corresponds with the formula  $3\text{CuBr} \cdot \text{N}_2\text{H}_5\text{Cl} \cdot \text{N}_2\text{H}_5\text{Br}$ . This substance, by the action of hydrobromic acid, gives the salt  $3\text{CuBr} \cdot 2\text{N}_2\text{H}_5\text{Br}$ , which crystallises in thin, lustrous laminae, which soften at  $160^{\circ}$ , melt to a pasty liquid at  $165$ — $166^{\circ}$ , and explode at a slightly higher temperature. The salt  $2\text{CuCN} \cdot \text{N}_2\text{H}_5\text{CN}$ , m. p.  $172$ — $173^{\circ}$  (decomp.), is obtained by adding a sufficient quantity of an aqueous solution of hydrazine hydrochloride to a solution of cuprous cyanide in potassium cyanide.

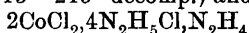
When mercuric cyanide is added to a warm aqueous-alcoholic solution of hydrazine hydrochloride, the salt  $\text{Hg}(\text{CN})_2 \cdot \text{N}_2\text{H}_5\text{Cl}$  is obtained; it has m. p.  $174$ — $175^{\circ}$  (decomp.).

Solutions of *hydrazine thiosulphate*,  $(\text{N}_2\text{H}_4)_2\text{H}_2\text{S}_2\text{O}_3$ , are obtained by adding barium thiosulphate to a solution of hydrazine sulphate until the filtered liquid gives no further precipitate with barium chloride. When freshly prepared silver chloride is shaken with a solution of hydrazine thiosulphate, the salt  $\text{Ag}_2\text{S}_2\text{O}_3 \cdot (\text{N}_2\text{H}_4)_2\text{H}_2\text{S}_2\text{O}_3$  is obtained; it forms lustrous, rectangular crystals, m. p.  $128$ — $129^{\circ}$  (becoming slightly brown at  $100^{\circ}$ ). Lead chloride and hydrazine thiosulphate yield the salt  $\text{PbS}_2\text{O}_3 \cdot (\text{N}_2\text{H}_4)_2\text{H}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ ; the product crystallises in thin, rectangular tablets, m. p.  $122$ — $123^{\circ}$  (becoming brown at  $100^{\circ}$ ). Cuprous chloride and hydrazine thiosulphate yield the salt  $\text{Cu}_2\text{S}_2\text{O}_3 \cdot (\text{N}_2\text{H}_4)_2\text{H}_2\text{S}_2\text{O}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ , but since the substance does not melt when heated to  $250^{\circ}$  this formula is perhaps doubtful.

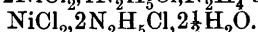
When an alcoholic solution of antimony trichloride is boiled with an excess of hydrazine hydrochloride, the salt  $\text{SbCl}_3 \cdot 3\text{N}_2\text{H}_5\text{Cl}$  is obtained; it forms a mass of silky needles. Bismuth trichloride yields the salt

$\text{BiCl}_3, 3\text{N}_2\text{H}_5\text{Cl}$ , which decomposes above  $100^\circ$ , melting at about  $220^\circ$  (decomp.). Arsenic trichloride also yields a double salt, but it could not be isolated in a pure state.

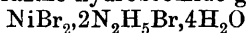
Cobalt chloride and hydrazine hydrochloride form the double salts  $\text{CoCl}_2, 2\text{N}_2\text{H}_5\text{Cl}, 2\frac{1}{2}\text{H}_2\text{O}$  (wine-red crystals which become pale violet at  $120^\circ$  and have m. p.  $213\text{--}215^\circ$  decomp.) and



(tufts of dark violet needles, m. p.  $221\text{--}223^\circ$  decomp.). Cobalt bromide and hydrazine hydrobromide yield a dark blue salt, which was obtained in fractions of different m. p., but of the approximate composition  $2\text{CoBr}_2, 4\text{N}_2\text{H}_5\text{Br}, \text{N}_2\text{H}_4$ . Nickel chloride and hydrazine hydrochloride yield the salts  $2\text{NiCl}_2, 4\text{N}_2\text{H}_5\text{Cl}, \text{N}_2\text{H}_4$  and



Nickel bromide and hydrazine hydrobromide give (1)

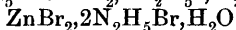


(compare Franzen and Lucking, *loc. cit.*); (2)  $2\text{NiBr}_2, 4\text{N}_2\text{H}_5\text{Br}, \text{N}_2\text{H}_4$ . In all these preparations with cobalt and nickel compounds the hydrazinates described by Franzen and Meyer (Abstr., 1909, ii, 40) were also obtained.

Ferric chloride and hydrazine hydrochloride produce the salt  $\text{FeCl}_3, 3\text{N}_2\text{H}_5\text{Cl}$ . From manganous chloride and hydrazine hydrochloride the salt  $\text{MnCl}_2, 3\text{N}_2\text{H}_5\text{Cl}$  was obtained, m. p.  $238\text{--}242^\circ$ .

The double salt  $\text{HgI}_2, 2\text{N}_2\text{H}_5\text{I}, \text{H}_2\text{O}$  crystallises in slightly yellow, prismatic tablets, m. p.  $92\text{--}93^\circ$ . The salt  $\text{HgBr}_2, 2\text{N}_2\text{H}_5\text{Br}, \text{H}_2\text{O}$  crystallises in colourless prisms, m. p.  $72\text{--}74^\circ$ , and in its preparation the anhydrous salt  $\text{HgBr}_2, 2\text{N}_2\text{H}_5\text{Br}$  is obtained.

Zinc iodide and hydrazine hydriodide yield products of compositions varying from  $\text{ZnI}_2, 2\text{N}_2\text{H}_5\text{I}$  to  $\text{ZnI}_2, 2\text{N}_2\text{H}_5\text{I}, \text{H}_2\text{O}$ . The salt



crystallises in rhomboidal tablets, m. p.  $66\text{--}68^\circ$ .

The compound  $\text{CdI}_2, 2\text{N}_2\text{H}_5\text{I}$  crystallises in prisms, which soften at  $140^\circ$  and melt at  $158\text{--}159^\circ$  (decomp.). Cadmium bromide and hydrazine hydrobromide yield two products, of which one has m. p.  $169\text{--}170^\circ$  and the probable composition  $\text{CdBr}_2, 3\text{N}_2\text{H}_5\text{Br}$ .

R. V. S.

**Nitrogen Hexa-oxide,  $\text{NO}_6$ .** FRITZ RASCHIG (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [i], 199—201).—When dry nitric oxide is passed into liquid oxygen, green flocks separate, and ultimately the mass forms a thick, green paste. The excess of oxygen is then allowed to evaporate, and the mass pressed together with a glass pestle. Decomposition begins shortly above the boiling point of oxygen, but by allowing all the excess of oxygen to escape and then dissolving the residue in sulphuric acid and analysing in the usual way, the composition may be determined. A little less than three atoms of oxygen are found for each atom of nitrogen, giving the formula  $\text{NO}_3$ . The products of decomposition are oxygen and  $\text{N}_2\text{O}_3$ . The result is held to confirm the author's view (Abstr., 1907, ii, 455), that the product of the action of air or oxygen on nitric oxide is not  $\text{NO}_2$ , but a mixture of oxides varying from  $\text{N}_2\text{O}_4$  to  $\text{N}_2\text{O}_7$ .

C. H. D.

**Revision of the Atomic Weight of Phosphorus. II. Analysis of Phosphorus Tribromide.** GREGORY P. BAXTER, CHARLES JAMES MOORE, and ARTHUR CLARENCE BOYLSTON (*J. Amer. Chem. Soc.*, 1912, 34, 259—274\*).—By the analysis of silver phosphate, Baxter and Jones (*Abstr.*, 1910, ii, 288) have found the atomic weight of phosphorus to be 31.04 ( $Ag = 107.88$ ), whereas Ter Gazarian (*Abstr.*, 1909, ii, 568; 1911, ii, 201), from determinations of the density of hydrogen phosphide, obtained the value 30.91. In view of the divergence of these results, the atomic weight has now been re-determined by the analysis of phosphorus tribromide.

Phosphorus tribromide was prepared by the action of pure dry bromine on pure dry phosphorus in a vacuum. The product was fractionally distilled in a vacuum, and when the excess of bromine had been eliminated, several fractions were collected for analysis. The method is fully described.

In order to estimate the bromine, the compound was decomposed with water and, after the phosphorous acid had been oxidised with hydrogen peroxide, the bromine was precipitated in the usual way as silver bromide. Three different series of samples of phosphorus tribromide were prepared, and the bromine in each case was estimated (1) by finding the amount of silver required to combine with it, and (2) by weighing the silver bromide formed. The values of the atomic weight of phosphorus obtained from the average of thirty-six analyses were 31.027 ( $Ag = 107.88$ ) and 31.024 ( $Ag = 107.87$ ), which agree closely with those found by Baxter and Jones (*loc. cit.*). E. G.

**Combustion of Carbon Monoxide.** HEINRICH WIELAND (*Ber.*, 1912, 45, 679—685).—The author finds that carbon monoxide is oxidised to carbon dioxide by palladium-black in the presence of water, the reaction taking place readily in the cold and in the absence of oxygen, according to the scheme:  $CO + H_2O \rightarrow CO_2 + H_2$ . The first product of the reaction is really formic acid, which then breaks down into carbon dioxide and hydrogen, the hydrogen being retained by the palladium. The formic acid was isolated as barium formate and identified by its reactions.

It was also shown that formic acid is an intermediate product in the hot combustion of carbon monoxide. A flame of carbon monoxide was allowed to play upon ice; formic acid was identified in the water formed by the melting of the ice. The combustion of the hydrogen produced by the breaking down of the formic acid furnishes the water necessary for the combustion of the carbon monoxide to proceed, and at the same time prevents the reversible reaction taking place.

These experiments are in agreement with Armstrong's views, and indicate that Traube's theory, according to which hydrogen peroxide plays an important part in combustion, is incorrect. Hydrogen peroxide occurs only as a subsidiary product formed in the first stage of the combustion of the hydrogen produced from the formic acid.

It is well known that the finely divided platinum metals catalyse

\* and *Zeitsch. anorg. Chem.*, 1912, 74, 365—383.

the fission of formic acid into carbon dioxide and hydrogen. In the case of palladium-black the catalytic action is so strong that it exceeds its hydrogen absorbing capacity, and hydrogen is evolved. Ignition of the palladium-black destroys its catalytic power, and this may account for the erroneous statement of Saint Claire-Deville and Debray that platinum-black has no catalytic effect; it is possible that they had ignited the black.

The reverse action, the formation of formic acid from carbon dioxide and hydrogen, is found to take place to a very slight extent under the catalytic influence of either a colloidal palladium solution or of palladium-black.

T. S. P.

**The Equilibrium Diagram of Alloys of Potassium and Sodium.** G. L. C. M. VAN ROSSEN HOOGENDYK VAN BLEISWYK (*Zeitsch. anorg. Chem.*, 1912, 74, 152—156).—The thermal analysis of alloys of potassium and sodium gives results in general agreement with those obtained by Kurnakoff and Puschin (Abstr., 1902, ii, 136). The purified metals are melted in Jena glass tubes under purified petroleum. Only one compound is formed,  $\text{Na}_2\text{K}$ , which decomposes at  $+6.9^\circ$  into sodium and liquid. The eutectic point is at  $-12.60^\circ$  and 66.6 atomic % of potassium. The formation of the compound from sodium and liquid is only complete after many days at  $0^\circ$ . Solid solutions are not formed at any part of the system.

C. H. D.

**The Solubility of Sodium Dihydrogen Phosphate and the Transition Points of the Hydrates.** AKIRA IMADSU (*Mem. Koll. Sci. Eng. Kyōtō*, 1912, 3, 257—263).—The solubility of sodium dihydrogen phosphate in water between  $0^\circ$  and  $99^\circ$  has been determined, and the existence of the anhydrous salt, monohydrate, dihydrate, and tetrahydrate has been confirmed. Dimorphism in the monohydrate was not noticed.

The transition points of the anhydrous salt and monohydrate, and of the monohydrate and dihydrate, have been estimated respectively to be  $57.4^\circ$  and  $40.8^\circ$ .

H. W.

**The Lithium Amalgam Richest in Mercury.** GEORGE MCPHAIL SMITH (*Zeitsch. anorg. Chem.*, 1912, 74, 172—173).—It has been shown by Schukoffsky (Abstr., 1911, ii, 882) that lithium does not form a compound richer in mercury than  $\text{LiHg}_8$ . This has also been shown by chemical means by Smith and Bennett (Abstr., 1910, ii, 500).

C. H. D.

**Solubility in Water of Nearly Insoluble Salts, Especially Silver Chloride.** C. VAN ROSSEM (*Chem. Weekblad*, 1912, 9, 203—209).—The mean values found by Ostwald's *E.M.F.* method for the solubility of silver chloride in water are: at  $18^\circ$   $1.019 \times 10^{-5}$ , and at  $25^\circ$   $1.429 \times 10^{-5}$  gram-equivalents  $\text{AgCl}$  per litre.

A. J. W.

**Preparation and Properties of an Oxybromide of Silver.** ALPHONSE SEYEWETZ (*Compt. rend.*, 1912, 154, 355—357).—Finely divided silver, prepared by reducing silver nitrate with formaldehyde,

is treated with a saturated solution of *p*-benzoquinone containing 2.5% of potassium bromide. When the odour of *p*-benzoquinone has disappeared, the liquid is decanted and replaced by a fresh quantity of the solution, the process being repeated until the quinone is no longer reduced. The product is washed and purified from silver by two crystallisations from boiling aqueous ammonia, from which it separates in colourless, shining lamellæ, having the composition of *silver oxybromide*,  $\text{Ag}_7\text{OBr}_7$ . The substance becomes brown on exposure to light; it is less soluble in ammonia than silver bromide. *Silver oxyiodide* is obtained by treating the oxybromide with potassium iodide. W. O. W.

**Preparation of Alkaline Earth Metals by the Electrolysis of Fused Salts.** MAX TRAUTZ (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 196—199).—Strontium is best obtained by electrolysing a mixture of strontium chloride (2 mols.) and potassium chloride (1 mol.) at bright redness. The crucible tapers sharply downwards, and a pointed iron cathode, cooled externally by water, passes through it. A thick carbon cylinder is used as anode. Using 30 amperes and 10 volts, a current efficiency of 29—48% is obtained, and masses of strontium up to 90 grams may be prepared. The product contains, on the average, 97.3% strontium, 0.3% chlorine, and 0.84% potassium, and has D 2.50.

Only small masses of barium can be prepared by the same method.

C. H. D.

**Hydration of Calcium Oxide.** S. CHUMANOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 201—204).—Definite weights of pure lime were left for three days in contact with different proportions of boiled water in vessels which were free from carbon dioxide and were frequently shaken. The solid phases were subsequently separated by filtration and dried at 112—115° until of constant weight, carbon dioxide being excluded during these operations. The proportion of water remaining in each of these phases after drying was then determined by ignition. In the following table *p* shows the number of parts of water originally taken per 1 part of lime, and *n* the number of mols. of water per mol. of lime in the dried solid phase:

<i>p</i> .....	17.962	35.917	179.65	353.17	718.67
<i>n</i> .....	1.0725	1.0996	1.1592	1.1866	1.5563

T. H. P.

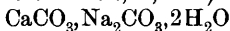
**The Constitution of Tetracalcium Phosphate and its Reduction by Iron.** EUGEN STEINWEG (*Metallurgie*, 1912, 9, 28—40).—The phosphorus in basic slag is present as tetracalcium phosphate,  $4\text{CaO}, \text{P}_2\text{O}_5$ . Less basic phosphates are reduced by molten iron, forming iron phosphide,  $\text{Fe}_3\text{P}$ .

It has not been found possible to fuse tetracalcium phosphate, on account of its action on all crucibles at a high temperature.

Silica, alumina or ferric oxide removes a part of the lime, and the remaining tricalcium phosphate is reduced by carbon. In the absence of these acid oxides, tetracalcium phosphate is not reduced by iron containing carbon.

C. H. D.

**Double Carbonates of Calcium.** MAURICE BARRE (*Compt. rend.*, 1912, 154, 431. Compare this vol., ii, 254).—The salt



described in the previous communication has also been studied by de Schulten (*Abstr.*, 1897, ii, 146). W. O. W.

**Thermal Analysis of Binary Mixtures of Chlorides of Bivalent Elements.** CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 208—213. Compare Sandonnini and Scarpa, *Abstr.*, 1911, ii, 984).—This paper deals with the systems  $\text{BaCl}_2\text{--MnCl}_2$ ,  $\text{CdCl}_2\text{--PbCl}_2$ ,  $\text{CdI}_2\text{--HgI}_2$ , and  $\text{HgBr}_2\text{--PbBr}_2$ .

Barium chloride and manganous chloride probably form a compound which contains 30—40 mol. % of manganous chloride; it is revealed by a pause which varies from 533° to 544°. The eutectic mixture corresponds with about 64 mol. % of manganous chloride and 503°.

In regard to the system  $\text{CdCl}_2\text{--PbCl}_2$ , the author obtains the same results as Herrmann (*Abstr.*, 1911, ii, 801).

The m. p. of cadmium iodide is 380° (Carnelley, *Trans.*, 1878, gave 404°; Ruff and Plato, *Abstr.*, 1903, ii, 588, gave 350°). For mercuric iodide the author finds m. p. 253°, and transformation point 128°; these differ slightly from the results of previous observers. The two substances form mixed crystals in all proportions.

Mercuric bromide and lead bromide form a eutectic which lies at 232° (5 mol. % of lead bromide). R. V. S.

**Action of Magnesium on the Water of Crystallisation of Crystallohydrates: Activation of the Magnesium by Salts.** JAKOV I. MICHAILENKO and P. G. MUSHINSKY (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 181—201).—Powdered magnesium reacts with the water of crystallisation of crystalline salts with evolution of hydrogen, and the authors have studied the temperatures at which this reaction takes place and the proportion of the total water decomposed in a number of cases. The halogen salts are most active in this respect, and of these, stannous chloride (+ 2H<sub>2</sub>O) and ferric chloride (+ 6H<sub>2</sub>O) show the greatest activity, the reaction occurring immediately on mixing with the magnesium.

The action is intensified by the addition of one of a number of salts, such as zinc, mercury, aluminium, etc., chlorides, which function as activators.

Hydroxides, such as those of calcium, lead, and aluminium, which contain no water of crystallisation, do not react with magnesium even when heated to 200°. With sodium hydroxide, the reaction is slight, and the evolution of hydrogen small in amount, but with potassium hydroxide extremely energetic action occurs. Crystalline barium hydroxide and peroxide, which contain water of crystallisation, react with magnesium. Anhydrous acids and acid salts, such as boric, antimonie, phosphoric and cinnamic acids, potassium and sodium hydrogen sulphates, and sodium hydrogen carbonate, do not react with magnesium, ammonium hydrogen fluoride being, however, an exception to this rule. Acids and acid salts crystallising with

water of crystallisation, such as  $\text{H}_3\text{AsO}_4 + \frac{1}{2}\text{H}_2\text{O}$ ,  $\text{H}_2\text{C}_2\text{O}_4 + 2\text{H}_2\text{O}$ ,  $\text{C}_6\text{H}_4(\text{OH})_3 \cdot \text{CO}_2\text{H} + \text{H}_2\text{O}$ ,  $\text{C}_3\text{H}_4(\text{OH})(\text{CO}_2\text{H})_3 + \text{H}_2\text{O}$ , all react with magnesium to approximately the same extent as other crystalline hydrates. T. H. P.

**The Solubility of Zinc Hydroxide in Alkalies.** OSKAR KLEIN (*Zeitsch. anorg. Chem.*, 1912, 74, 157—169).—It has been maintained by Hantzsch (Abstr., 1902, ii, 395) on the ground of conductivity measurements that zinc hydroxide in alkaline solutions is mainly present in the colloidal form, and not as zinc oxide. It is, however, known that the solubility is proportional to the quantity of alkali present. The separation of zinc hydroxide on boiling may be explained, as has been done by Ostwald for glucinum hydroxide, by the assumption of a less soluble and more stable form of the hydroxide.

If a solution of zinc sulphate is allowed to drop into one of potassium hydroxide until the white precipitate just fails to redissolve, the solution is saturated with respect to the modification *A*. In time this solution deposits a modification *B*, which often forms regular crystals. If collected and dried, *B* passes into a still less soluble modification *C*. The solubility of all three modifications in solutions of different concentrations has been determined. *A* has the composition  $\text{H}_2\text{ZnO}_3$ , *B* and *C* have the composition  $\text{Zn}(\text{OH})_2$ . There is no evidence for the presence of colloidal zinc hydroxide in the solutions.

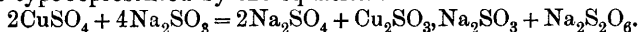
An application of the law of mass action, assuming that the hydroxides yield hydrogen ions on dissociation, gives the value for *A*:  $[\text{H}^+]^2 \cdot [\text{Zn}_2\text{O}_3] = k_1 = 0.68 \times 10^{-29}$ , the corresponding values for *B* and *C* being  $k_2 = 0.71 \times 10^{-29}$  and  $k_3 = 0.27 \times 10^{-29}$ . C. H. D.

**Copper Amalgam.** ANTOINE GUNTZ and DE GRIEFT (*Compt. rend.* 1912, 154, 357—358).—The composition of amalgams obtained by electrolysing copper sulphate solutions with a mercury cathode at the ordinary temperature vary with the pressure subsequently employed to free them from mercury. Comparison of such amalgams with those made by heating the two metals together shows that in the former case an amalgam having the composition  $\text{CuHg}$  is formed, but remains dissolved in mercury, whilst in the latter instance no combination occurs at  $135^\circ$ , the product on cooling consisting of a solution of copper in mercury, from which pure copper may be separated by pressure. Such a solution is unstable, and passes in three days into a stable solution of the compound,  $\text{CuHg}$ . W. O. W.

**The Fusion of Cuprous Oxide with Silica.** C. NICOLSCU OTIN (*Metallurgie*, 1912, 9, 92—99).—It has not been found practicable to make a thermal analysis of the binary system cuprous oxide-silica, on account of oxidation to cupric oxide, and a ternary system is thus formed. Basic mixtures contain crystals of cuprous oxide, together with a eutectic. The thermal results, together with the determinations of density, indicate that several silicates are formed, the composition of which is uncertain. C. H. D.

**Action of Alkali Sulphites on Copper Salts.** HENRI BAUBIGNY (*Compt. rend.*, 1912, 154, 434—437).—On heating copper sulphate solution with excess of an alkali sulphite so that the precipitate first

formed redissolves, and then heating the resulting colourless solution on the water-bath, a red precipitate is formed, and the filtrate is found to contain an alkali dithionate. The latter arises through a reaction of the type represented by the equation :



The composition of the red precipitate is difficult to determine owing to the ease with which it loses sulphur dioxide, but it undoubtedly contains cuprous sulphite, and is apparently a decomposition product of the double alkali cuprous sulphite first formed. W. O. W.

**Compounds of Neodymium.** PAUL JOYE and CHARLES GARNIER (*Compt. rend.*, 1912, 154, 510—511).—Neodymium hydroxide,  $\text{Nd}(\text{OH})_3$ , is known to show a different absorption spectrum by reflection from that given by the oxide.

The existence of two new hydrated oxides has now been recognised by heating the hydroxide between  $300^\circ$  and  $700^\circ$ , and examining the spectra. The first, formed at  $310$ — $325^\circ$ , is a greyish-brown substance having the composition  $2\text{Nd}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ; its spectrum is characterised by broad, diffuse bands showing more than one maximum of absorption.

At  $525^\circ$ , the second hydrate,  $2\text{Nd}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ , is slowly formed as a grey compound. The spectrum has been studied by Waegner, who attributed it to a higher oxide,  $\text{Nd}_4\text{O}_7$ . W. O. W.

**The Annealing of Aluminium Bronzes.** A. PORTEVIN and G. ARNOU (*Compt. rend.*, 1912, 154, 511—514).—The effect of annealing industrial, tempered aluminium bronzes at different temperatures on the structure and mechanical properties of the alloy has been studied. With bronzes containing 89—90% of copper, annealing at  $400^\circ$  increases the hardness and diminishes the elongation; above  $500^\circ$  the hardness and elastic limit diminishes, whilst the elongation continues to increase. The tempered bronzes contain an eutectic which disappears above the transition point, its place being taken by a constituent crystallising in needles, recalling by their appearance the martensitic structure of steel. The higher the temperature and the longer the duration of annealing, the more complete is the transformation. In this respect aluminium bronzes resemble steel and copper-tin alloys.

The paper is illustrated with two microphotographs. W. O. W.

**Italian Pozzuolanas.** A Sicilian Pozzuolana. EUGENIO MANZELLA (*Gazzetta*, 1911, 41, ii, 730—747).—The paper records the results of the physical and chemical determinations of a pozzuolana from the neighbourhood of Catania. The pozzuolana in question has the following composition :

Loss on heating.	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .	$\text{SO}_3$ .	Total.
0.90	45.81	21.94	9.79	7.15	1.90	3.81	2.09	0.28	99.70

The hydraulic value of the material was also compared with that of other pozzuolanas by the method previously described (*Abstr.*, 1906,

ii, 493), which is to be preferred to Gallo's modification (Abstr., 1908, ii, 844). Attention is drawn to the great influence of temperature on the results obtained in this measurement. The resistance of mortar made from the substance to tension and compression was also determined. Experiments on the hydraulic value of the pozzuolana were also made by the electrical method of Giorgis and Gallo (Abstr., 1906, ii, 447).  
R. V. S.

**The System Iron-Carbon.** OTTO RUFF (*Zeitsch. Elektrochem.*, 1912, 18, 158. Compare Smits, this vol., ii, 165).—A claim for priority.  
G. S.

**The System Iron-Carbon.** WILLIAM C. McC. LEWIS (*Zeitsch. Elektrochem.*, 1912, 18, 158—159).—Smits (this vol., ii, 165) has suggested that in the homogeneous liquid phase of the iron-carbon system, iron, carbon and iron carbide are in equilibrium according to the equation  $3\text{Fe} + \text{C} \rightleftharpoons \text{Fe}_3\text{C}$ . Support is lent to this assumption by a calculation of the molecular weight of dissolved carbon according to the known cryoscopic formula  $dT = RT^2(x_1 - x_2)/LM$ , where  $x_1$  and  $x_2$  are the concentrations of carbon in the solid and liquid phases. For the purposes of the calculation, the latent heat,  $L$ , of the solvent is required, but is not known with certainty. Taking  $L$  as 30 calories, the molecular weight of dissolved carbon is about 12, so that 30 calories is probably about the true value for  $L$ . The value of 12 obtained for the atomic weight of carbon is in accord with the view that it is present mainly as a compound  $\text{Fe}_n\text{C}$ , probably  $\text{Fe}_3\text{C}$ .  
G. S.

**Complex Ferric Compounds. Ferric Fluoride.** ALBERT RECOURA (*Compt. rend.*, 1912, 154, 655—657. Compare this vol., ii, 165).—The constitution of ferric fluoride,  $\text{Fe}_2\text{F}_6 \cdot 6\text{H}_2\text{O}$ , should probably be represented as  $\text{FeF}_4(\text{OH})_2(\text{HF})_2 \cdot 4\text{H}_2\text{O}$  for the following reasons. Only one-third of the fluorine enters into double decomposition when an aqueous solution is treated with barium chloride, although in practice the phenomenon is complicated by precipitation of the salt  $\text{Fe}_2\text{F}_6 \cdot 3\text{BaF}_2$ . When the solid is boiled with alcohol, one-third of the fluorine is rapidly eliminated as hydrogen fluoride, the remainder being lost extremely slowly. At  $95^\circ$  the salt loses water rapidly and proportionally to the loss of fluorine, until one-third of the latter has been eliminated, when no more water is lost. On prolonged heating, decomposition slowly occurs with change in colour, probably in accordance with the equation:  $\text{Fe}_2\text{F}_4(\text{OH})_2(\text{HF})_2 = \text{Fe}_2\text{OF}_4 + \text{H}_2\text{O} + 2\text{HF}$ .  
W. O. W.

**Colloidal Ferric Oxide.** G. D. KRATZ (*J. Physical Chem.*, 1912, 16, 126—130).—The author has investigated Wright's method of preparing colloidal ferric oxide solutions (Trans., 1883, 43, 156). When 10% ferric chloride solution is poured into a large excess of concentrated ammonia, the colloidal ferric oxide produced is coagulated by the ammonium chloride. On evaporating to dryness and washing with water, the ammonium chloride is first washed out, and then the ferric oxide deflocculates and passes through the filter paper as a

dark or bright red colloidal solution. If the original precipitate is left for some time in contact with its ammoniacal mother liquor, spontaneous changes occur, so that after evaporation it is found to be insoluble.

Wright's method does not give concentrated solutions of the colloid, but it avoids the necessity of washing and dialysing a gelatinous precipitate. R. J. C.

**The Mineral Sulphides of Iron.** EUGENE T. ALLEN, J. L. CRENSHAW, and JOHN JOHNSTON; with Crystallographic Study by ESPER S. LARSEN (*Amer. J. Sci.*, 1912, [iv], 33, 169—236).—Some of the main facts arrived at in the long series of experiments here recorded in detail have already been given in a preliminary paper (Abstr., 1911, ii, 1093); additional conclusions are now stated respecting pyrrhotite. The change from iron-pyrites to pyrrhotite is a reversible one,  $\text{FeS}_2 \rightleftharpoons \text{FeS(S)}_x + (1-x)\text{S}$ , on either side of the temperature  $565^\circ$ . The composition of pyrrhotite depends, not only on the temperature, but also on the pressure of the sulphur vapour in which it is heated. The variation in composition is explained by the solid solution of sulphur in ferrous sulphide, and the sp. gr. varies continuously with the composition (D 4.755 with 0.41% dissolved sulphur to D 4.520 with 6.04%). The maximum amount of dissolved sulphur (6.04%) was obtained at a temperature of  $600^\circ$ , and extrapolation on the curve gives the saturated solution with 6.5% sulphur at  $565^\circ$ . The melting point of pure ferrous sulphide in a vacuum is  $1170^\circ \pm 5^\circ$ ; in an atmosphere of hydrogen sulphide, sulphur is absorbed and the m. p. is raised. Troilite is merely the end member of the pyrrhotite series; it contains no dissolved sulphur, having been formed in contact with free iron in meteorites. Crystals of pyrrhotite, 0.3—1.0 mm. in length, were formed at various temperatures between  $80^\circ$  and  $225^\circ$  by the action of hydrogen sulphide on slightly acid solutions of a ferrous salt containing some ferric iron. The crystals of  $\alpha$ -pyrrhotite formed at the higher temperatures appear to be orthorhombic with  $a:b:c=0.5793:1:0.9267$  to  $0.5793:1:0.9927$ . Those of  $\beta$ -pyrrhotite formed at the lower temperatures are hexagonal with the  $c$  axis ranging from 0.8632 to 0.8742. L. J. S.

**The Solubility of Carbon in Nickel.** OTTO RUFF and WALTER MARTIN (*Metallurgie*, 1912, 9, 143—148).—The solubility of carbon in molten nickel, determined by the method already employed for iron (Abstr., 1911, ii, 897), increases with the temperature, reaching a maximum value of 6.42% at  $2100^\circ$ , corresponding with the composition of *nickel carbide*,  $\text{Ni}_3\text{C}$ . Above  $2100^\circ$  the solubility remains constant. The carbide is much less stable than iron carbide, and not more than 1% of carbon is retained in the combined state, even on rapid quenching. The carbide appears as a distinct micrographic constituent in etched specimens. C. H. D.

**Solubility of Nickel Perchlorate and Cobalt Perchlorate.** H. GOLBLUM and F. TERLIKOWSKI (*Bull. Soc. chim.*, 1912, [iv], 11, 146—159. Compare this vol., ii, 261).—With a view to constructing

a complete solubility diagram for each of these salts a number of their solubility constants have been determined. Tables are given in the original showing the solubilities of the salts at  $-30.7^{\circ}$ ,  $-21.3^{\circ}$ ,  $0^{\circ}$ ,  $7.5^{\circ}$ ,  $18^{\circ}$ ,  $26^{\circ}$ ,  $45^{\circ}$  and the densities of saturated solutions at these temperatures. A second set of tables shows the composition of solutions of the salts which are in equilibrium with ice at  $-10.9^{\circ}$ ,  $-21.3^{\circ}$ , and  $-30.7^{\circ}$ . Brief crystallographic descriptions of four perchlorates are also given.

The chief results obtained are as follows: Cobalt perchlorate forms long, hexagonal prisms, which are pale pink in colour, uniaxial negative, and show feeble polychroism. The cryohydric point for this salt is  $-62.20^{\circ}$ . Nickel perchlorate crystallises in the same form as the cobalt salt, but the prisms are longer. The colour is bluish-green, and the polychroism very feeble. The cryohydric point is  $-49^{\circ}$ . Chromium perchlorate also crystallises in the same form, but the prisms are thicker and shorter. The colour is pale brownish-green, and the polychroism inappreciable. Didymium perchlorate forms cubic crystals or octahedral grains, arranged in dendritic or hopper forms. Nickel and cobalt perchlorates crystallise with  $9H_2O$  at  $-21.3^{\circ}$ . They can be estimated in solution by electrolytic deposition of the metal and titration of the perchloric acid liberated. They are very soluble in water, and the solubility increases with the temperature.

T. A. H.

**The Isomerism of the Stannic Acids. II.** WERNER MECKLENBERG (*Zeitsch. anorg. Chem.*, 1912, 74, 207—280. Compare Abstr., 1910, ii, 41).—The explanation previously offered, that  $\alpha$ - and  $\beta$ -stannic acids differ in the size of their particles, is found to account satisfactorily for other facts in the behaviour of the acids. For the further experiments, a solution of stannic sulphate, prepared by dissolving pure tin in boiling concentrated sulphuric acid and filtering from sulphur, is allowed to drop into water at different temperatures. Five such preparations have been used, the hydrolysis being performed at  $0^{\circ}$ ,  $25^{\circ}$ ,  $50^{\circ}$ ,  $75^{\circ}$ , and  $100^{\circ}$  respectively. The precipitated stannic acid is in each case washed repeatedly with water by decantation, and the milk coagulated by the addition of ether, filtered, and washed until the washings are free from sulphuric acid, an operation sometimes requiring several weeks. The masses dried in air differ in appearance, the  $0^{\circ}$  acid being almost transparent, whilst the  $100^{\circ}$  acid is opaque, like starch, the other preparations being of an intermediate character. The proportion of adsorbed water decreases with increasing temperature of hydrolysis.

Hydrochloric acid acts less readily on the colloids prepared at high temperatures than on those prepared at a low temperature. The adsorptive power for phosphoric acid falls off in the same order, indicating that the differences between the acids consist in differences of adsorbing surface, that is, of size of particles. The colloidal solutions obtained by the action of concentrated hydrochloric acid on the stannic acids, followed by dilution with water, show the same order of decreasing stability, although the  $50^{\circ}$  acid is more difficult to bring into colloidal solution than any of the other four. The velocity of pre-

cipitation of such solutions by sodium sulphate increases with increasing quantity of the reagent, and is also dependent on the age, concentration, and source of the colloidal stannic acid solution. Precipitation by hydrochloric acid follows the same order, but up to a certain limit hydrochloric acid increases the stability of the solution.

The colloidal solutions have been optically examined by means of an instrument in which the intensity of the "Tyndall cone" may be measured. A relation between the opacity of a colloidal solution of stannic acid and its chemical stability has not been recognised, and it is possible to prepare from the same colloid solutions of very different turbidity, using the same concentrations of stannic and hydrochloric acids. The 50° acid, however, yields exceptionally turbid solutions.

In mixtures of colloidal solutions of two preparations, such as the 0° and 100° acids, the acid prepared at the lower temperature exerts a protective action on the other in respect to precipitation by sodium sulphate.

The experiments indicate that there are not two definite compounds, *a*- and *b*-stannic acid, but that two kinds of particles, termed "primary" and "secondary" particles, the second of which are aggregates of the first, exist, and that the properties of the colloids depend on the relative proportions of the two kinds present.

C. H. D.

**Electrolytic Preparation of Tervalent Vanadium Salts.** EUGEN RENSCHLER (*Zeitsch. Elektrochem.*, 1912, 18, 137).—Ammonium metavanadate can readily be reduced electrolytically to tervalent vanadium salts. For this purpose an ordinary porous cell is used as cathode compartment, and both anode and cathode, which are cylinders of lead foil, dip in 50% sulphuric acid. Ammonium vanadate is added to the cathode liquid, which is kept stirred, and a current of 4 amperes passed through until the solution becomes green. It is then removed from the pot, and, when kept, vanadium ammonium alum separates in good yield.

G. S.

**Reduction of Vanadic Acid in Concentrated Sulphuric Acid Solution by Hydrogen Peroxide and by Persulphates.** JOHN R. CAIN and J. C. HOSTETTER (*J. Amer. Chem. Soc.*, 1912, 34, 274—276).—In attempting to substitute hydrogen peroxide for potassium chlorate in Gregory's method of estimating vanadium (*Proc.*, 1909, 25, 232), it was found that the vanadium was quantitatively reduced from the quinquevalent to the quadrivalent state. Molybdenum, titanium, and iron compounds are not reduced under similar conditions. Solutions of vanadium pentoxide in concentrated sulphuric acid are also reduced by potassium and ammonium persulphates, and it is shown that in these cases the reaction is probably due to Caro's acid.

E. G.

## Mineralogical Chemistry.

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**Nomenclature of Aluminium Hydroxides.** EMIL DITTLER and CORNELIO DOELTER (*Centr. Min.*, 1912, 104—106).—As applied for technical purposes the term bauxite includes a variety of mixtures which are to be regarded as rocks. Such material consists of the crystallised aluminium hydroxides diaspore and hydrargillite (= gibbsite), and the amorphous aluminium hydroxide bauxite, together with intermixed limonite, hæmatite, and kaolin (clay). Such mixtures may be named diasporite, gibbsitite, or bauxitite, according to the predominance of one or other of these constituent minerals. The two former are referred to as crystalloidal alumolites (Kristalloid-Alumolithe), and the latter as colloidal alumolites (Kolloid-Alumolithe).

L. J. S.

**Concretions of the Geysers and Springs of the Yellowstone Park.** JOSE CASARES and S. PIÑA R. (*Anal. Fis. Quim.*, 1912, 10, 18—20).—A specimen of compact sopal having D 2·0285 gave H<sub>2</sub>O at 100° 2·78, at red heat 4·61; SiO<sub>2</sub>, 88·45; Al<sub>2</sub>O<sub>3</sub>, 4·38; CaO, 0·10; K<sub>2</sub>O and Na<sub>2</sub>O, traces.

A concretion from the Mammoth Hot Springs gave H<sub>2</sub>O, 0·86; SiO<sub>2</sub>, 0·06; Fe<sub>2</sub>O<sub>3</sub>, 0·10; Al<sub>2</sub>O<sub>3</sub>, 0·16; CaO, 53·31; CO<sub>2</sub>, 38·18; SO<sub>3</sub>, 6·67.

G. D. L.

**Baeumlerite, a New Potash-salt Mineral.** O. RENNER (*Centr. Min.*, 1912, 106—107).—This new mineral occurs as thin bands in the rock-salt of the Desdemona salt mine in the Leine valley. It is colourless and transparent, extremely deliquescent, and becomes phosphorescent when broken or rubbed. It is frequently intermixed with rock-salt and tachhydrite. Analysis gives the formula KCl, CaCl<sub>2</sub>. The material possesses three perfect cleavages at right angles, or approximately at right angles, to one another; it is optically biaxial and negative; *n* about 1·52; H 2½—3.

L. J. S.

**Observations on the Action of Fluorine in Nature.** UGO ALVISI (*Gazzetta*, 1912, 42, i, 25—30).—The author discusses the mode of origin of the minerals containing fluorine found in the vein of "The Three Princes" near Freiberg i.S. He supposes that by the action of hydrofluoric acid on material containing silicon and calcium, calcium silicofluoride is formed. When this is decomposed by heat, calcium fluoride and silica are produced. Barium sulphate and calcium fluoride when heated with water at 240° yield in small quantity the compound BaSO<sub>4</sub>, CaF<sub>2</sub> (Scheerer and Drechsel, this Journ., 1874, 234). All these substances are found in the vein in question.

R. V. S.

**Solution Phenomena on Anhydrite.** WILHELM [FRIEDRICH] BURKHARDT (*Zeitsch. Kryst. Min.*, 1912, 50, 209—230).—A detailed description is given of the forms of the etched figures and of the final

forms due to solution when cleavage blocks of anhydrite are treated with cold and with hot sulphuric acid, nitric acid, hydrochloric acid, and distilled water. The resulting forms differ in character according to the nature of the solvent.

L. J. S.

[Canadian Minerals.] ROBERT A. A. JOHNSTON (*Summary Rep. Geol. Surv. Canada*, for 1910, 1911, 256—263).—*Hexahydrate*.—This new name is applied to a hydrated magnesium sulphate (anal. I.) with the composition of the artificial hexahydrate,  $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ . It occurs as seams, up to  $\frac{1}{2}$  in. thick, and patches in an altered rock on the bank of the Bonaparte river, Lillooet district, British Columbia. The material is white and opaque, with a columnar to fibrous structure.

	$\text{SO}_3$ .	$\text{MgO}$ .	$\text{H}_2\text{O}$ .	Insol. ( $\text{SiO}_2$ ).	Total.	Sp. gr.
I.	34.52	17.15	46.42	1.78	99.87	1.757

*Awaruite*, *magnetite*, and *almandine* are found in the gold-washings on the Pelly river, Yukon. The awaruite (anal. II.) has the form of small, irregular grains, rarely exceeding 1 mm. diameter, and showing no definite crystalline structure. It is steel-grey with a pale yellow tarnish, and is malleable and strongly magnetic. The associated almandine (anal. III) has the form of minute, angular grains with a pale reddish colour.

	Ni.	Fe.	Co.	Cu.	P.	S.	Insol.	Total.	Sp. gr.
II.	74.34	21.35	1.34	0.48	0.08	0.03	1.72	99.34	7.746

*Axinite* (anal. IV of crystals) occurs as hair-brown crystals and crystalline masses at the contact of monzonite and sedimentary rocks, at Nickel Plate mountain, Yale district, British Columbia.

	$\text{SiO}_2$ .	$\text{B}_2\text{O}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{FeO}$ .	$\text{MnO}$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{H}_2\text{O}$ .	Total.	Sp. gr.
III.	37.7	—	21.1	2.4	31.9	1.5	nil	5.1	—	99.7	3.991
IV.*	42.18	5.22	18.12	0.98	7.20	3.89	19.91	1.43	0.35	99.37	3.296
V.	42.76	—	4.32	2.57	—	—	1.92	25.30	23.13	100.00	2.162

\* Also  $\text{ZnO}$ , 0.09.

An *alteration product* after *amphibole* (anal. V) occurs at several spots in the Gatineau valley, province of Quebec. The pale yellowish-grey material is waxy and clay-like, and is decomposed by cold dilute hydrochloric acid with the separation of gelatinous silica. In composition it is near to saponite.

*Linarite* (anal. VI) is found as fine twinned crystals associated with anglesite, galena, and copper-pyrites at Beaver mountain, West Kootenay, British Columbia.

	$\text{PbSO}_4$ .	$\text{CuO}$ .	$\text{H}_2\text{O}$ .	Total.	Sp. gr.
VI.	75.17	19.88	4.73	99.78	5.23

*Diamond* has been detected as minute particles in the insoluble residues of the chromite from altered peridotite and serpentine at Olivine mountain, Yale district, British Columbia.

L. J. S.

**Amphiboles from Mount Plebi near Terranova Pausania (Sardinia).** DOMENICO LOVISATO (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 109—116).—The author gives a detailed account of the minerals

in this situation. Among them is an actinolite, which when unaltered has a pale emerald-green colour. Its hardness is from five to six, D<sup>29</sup> 2·913. Analysis gave the following results :

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.	MgO.	CuO.	NiO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total.
56·50	0·81	1·15	6·90	0·09	13·00	19·22	0·19	0·15	1·07	0·19	0·90	100·17

Even spectroscopic examination failed to reveal the presence of lithium, fluorine, zinc, titanium, chromic acid, or phosphoric acid, but the presence of copper and nickel is noteworthy.

R. V. S.

**Experimental Investigation of Some Metasilicates.** GUSTAV ZINKE (*Jahrb. Min.*, 1911, ii, 117—142).—Artificial products and natural minerals mixed together in various proportions were fused in crucibles; the melting and consolidation points are noted, and the optical characters of the crystalline products are described in detail. The series experimented with were:  $m\text{MgSiO}_3 + n\text{FeSiO}_3$ ;  $m\text{MgSiO}_3 + n\text{CaSiO}_3$ ;  $m\text{MgSiO}_3 + n\text{MnSiO}_3$ ;  $m\text{MgSiO}_3 + n\text{CaMgSi}_2\text{O}_6$ ;  $m\text{MgSiO}_3 + n\text{CaFeSi}_2\text{O}_6$ , and  $\text{MgSiO}_3$  + crystallising agents (bismuth,  $\text{MgF}_2$ ,  $\text{MgCl}_2$ , or  $\text{CaF}_2$ ). The products include rhombic pyroxenes, clinoenstatite, diopside, wollastonite, hexagonal calcium silicate, and glassy material. The presence of the “crystallising agents” had no effect.

L. J. S.

**Analyses of French Felspars.** FERDINAND GONNARD and PHILIPPE BARBIER (*Bull. Soc. franç. Min.*, 1911, 34, 235—239. Compare Abstr., 1910, ii, 419).—(I) Microcline from Runchy; pink crystalline masses associated with black and white mica (biotite and hallerite) in pegmatite. (II) Microcline from Vizézy, near Montbrison; large, milk-white, crystalline masses and crystals in pegmatite. (III) Orthoclase (soda-orthoclase) from Pardines; occurring as enclosures in basalt, and probably derived from a granite; the felspar encloses some apatite and magnetite. (IV) Orthoclase from puy de Montaudou; as enclosures in basalt.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	SrO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Total.
I.	66·64	18·59	trace	trace	10·29	4·34	99·86
II.	66·01	18·36	—	—	11·02	4·41	99·80
III.	66·43	19·00	1·22	0·38	5·37	7·36	99·76
IV.	66·56	19·18	0·52	—	6·94	6·56	99·76

L. J. S.

**Laumontite from Heimbach, Oberstein, Germany.** V. DÜRRFELD (*Zeitsch. Kryst. Min.*, 1912, 50, 257—258).—A new railway tunnel at Heimbach penetrates a basaltic melaphyre, which in numerous cavities contains chalcedony, quartz, calcite, hæmatite, limonite, chabazite, harmotome, and laumontite. The last of these minerals forms large (up to  $3\frac{1}{2}$  cm.), white to reddish-white crystals; analysis gave:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
50·64	22·75	11·69	0·53	0·21	14·80	100·62

L. J. S.

**Beryl from Madagascar.** LOUIS DUPARC, M. WUNDER, and R. SABOT (*Bull. Soc. franç. Min.*, 1912, **34**, 239—242. Compare Abstr., 1910, ii, 312; 1911, ii, 736, 1105).—The following new analyses are given: (I) Blue aquamarine of prismatic habit from Ambatolampy, with  $\omega = 1.5834$ ,  $\epsilon = 1.5774$ ,  $D = 2.7186$ . (II) Green aquamarine of prismatic habit from Sahanivotry,  $D = 2.7181$ .

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	GlO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Li <sub>2</sub> O.	Cs <sub>2</sub> O.	Rb <sub>2</sub> O.	Loss on ignition.	Total.
I.	64.56	18.02	0.61	13.49	0.32	1.43	0.12	nil	nil	1.96	100.51
II.	64.28	17.44	1.05	13.89	0.28	1.18	0.30	,,	,,	1.85	100.29

This type of beryl is distinct from the vorobyevite type in which the habit of the crystals is tabular, and rubidium and caesium are present. Colour affords no criterion for distinguishing the two types—the crystals of both may be blue, pink or colourless.

L. J. S.

**Augite and Hornblende from Volcanic Rocks of Central France.** FERDINAND GONNARD and PHILIPPE BARBIER (*Bull. Soc. franç. Min.*, 1911, **34**, 228—235).—(I) Hornblende as large crystals in the peperite of the Puy de Chaumonteix. (II) Hornblende, crystal fragments showing a dark green colour on thin edges, from Pardines. (III) Augite, simple and twinned crystals in the volcanic sands of the Puy de Rodde. (IV) Augite, simple and twinned crystals from Maillargues, Cantal:

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Na <sub>2</sub> O, K <sub>2</sub> O.	Total.
I.	45.25	1.03	18.11	14.28	12.23	8.77	—	99.67
II.	52.20	0.44	6.16	11.02	12.77	16.26	1.03	99.88
III.	{ 45.18	3.44	8.10	10.21	19.21	13.81	—	100.01
	{ 45.16	3.42	8.09	9.79	19.11	13.51	0.81	99.89
IV.	45.50	3.12	10.93	6.46	19.01	13.94	0.91	99.87

L. J. S.

**Ilmenite-rocks containing Rutile and Sapphirine from St. Urbain, Quebec.** CHARLES H. WARREN (*Amer. J. Sci.*, 1912, [iv], **33**, 263—277).—Large dyke-like masses composed largely of ilmenite occur in anorthosite rocks in the parish of St. Urbain. The ilmenite grains contain a lamellar intergrowth of hæmatite (forming about one-fifth of the whole), and are associated with accessory andesine, green spinel, and biotite. In one mass (anal. II) rutile (about 20%) and sapphirine (3—5%) are also present. These rocks are believed to be of igneous origin, and for the ilmenite-rutile-sapphirine-rock the name urbainite is proposed. The sapphirine (a mineral previously known only from Greenland and Madras) is present as small, greenish-black grains, which under the microscope show a strong pleochroism (pale brown to deep sapphire-blue). The ratios of analysis I lie between those of the formulæ  $Mg_5Al_{12}Si_2O_{27}$  and  $Mg_4Al_{10}Si_2O_{23}$ , deduced from analyses of Greenland sapphirine:

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	MgO.	CaO.	Total.	Sp. gr.
I.	13.44	—	62.98	—	9.08	—	15.28	—	100.78	3.5
II.	2.24	53.35	1.65	13.61	24.49	0.30	4.04	0.30	99.98	—

L. J. S.

**The Meteorite of El Nakhla El Baharia.** JOHN BALL (*Egypt, Survey Dept. Paper No. 25, 1912, 1—20. Compare Abstr., 1911, ii, 1106*).—A shower of meteoric stones, accompanied by a series of explosions, fell in the neighbourhood of the village of El Nakhla El Baharia, near Abu Hommos, in the north-western portion of the Nile Delta, on June 28th, 1911. About forty stones, ranging in weight from 20 to 1813 grams and with a total weight of nearly 10 kilos., were picked up over an area  $4\frac{1}{2}$  kilometres in diameter. The stones are covered with a glossy black skin, but some surfaces (formed by the later explosions) show the fusion of only the hypersthene grains. The material consists of a friable aggregate of crystalline grains (averaging  $\frac{1}{2}$  mm. diam.) of pale green augite (forming three-quarters of the mass) and of reddish-brown hypersthene (one-quarter of the mass). There is no chondritic structure, and metallic iron is absent. A few scattered grains of chromite were detected under the microscope. Analysis I by W. B. Pollard, and II of the portion decomposed by digestion with hydrochloric acid. The latter accounts for almost the whole of the hypersthene, and corresponds with  $2\text{FeSiO}_3, \text{MgSiO}_3$ . The augite has the composition  $2\text{FeO}, 3\text{CaO}, 3\text{MgO}, 8\text{SiO}_2$ :

	SiO <sub>2</sub>	Cr <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub> .*	FeO.	CaO.	MgO.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.	Sp. gr.
I.	49·98	0·23	1·65	19·58	15·12	12·20	n. d.	0·35	99·11	3·40
II. [11·00]	—	—	8·23	—	0·75	2·20	—	—	22·18	—

\* Including traces of MnO, TiO<sub>2</sub>, and V<sub>2</sub>O<sub>5</sub>.

As representing a new type of meteoric stone, the class name *nakhlite* is proposed.

L. J. S.

**Analyses of Stone Meteorites.** OLIVER C. FARRINGTON (*Field Museum Nat. Hist. Chicago, 1911, Geol. Ser. 3, 195—229*).—A tabulated collection of 125 published analyses of meteoric stones. The average of these is given under I. A few additional analyses are also given of meteoric irons (Abstr., 1907, ii, 706). II gives the average composition of 318 meteoric irons; and III the average of all meteorites, both stones and irons. The last probably represents the composition of the earth as a whole, and corresponds with iron 72·06, oxygen 10·10, nickel 6·50, silicon 5·20, magnesium 3·80, other elements being only in fractional percentages.

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	FeO.	MnO.	NiO.	MgO.	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O.
I.	39·12	2·62	0·38	0·41	16·13	0·18	0·21	22·42	2·31	0·81	0·20	0·20
II.	11·07	0·74	0·11	0·12	4·55	0·04	0·06	6·33	0·65	0·23	0·05	—
	Fe.	Ni.	Co.	S.	P.	C.	Cr.	Cu.	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	SnO <sub>2</sub>	Total.
I.	11·46	1·15	0·05	1·98	0·04	0·06	—	—	0·03	0·02	0·02	99·82*
II.	90·85	8·52	0·59	0·04	0·17	0·03	0·01	0·02	—	—	—	100·23
III.	68·43	6·44	0·44	0·49	0·14	0·04	0·01	0·01	0·01	0·01	0·01	99·98

\* Including "Ni, Mn, Cu, Sn," 0·02.

The collected analyses are used as a basis for the establishment of a quantitative chemical classification of meteoric stones on the same lines but with some modifications, as the American quantitative

classification of rocks. A few of the groups correspond with those for terrestrial rocks, but, owing to the presence of free metal, several new sub-classes have to be introduced.

L. J. S.

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## Physiological Chemistry.

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**The Effect of Inhalation of Oxygen on the Pulse in Health.** JOHN PARKINSON (*Proc. physiol. Soc.*, 1911—12, xxxviii—xxxix; *J. Physiol.*, 43).—During inhalation of oxygen in man there is a slight drop in the pulse rate. The average rates given are 68 before, 64.2 during, and 66.6 after the inhalation. W. D. H.

**The Nitrogen Content of Blood.** GEORGE A. BUCKMASTER and JOHN A. GARDNER (*J. Physiol.*, 1912, 43, 401—417).—The amount of oxygen dissolved in cats' blood is greater than is calculated from physical constants even if the latter are 20% wrong, and it does not follow the ordinary laws of absorption with varying nitrogen pressures. After oxygen inhalation, the amount of nitrogen rises in venous as compared with arterial blood. This is probably due to leakage of nitrogen from fatty tissues; the excess of nitrogen is not due to metabolism. W. D. H.

**Blood Tests before Transfusion.** REUTER OTTENBERG and DAVID J. KALISKI (*Biochem. Bulletin*, 1911, 1, 5—6).—Some human blood agglutinates and hæmolyses other human blood, even if both bloods are apparently healthy. The conditions for this are not known, but the existence of the fact renders it necessary to test the bloods *in vitro* before transfusion in order to prevent danger and even death afterwards. W. D. H.

**Ester Hydrolysis by the Blood.** PETER RONA and JOSINE EBSSEN (*Biochem. Zeitsch.*, 1912, 39, 21—35).—The course of the reaction of the blood on tributyrin follows apparently only the course of a unimolecular reaction. It deviates from the strict course of such a reaction in that the constant varies with the initial concentration of the ester, to which it is approximately reciprocally proportional. The deviation from the course of a strictly unimolecular reaction is due apparently to the inhibitory effect of the tributyrin. The previously observed fact that the reaction rate is directly proportional to the amount of ferment, is confirmed by investigations over a wide range of concentrations. S. B. S.

**The Reaction between Ferments and Anti-ferments.** D. MINAMI (*Biochem. Zeitsch.*, 1912, 39, 75—80).—Ferment solutions on baking or warming lose their activity. The changes in the com-

binning capacity for the anti-ferment of serum when treated thus were also investigated. In the cases of trypsin and pepsin, it was found that the loss of activity was not proportional to the alteration in the combining power with anti-ferment, the latter decreasing, as a rule, more than the former. S. B. S.

**Rotatory Power of the Protein Substances from the Serum of Dog's Blood.** PAUL DELAVA (*Bull. Acad. roy. Belg.*, 1912, 35—40).—Contrary to the results of Fredericq, who found  $[\alpha]_D - 44^\circ$  for the albumin from the serum of dog's blood, the author finds the value  $-54.41^\circ$  when the albumin is obtained pure from the same source. This value is approximately in accord with the  $[\alpha]_D - 57.3^\circ$  obtained from other mammals. He confirms Fredericq's value  $[\alpha]_D - 47.84^\circ$  for paraglobulin from the same source, and finds that the serum of dog's blood contains 3% of paraglobulin and 3.25% of albumin. W. G.

**The Specific Inhibition of Rennet Action.** SVEN G. HEDIN (*Zeitsch. physiol. Chem.*, 1912, 76, 355—368. Compare Abstr., 1911, ii, 998).—Freshly prepared neutral infusions of the gastric mucous membrane of calf, pig, guinea pig, and pike show, after treatment with dilute ammonia and neutralising, the presence of substances which inhibit rennetic activity. The inhibiting power is retained in part after boiling. Treatment of the ammoniacal solution with hydrochloric acid and again neutralising does not restore rennetic action. If the original zymogen is first treated with hydrochloric acid, rennet is activated; if this is treated with ammonia and neutralised, inhibitory action is absent. The inhibitory substances from calf and pig are not specific. The rennet of guinea pig and pike gave no inhibition after boiling. W. D. H.

**Nitrogen Retention and Nitrogen Equilibrium on Feeding with Ammonium Salts.** E. GRAFE and V. SCHLÄPFER (*Zeitsch. physiol. Chem.*, 1912, 77, 1—21).—The experiments were made on dogs. The animal was subjected to eight days' inanition; then fed on a diet rich in carbohydrates, but poor in nitrogen; then for a third period ammonium salts (chloride or citrate) were added, and finally it returned to the nitrogen poor diet. During the third (the important) period, which lasted four days, the animal retained nitrogen, and with the citrate reached nitrogenous equilibrium, and the body-weight increased. The question is what becomes of the retained nitrogen: is it simply excreted as urea or amino-acids? Is protein formed from it by bacteria in the intestine and subsequently absorbed? Or are the body cells capable of synthesising protein from it? These questions are discussed, and the evidence in favour of the third view is regarded favourably. W. D. H.

**Feeding Investigation with Completely Digested Nutrient.** Solution of the Problem of the Artificial Preparation of Nutritive Material. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1912, 77, 22—58).—A fresh series of experiments are given which

support the author's previous conclusions that animals can maintain their health, weight, and nitrogenous equilibrium when they are fed on the ultimate cleavage products of proteins. They further support the view that certain cleavage products, such as tryptophan, are more important than others, such as glycine or proline. Such feeding does not increase the amino-acid output in the urine. Other experiments support Michaud's idea that proteins nearly allied to those of the animal are more valuable than foreign proteins, such as those derived from the vegetable world; this may be largely rectified by adding the missing cleavage products, and a list of the various amino-acids and their relative quantity is given, embodying the author's views of what is advisable and necessary. To this is added a list of the cleavage products of fats and of carbohydrates, of nucleic acid, and cholesterol. The general conclusion is drawn that the animal organism is capable of synthesising the complex components of its body from such simple materials.

W. D. H.

**Protein Metabolism from the Standpoint of Blood and Tissue Analysis. II. The Origin and Significance of the Ammonia in the Portal Blood.** OITO FOLIN and W. DENIS (*J. Biol. Chem.*, 1912, 11, 161—167).—Portal blood does not contain more ammonia than systemic blood, but the values are much smaller with improved technique than those previously recorded. The excess in the tributaries from the small intestine is, however, small when compared to that in those from the large intestine, where it originates from bacterial decomposition.

W. D. H.

**Digestion and Absorption of Nucleic Acid in the Alimentary Canal. III.** EFIM S. LONDON, ALFRED SCHITTENHELM and KARL WIENER (*Zeitsch. physiol. Chem.*, 1912, 77, 86—91).—The experiments were made on four dogs, one normal, one without a stomach, one with pancreatic ducts ligatured, and one without a pancreas. The chyme was in all cases collected from a fistula in the lower ileum. In respect to the digestion of nucleic acid, there was no important difference between the four animals. Undecomposed nucleic acid was present in quite small amount; free purine bases were never found; they are present mainly as nucleosides, and guanosine was isolated.

Experiments *in vitro* showed that pancreatic juice had no action, but intestinal juice had a marked action in producing this result, which coincides with the statements of Levene and Medigreceanu.

W. D. H.

**Physiological Effects on Growth and Reproduction of Rations Balanced from Restricted Sources.** EDWIN B. HART, ELMER V. MCCOLLUM, and H. STEENBOCK (*Proc. Amer. Soc. Biol. Chem.*, 1911, xii-xiii; *J. Biol. Chem.*, 11).—Animals fed on rations from different plant sources of equivalent chemical and thermal value are not alike in growth, vigour, strength of offspring, and capacity for producing milk; for instance, oats are inferior in such respects to wheat and especially to maize. Wheat-fed animals have acid urine, whereas the others have alkaline urine. Correction of the acidity

by alkali carbonates did not bring the wheat-fed animals to full vigour. No solution of the problem is at present offered.

W. D. H.

**The Fate of Ingested Fat in the Animal Body.** H. S. RAPER (*Proc. Amer. Soc. Biol. Chem.*, 1911, ix—x; *J. Biol. Chem.*, 11).—Cocoanut oil yielding 40% of acids volatile with steam can be recovered from a mixture of 1 gram of the oil with the minced liver of a cat to the extent of 80%, when the fatty acids are subjected to steam distillation. If a cat is fed on the oil, considerable quantities of volatile acids are obtained from the liver. If an emulsion of the oil is slowly introduced into a vein, from 30 to 50% of the volatile acids can be recovered from the liver two or three hours later, which is about the same proportion found when the oil is absorbed from the intestine.

W. D. H.

**Intestinal Absorption.** HAROLD C. BRADLEY and H. S. GASSER (*Proc. Amer. Soc. Biol. Chem.*, 1911, xx; *J. Biol. Chem.*, 11).—An emulsified mixture of olive oil and petroleum was given to a dog. The thoracic lymph contained subsequently both substances in the same proportion, which suggests absorption of droplets.

Isolated intestinal loops were perfused with defibrinated blood at the height of digestion, or after the introduction of amino-acid and peptone into the loops. Tyrosine was not found in the perfusate, nor any other amino-acid.

W. D. H.

**Carbohydrate Esters of the Higher Fatty Acids. II. Mannitol Esters of Stearic Acid.** W. R. BLOOR (*J. Biol. Chem.*, 1912, 11, 141—159).—A fat with some characteristic property which enables it to be traced through the processes of absorption and transport was sought, in order to test the usually accepted theories of fat absorption. The substances selected were stearic acid esters of mannitol, which are optically active.

Mannitol distearate shows with human pancreatic juice a digestibility of about one-third that of cotton oil, and with castor bean lipase about half that of cotton oil.

Mannitan distearate is not attacked by castor bean lipase, and is only slightly digested by various preparations of pancreas. The amount of digestion of these compounds in cats is also small, so that the main object of the research was not attained. Further work is in progress.

W. D. H.

**Experiments in Feeding "Dissected" Milk.** ELMER V. MCCOLLUM and EDWIN B. HART (*Proc. Amer. Soc. Biol. Chem.*, 1911, xvi—xvii; *J. Biol. Chem.*, 11).—Experiments on pigs indicate that they can grow to a considerable extent on caseinogen as the sole protein, and that milk treated so as to disturb any specific complexes between organic and inorganic radicles is still capable of maintaining a fairly vigorous growth.

W. D. H.

**The Metabolism of Hypophysectomised Dogs.** FRANCIS G. BENEDICT and JOHN HOMANS (*J. Med. Research*, 1912, 25, 409—502).—Dogs, especially young ones, continue to live for a considerable time

after complete or almost complete removal of the pituitary gland; one died three months after the operation, but the others lived longer, in fact, until they were killed seven to sixteen months later for the purpose of examination. Their normal growth is retarded; there is a tendency to a low body temperature, a disturbance of the heat-regulating mechanism, and a fall in pulse and respiration rates. The total metabolism as measured by carbon dioxide production is very low; the body tends to become fat, and a condition of sexual infantilism persists.

W. D. H.

**A Comparison of the Nutritive Value of the Nitrogen of the Oat and Wheat Grains for the Growing Pig.** ELMER V. MCCOLLUM (*Proc. Amer. Soc. Biol. Chem.*, 1911, xv; *J. Biol. Chem.*, 11).—Little if any difference exists in the utilisation of the nitrogen of these grains by the pig for growth during a period of sixty days.

W. D. H.

**The Relation between Nitrogen Retention and Rise of Creatinine Excreted During Growth in the Pig.** ELMER V. MCCOLLUM (*Proc. Amer. Soc. Biol. Chem.*, 1911, xv—xvi; *J. Biol. Chem.*, 11).—Young pigs show a steady rise in creatinine output during growth. In a pig fed on oats, there was a rise of 1 mg. of creatinine nitrogen for each 2.01 grams of nitrogen retained; in the wheat fed pig the figures are 1 to 2.55. It is suggested that certain protein mixtures may supply an abundance of complexes necessary to the formation of tissues concerned with creatinine formation.

W. D. H.

**Effect of the Quantity of Protein Ingested on the Nutrition of Animals. VI. The Chemical Composition of the Entire Body of Swine.** A. D. EMMETT, W. E. JOSEPH, and R. H. WILLIAMS (*Proc. Amer. Soc. Biol. Chem.*, 1911, xxxv—xxxvi; *J. Biol. Chem.*, 11).—Three lots of young pigs were fed on low, medium, and high protein planes. Various parts were analysed after slaughter. The medium group made the best showing. Certain differences in water, ash, fat, protein, and phosphorus are noted, but they are not great.

W. D. H.

**Absorption and Distribution of Aluminium from Aluminised Foods.** MAX KAHN (*Biochem. Bulletin*, 1911, 1, 235—244).—In the dog, aluminium from alum biscuits passes into the blood, and is subsequently found in varying degrees in many organs, and is excreted in both bile and urine.

W. D. H.

**The Preparation of Secretin.** WILHELM STEPP (*J. Physiol.*, 1912, 43, 441—448).—Pancreatic secretin is a single substance, is soluble in water, and may occasionally be free in the intestinal mucous membrane. Usually it is present as prosecretin, which is insoluble in water. Secretin is obtainable from prosecretin by treatment with dilute acids, 70% alcohol, or strong soap solution. Feebler extracts can be made with glycerol or bile salts. It is insoluble in acetone, ether, or absolute alcohol; this fact may be utilised to

prepare dry powdered mucous membrane which keeps indefinitely; from this secretin can be always prepared by boiling with dilute acid.

W. D. H.

**The Absence of Temperature Changes During the Transmission of a Nerve-impulse.** ARCHIBALD V. HILL (*J. Physiol.*, 1912, 43, 433—440).—The absence of heat formation in active nerve noted by Rolleston is here confirmed by improved methods. For every single impulse the change of temperature, if any occurs, is less than a hundred millionth of a degree. This suggests, but does not finally prove, that the propagated nervous impulse is not a wave of irreversible chemical breakdown, but a reversible change of a physical nature.

W. D. H.

**The Control by the Splanchnic Nerve of Adrenaline Secretion.** T. R. ELLIOTT (*Proc. physiol. Soc.*, 1911—12, xxxii—xxxiii; *J. Physiol.*, 43).—The suprarenals lose much of their adrenaline from the irritation of a cerebral puncture and hæmorrhage, and by ether anæsthesia. There is a similar loss centrally excited as a result of alarm. No exhaustion, however, was noted after direct excitation of the splanchnic nerves, nor after the administration of pilocarpine.

W. D. H.

**The Relations to Electrolytes of the Hearts of Different Species of Animals. I. Elasmobranchs and Pecten.** GEORGE R. MINES (*J. Physiol.*, 1912, 43, 467—506).—The hearts of elasmobranch fishes and of the common scallop (*Pecten*) show close resemblances to that of the frog in relation to electrolytes. The action of magnesium accords with the hypothesis that it acts by altering the electric charge of the surfaces which are affected by the hydrogen ion and by trivalent cations.

Differences in the quantitative relations of the hearts to those electrolytes which act by altering the electric charge of surfaces in the heart indicate the existence of differences in the isoelectric points of the materials of which the different hearts are composed.

W. D. H.

**The Oxygen Exchange of the Suprarenal Gland.** K. O. NEUMANN (*Proc. physiol. Soc.*, 1911—1912, xxxi; *J. Physiol.*, 43).—The amount of oxygen used per gram per minute in the suprarenal gland averaged in 10 cats, 0.035 c.c., and in 4 rabbits, 0.03 c.c. The blood flow per gram of gland per minute was in the mean for the cats, 2.7 c.c., and in the rabbits, 2.6 c.c. Injection of 0.1 mg. of adrenaline caused a slight increase of blood flow.

W. D. H.

**The Presence of Glycerophosphatase in Animal Organs.** PAUL GROSSER and JOSEPH HUSLER (*Biochem. Zeitsch.*, 1912, 39, 1—5).—Within twenty-four hours, the dried tissue or extracts from kidneys and mucous membrane of the small intestine of cats were able to cause the scission of 100% of the phosphoric acid from a 1% solution of sodium glycerophosphate (optically inactive). During the same period,

the lung tissue caused a scission of 62%, the liver 16%, the spleen of traces, whereas the blood and muscular tissue were quite inactive. If the tissues or the extract be heated, they are quite inactive, so that certain tissues, especially the kidneys and small intestine, contain a glycerophosphatase. The action of pepsin, trypsin, and other ferments on glycerophosphates was also investigated. With the exception of erepsin, they were found to be inactive. The faeces also contain a glycerophosphatase, which the authors believe is not due to the presence of bacteria. The natural glycerophosphates from lecithin are also hydrolysed by the glycerophosphatase. S. B. S.

**Synthetic Action of Enzymes.** HAROLD C. BRADLEY (*Proc. Amer. Soc. Biol. Chem.*, 1911, xxviii; *J. Biol. Chem.*, 11).—A quantitative comparison of lipolytic activity appears of doubtful value in supporting the theory of the synthetic functions of enzyme in tissues. Mammary glands at the height of lactation showed no lactase, the enzyme which should synthesise as well as hydrolyse lactose. No definite evidence of the synthetic function of enzymes in living tissues was obtained. W. D. H.

**Glycolysis.** PHOEBUS A. LEVENE and GUSTAVE M. MEYER (*Proc. Amer. Soc. Biol. Chem.*, 1911, xxix—xxx; *J. Biol. Chem.*, 11).—The experiments recorded definitely establish for the first time the fact that lactic acid is an intermediate product of glycolysis in living tissues. W. D. H.

**Glycolysis as Modified by Removal of the Pancreas and by the Addition of Antiseptics.** HUGH MCGUIGAN and C. L. VON HESS (*Proc. Amer. Soc. Biol. Chem.*, 1911, xxxiv—xxxv; *J. Biol. Chem.*, 11).—Mixtures of extracts of normal muscle and pancreas with toluene or chloroform added as antiseptics cause little or no glycolysis, or not more than muscle alone does. Muscle of de-pancreatized dogs had no action on dextrose either with or without the addition of pancreatic extract. The results, however, are valueless, as it was found that the antiseptics added are quite sufficient in themselves to inhibit glycolysis. W. D. H.

**Synthesis of Lecithin in the Hen.** ELMER V. MCCOLLUM and J. G. HALPIN (*Proc. Amer. Soc. Biol. Chem.*, 1911, xiii—xiv; *J. Biol. Chem.*, 11).—From examining the eggs, the conclusion is drawn that the synthesis of phosphatides is readily accomplished in the body of the hen on rations which are free from those substances. W. D. H.

**Composition of the Egg-shells of *Pollachius brandti*.** K. MIYAKE and T. TADOKORO (*J. Coll. Agric. Tohoku Imp. Univ. Sapporo*, 1911, 4, 269—277. Compare Buchtala, *Abstr.*, 1908, ii, 610).—The substance was prepared by washing the crushed eggs with water, treating for some days with 1% hydrochloric acid, again washing with water, and extracting with alcohol and ether. The dried skins contained C, 51.24; H, 8.41; N, 14.57; S, 0.67; and O, 25.11%, and

are therefore similar in composition to the egg-skins of *Scyllium catulus* (Krukenberg, Abstr., 1885, 826); it resembles keratin in its behaviour towards various reagents. The distribution of the nitrogen, as determined by boiling with strong hydrochloric acid, was found to be as follows: Ammonia-N, 5.97; melanin-N, 0.96; monamino-N, 78.24, and diamino-N, 14.83%.

The following amounts of cleavage products were obtained from the skins: tyrosine, 0.53; leucine, 2.4; glutamic acid, 1.40; arginine, 2.30, and lysine, 1.75%. Histidine was also present.

N. H. J. M.

**Egg Capsules of Two Species of Shark.** LOUIS HUSSAKOF and WILLIAM H. WELKER (*Biochem. Bulletin*, 1911, 1, 216—221).—The egg capsules of the skate and Port Jackson shark are composed of a keratinous material which differs in certain points from other keratins; the two new keratins also differ in solubilities from each other. There is also a slight difference in their colour; the pigments are probably melanins.

W. D. H.

**Physiology of Marine Organisms. II. Influence of the Carbon Dioxide and Oxygen Tensions on Rhythmical Movements.** HERBERT E. ROAF (*J. Physiol.*, 1912, 43, 449—454).—By adding sodium hydrogen carbonate to sea-water, it is possible to alter the hydrogen ion concentration independently of the carbon dioxide tension. The rates of movement of fish and barnacles are influenced by this concentration in opposite directions. The influence of carbon dioxide is due to its effect on the hydrogen ion concentration. The oxygen tension has no influence on rate of movement.

W. D. H.

**The Effect of the Chemical Composition of the Medium on the Life Cycle of Hydatina Senta.** A. FRANKLIN SHULL (*Biochem. Bulletin*, 1911, 1, 174—193).—This animal is a rotifer in which reproduction occurs alternately, sexually, and parthenogenetically. Urea, ammonium salts, beef extract, creatine, horse manure (boiled or not) all reduce or may wholly prevent male producers from appearing.

W. D. H.

**Fasting Studies. VI. Distribution of Nitrogen During a Fast of One Hundred and Seventeen Days.** PAUL E. HOWE, H. A. MATTILL, and PHILIP B. HAWK (*J. Biol. Chem.*, 1912, 11, 103—127).—The subject of the fast was a collie dog; after the fast, during which the dog took water only, it was brought back to its original weight and subjected to a second fast, the details of which will be published later. Details of the elimination of nitrogen in urine and faeces are given. There was no indication of a pre-mortal rise in the nitrogen excretion, or of "creatinine crossing," that is, an excess of creatine over creatinine.

W. D. H.

**Studies in Water-Drinking. XIII. (Fasting Studies. VIII.) Hydrogen Ion Concentration of Faeces.** PAUL E. HOWE and PHILIP B. HAWK (*J. Biol. Chem.*, 1912, 11, 129—140).—The hydrogen

ion concentration was estimated in the faeces of three men, two in water-drinking experiments, and one in a fasting test. The hydrogen electrode of the Salm type was used. The reaction was uniformly alkaline, the hydrogen ion concentration varying between  $0.15 \times 10^{-8}$  and  $9.8 \times 10^{-8}$ . Water drinking with meals tended to increase the concentration. Changes in diet caused very small variations. Previous investigators have reported acid stools in fasting, but this was not confirmed in the present investigation. W. D. H.

**The Effect of High Magnesium Intake on Calcium Excretion by Pigs.** EDWIN B. HART and H. STEENBOCK (*Proc. Amer. Soc. Biol. Chem.*, 1911, xiv; *J. Biol. Chem.*, 11).—An increased intake of magnesium salts leads to an increased excretion of calcium in the urine. Faulty calcium retention for bone formation incident to a diet of grains or grain by-products only does not lie in an improper ratio of these elements in the food, but rather to a lack of supply of calcium. W. D. H.

**The Reducing Properties of Normal Urine.** FRIEDRICH N. SCHULZ (*Zeitsch. physiol. Chem.*, 1912, 77, 121—128).—Normal urine free from sugar gives a positive reaction with Trommer's test, if the copper sulphate is added first and then the sodium hydroxide. This is attributed to creatinine, which reacts in the same way. W. D. H.

**The Excretion of Silicic Acid in Human Urine.** HUGO SCHULZ (*Pflüger's Archiv*, 1912, 144, 350—360).—The amount of silicic acid in the author's urine varied from 0.04 to 0.16 gram per litre. Higher figures are obtained in dogs when a large amount of vegetable food was taken; the greater quantity originates in this way; silicic acid is, however, a small but constant constituent of connective tissue, so the urinary silicic acid has, in part, a metabolic origin. W. D. H.

**The Excretion of Amino-acids in the Urine under the Influence of Strenuous Exercise at High Altitudes.** ERNESTO SIGNORELLI (*Biochem. Zeitsch.*, 1912, 39, 36—49).—The amino-acids were estimated by the Sørensen-Henriques method. The quantity of total nitrogen excreted in the urine diminishes in high altitudes (3000—4000) metres as compared with the normal. It increases again with strenuous bodily exercise. The amount of amino-acids excreted decreases also in high altitudes, both during rest and work. This result may be possibly ascribed to the increased oxidative capacity of the tissues. S. B. S.

**The Lipolytic Enzyme of the Urine.** HUGO PRIBRAM and JULIUS LÖWY (*Zeitsch. physiol. Chem.*, 1912, 76, 489—495).—Lipasuria may be nephrogenous as in nephritis, or it may be due to an increase in the lipase of the blood as in fever, and disintegration of leucocytes. It also occurs in disorders of the alimentary tract, such as jaundice and in polyuria. Food has no influence on it. W. D. H.

**The Urine of Late Pregnancy and the Puerperium.** JOHN R. MURLIN and H. C. BAILEY (*Proc. Amer. Soc. Biol. Chem.*, 1911, xvii—xviii; *J. Biol. Chem.*, 11).—Normal maternity cases on creatine-free diets containing less than 35 calories per kilo. show creatine in the urine. In a well-fed case, the ammonia-nitrogen ran as high as 12.2% of the total, and the amino-acid-nitrogen was 7.9%. Pre-eclamptic cases on a milk diet showed no high ammonia. In a case of interpartum eclampsia, the ammonia was not over 6% until after the convulsions; afterwards it ran up to 30%. In another case the ammonia fraction was high, but fell rapidly as the patient's condition improved. W. D. H.

**Excretion of Formaldehyde, Ammonia, and Hexamethylenetetramine.** HUGH MCGUIGAN (*Proc. Amer. Soc. Biol. Chem.*, 1911, xxxiii—xxxiv; *J. Biol. Chem.*, 11).—The intravenous injection of formaldehyde is followed by its oxidation with surprising rapidity; 100 c.c. of a 1% solution injected into a dog completely disappeared from the blood within thirty minutes. It is excreted with the urine as such only when large doses are given; as a rule, only formic acid is found there. It is also excreted and oxidised in the intestine, but more slowly. Hexamethylenetetramine injected in like manner is found in the blood several hours' later, and in most of the excretions. Ammonia is not excreted in the lungs, but combined with formaldehyde, however, it is found in the bronchial secretion. W. D. H.

**The Hæmolytic Power of Fatty Acids.** FLETCHER MCPHEDRAN (*Proc. Amer. Soc. Biol. Chem.*, 1911, x—xi; *J. Biol. Chem.*, 11).—Faust and Tallquist ascribe the anæmia due to *Bothriocephalus latus* to the unsaturation of oleic acid. Other more unsaturated acids occurring in the body may also be of importance in anæmia, but experiments show that increase in the number of unsaturated carbon atoms does not increase the hæmolytic power. Saturation of the free bonds with halogens actually increases it, but in the case of dihydroxystearic acid the saturation with hydroxyl groups diminishes it. W. D. H.

**The Purines and Purine-Enzymes of Tumours.** H. GIDEON WELLS (*Proc. Amer. Soc. Biol. Chem.*, 1911, x; *J. Biol. Chem.*, 11).—The liver is the chief or only organ of the human body capable of oxidising xanthine into uric acid *in vitro*. Secondary carcinomas of the liver cannot do this. Both malignant and benign tumours resemble normal tissues as regards content of purines and purine enzymes; guanase and nucleases are always present; adenase and xanthine-oxydase are absent. A tumour breeds true both histologically and chemically in secondary growths; that is, if secondary in the liver, they will not correspond to liver tissue. W. D. H.

**Studies in Experimental Glycosuria. VIII. The Relationship of the Adrenal Glands to Sugar Production by the Liver.** JOHN J. R. MACLEOD and R. G. PEARCE (*Amer. J. Physiol.*, 1912, 29, 419—435).—It is only when the adrenal glands are intact that it is possible by stimulating the nerves supplying the liver to excite hyperglycogenolysis. Some influence exerted by the adrenal

glands is evidently essential for the functional integrity of the nerves which control the process of glycogenolysis. W. D. H.

**The Pharmacology of Iodine.** OSWALD LOEB (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [2], 483—484).—When sodium iodide is administered to dogs, with the production of pleuritis, the exudations in the lungs and elsewhere contain from 30 to 50% of the original iodine in a form which is insoluble in alcohol, and therefore in the form of organic compounds. C. H. D.

**The Action of Phosphorus on the Calcium Metabolism of the Dog.** MARTIN KOCHMANN (*Biochem. Zeitsch.*, 1912, 39, 81—87).—Phosphorus influences the calcium and phosphoric acid metabolism in that it causes a retention, or, at any rate, a diminution, of the negative balance. The active doses approximate to the toxic doses, but the time during which administration takes place exerts no influence on the result. The method of action can be explained by assuming that the toxic products of metabolism, which under normal conditions combine with the calcium, are broken down under the influence of the phosphorus to non-toxic substances. The magnesium metabolism, which runs more or less parallel with that of nitrogen, is not directly influenced by phosphorus. S. B. S.

**The Action of Arsenic on the Blood-vessels.** ADAM LOEB (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [2], 489—491).—Small quantities of sodium arsenite produce a great increase in the quantity of blood passing through an artery, but the vessel still responds at once to barium salts or adrenaline. C. H. D.

**Influence of Certain Ions on the Electrical Charge of Surfaces and its Relationship to Problems in Colloidal Chemistry and Biology.** GEORGE R. MINES (*Koll. Chem. Beihefte*, 1912, 3, 191—236).—The action of ions in determining the electrical charge of surfaces in contact with aqueous solutions is discussed, and experiments are described relating to the influence of the valency and of the simple or complex character of multivalent ions in the action of aqueous solutions of salts on the frog's heart. Comparative observations with yttrium and hexamminecobalt chloride indicate that the influence of the latter is only about 1% of that of the former. The differences exhibited by different ions in this respect correspond with those which are found when various colloidal substances are examined in reference to their permeability towards different ions.

H. M. D.

**The Action of Substances of Homologous Series in Vital Processes.** OTTO WARBURG and RUDOLF WIESEL (*Pflüger's Archiv*, 1912, 144, 465—488).—Previous work has shown that the influence of ketones, nitriles, amides, etc., on the rapidity of oxidation in living cells is dependent on their concentration, is immediate and reversible, but is independent of chemical composition; two nitriles may differ enormously in their action, but a nitrite and a ketone may act alike. The effects coincide with those obtained by Meyer and Overton in their

study of narcosis. The present experiments deal with various kinds of living cells, bacteria, yeast, etc., and confirm those previously described in relation to blood corpuscles. In a series of urethanes, an increase of activity with a rise of molecular weight was found. The same was found in alcohols, nitriles, and ketones; this runs parallel with the precipitating influence of these reagents. A number of other experiments are described which tell in favour of the Meyer-Overton view that the interaction between narcotics and cell-lipoids is an important factor in narcosis.

W. D. H.

**Hindrance of the Action of Hydrogen Cyanide in the Living Cell.** OTTO WARBURG (*Zeitsch. physiol. Chem.*, 1912, **76**, 331—346).—Most substances such as alcohols, formaldehyde, urethanes, or substituted ureas are additive in their action on oxidative changes in the living cell, for example, if the retardation due to urethane is 30% of the total and that due to formaldehyde is 20%, the retardation caused by a mixture of both will be 50% or more. When, however, hydrogen cyanide is one of the components, the retardation effected is by no means equal to the sum of the retardations taken singly, it is always much less and sometimes 20% or even 50% less than the retardation caused by the hydrogen cyanide alone. The respiration of cells saturated with hydrogen cyanide is increased by the addition of substances which when used alone retard respiration. The influence is not a progressive one; methylurethane does not act any more strongly after six hours than after three hours; it cannot therefore be due to a gradual recovery from the poison. The higher members of a homologous series are more active than the lower in overcoming the effects of hydrogen cyanide.

The experiments were made with young erythrocytes of geese.

Increase of concentration of an active substance when used alone increases the retardation; in general, a given quantity of urethane diminishes the velocity of oxidation by a definite fraction.

E. F. A.

**The Influence of the Ingestion of Thiocyanates.** G. DIENA (*Biochem. Zeitsch.*, 1912, **39**, 12—20).—For the purpose of the experiments a protein-thiocyanogen compound (rhodazide) was administered to dogs with various fistulæ (submaxillary gland fistula, stomach fistula made by Pawloff's method, biliary and duodenal fistulæ). The secretions were tested for thiocyanate at intervals after administration of the medicament. There was always a marked thiocyanate reaction in the saliva, which lasted for twenty-four hours after administration of the medicament. There was a weak reaction from the other fistulæ, which was generally observed four to four and a-half hours after administration. The experiments of Kondo show also that the administration of thiocyanates increases the uric acid output.

S. B. S.

**The Relation between Chemical Constitution and Physiological Action in the Morphine and Strychnine Groups.** OSWALD LOEB and LUDWIG OLDENBERG (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [2], 481—483).—Dihydromorphine (Oldenberg, Abstr.,

1911, i, 668) and dihydrocodeine resemble the unreduced alkaloids in their physiological action, whilst tetrahydrothebaine and dihydrostrychnine have lost the power of producing tetanus. This property is thus connected with the presence of the double linking. In the case of dihydromorphine, re-oxidation to morphine may take place in the organism, this being prevented in tetrahydrothebaine by the presence of a hydroxyl group.

C. H. D.

**The Action Currents of Muscle Poisoned with Veratrine**  
PAUL HOFFMANN (*Zeitsch. Biol.*, 1912, 58, 55—80).—In the electromyogram obtained from veratrinised muscle, a study is made of the parallelism between the fibrillations and the oscillations of the electrogram. Differences, however, occur which show that "veratrine tetanus" is not on all fours with ordinary tetanus. [The details are of more interest to electro-physiologists than to chemists.]

W. D. H.

**The Action of Veratrine on Striped Muscle. II.** G. LAMM (*Zeitsch. Biol.*, 1912, 58, 37—54).—The fibrillary contractions seen in muscles poisoned with veratrine is spoken of as veratrine-tetanus. It penetrates the plasmatic membrane, but is not oxidised by the active muscle; excess of calcium salts in the fluid increases the action.

W. D. H.

**Aromatic Mercury Compounds. II.** FERDINAND BLUMENTHAL and KURT OPPENHEIM (*Biochem. Zeitsch.*, 1912, 39, 50—58).—The experiments were carried out on rabbits and rats. After administration of the sodium salt of diaminomercuridiphenyldicarboxylic [di-*p*-amino-*o*-mercuridibenzoic] acid, mercury was found only in the intestine, and never in the liver; after that of mercuridihydroxydiphenyldicarboxylic acid, it was found in the liver and intestines, and in smaller quantities in the blood; after that of the mercuridinitrodiphenyldicarboxylic acid, it was also found in the liver, intestines, and blood. After administration of the mercury salt of the diamino-derivative, the metal was found only in the intestine. This salt was toxic, whereas the three sodium salts were relatively innocuous.

S. B. S.

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### Chemistry of Vegetable Physiology and Agriculture.

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Sterilisation of Drinking Waters by the Action of Ozonised Oxygen and of Chlorine Compounds in the Nascent State. E. ROUQUETTE (*Compt. rend.*, 1912, 154, 447—450).—Sodium hypochlorite was employed successfully for the sterilisation of water during a recent cholera epidemic. Water containing 15,000 *B. coli* per litre was rendered sterile by the addition of 1 mg. of active chlorine per litre containing 1 mg. of organic matter.

The best form in which to use active chlorine for this purpose is as a mixture of one part of the salt,  $\text{Na}_2\text{S}_2\text{O}_9$  (obtained by mixing hydrogen peroxide and sodium hydrogen sulphate in concentrated solution), and two parts of the compound  $\text{Na}_2\text{O}_2\text{Cl}$  (prepared by addition of sodium sulphate to calcium hypochlorite solution, the calcium sulphate being removed by filtration). The mixture is added in the proportion of 0.02—0.1 part per 100,000, according to the degree of bacterial contamination. It is more rapid and intense in action than sodium hypochlorite, and the water thus treated is odourless, tasteless, and contains no chlorine, hydrochloric or sulphuric acid. W. O. W.

**A Recently Discovered Bacterial Decomposition of Sucrose.** W. L. OWEN (*J. Ind. Engin. Chem.*, 1911, 3, 481—486).—A summary of the results obtained by the Department of Bacteriology in its investigation of the part played by bacteria in the deterioration of sugars. Sugars were obtained from the most important sugar-producing countries, their bacterial flora carefully examined, and found to consist chiefly of members of the "potato bacilli," such as *B. vulgatus*, *B. mesentericus fuscus*, *B. mesentericus ruber*, *B. mesentericus niger*, and *B. mesentericus granulatus*, which are characterised by the very high resistance of their spores to heat, which power they appear to have developed more strongly by growth on sugar, as the spores of many of the most deteriorative type germinated freely after several hours' exposure to  $100^\circ$ , some even surviving the raising of the temperature to  $109^\circ$  during fifteen to thirty minutes, and as might be expected from this they were found to persist during all stages in the manufacture of sugar.

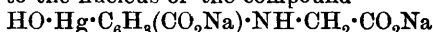
Further work has shown that the formation of the l  voro  tory gum levan isolated by Greig Smith is the product of the action of these bacteria directly on sucrose, and not on the nascent products of its inversion as believed by Smith; its production only takes place in the presence of sucrose, and more energetically in slightly alkaline solutions, whereas invertase is entirely inactive under alkaline conditions; this was also demonstrated by experiments with sugar solutions inoculated with only gum-forming bacteria, and others containing yeast in addition, when those containing only bacteria (the inverting powers of which are far less than yeast) yielded a much larger quantity of levan than those in which the yeast had produced dextrose and l  vulose.

Since reducing sugars are found to develop concurrently with levan in the fermentation of sucrose, the decomposition is considered to take place according to the equation:  $\text{C}_{12}\text{H}_{22}\text{O}_{11} = \text{C}_6\text{H}_{12}\text{O}_6 + \text{C}_6\text{H}_{10}\text{O}_5$ . The enzyme causing this decomposition of sucrose, for which the name *levanase* is proposed, has been isolated as a dark-coloured powder by cultivating *B. vulgatus* on agar agar, taking the ten-day old surface growth, grinding it with powdered glass, dissolving in water, and precipitating with alcohol; this product when introduced into sucrose solutions containing sufficient toluene to inhibit bacterial growth yielded levan and a reducing sugar, although microscopic examination showed the complete absence of living cells.

The errors introduced by the presence of levan in commercial sugar analysis are also discussed in the original. F. M. G. M.

**Effect of Quinine on Cultures of Pneumococci.** ORVILLE H. BROWN (*Proc. Amer. Soc. Biol. Chem.*, 1911, xxxvi; *J. Biol. Chem.*, 11).—Although the therapeutic use of quinine in pneumonia has given varying results, the effect of quinine in killing the *Pneumococcus* is undoubted. Pure quinine is better than its salts. Higher concentrations or longer exposure is necessary to kill *Streptococci* and *Staphylococci*. W. D. H.

**Disinfecting Power of Complex Organic Mercury Compounds. I. Aromatic Mercuricarboxylic Acids. II.** WALTER SCHOELLER and WALTHER SCHRAUTH (*Zeitsch. Hyg. Infekt-krankh.*, 1911, 70, 24—34. Compare *ibid.*, 1910, 66, 497).—The present paper deals with the influence on the disinfecting power of sodium *o*-hydroxymercuribenzoate,  $\text{HO}\cdot\text{Hg}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Na}$ , exerted by the introduction of various substituents into the *ortho*-position in regard to the carboxyl group. The experiments were executed chiefly with *Staphylococcus pyogenes aureus*, and in some cases with *B. anthracis* spores. Substitution of chlorine, iodine, methyl- and methoxy-groups raise the disinfecting power considerably. Hydroxyl and sulphoxyl groups lower the disinfecting power. Substitution of  $-\text{NH}_2$  also decreases the disinfecting power, but alkyl groups introduced into the amino-group raise it again to a degree corresponding with the number of groups introduced. The introduction of an acidic group into the amino-group decreases the disinfecting power of sodium *o*-hydroxymercurianthranilate. The removal of the carboxyl group attached to the nucleus of the compound



increases the disinfecting power. The introduction of a second hydroxymercuri-group into the benzene nucleus increases the disinfecting power. R. V. S.

**The Influence of Potassium Hexatantalate on the Action of Antimony Compounds in Experimental Trypanosome Infection.** JULIUS MORGENROTH and F. ROSENTHAL (*Zeitsch. Hyg. Infekt-Krankh.*, 1911, 68, 506—534).—A continuation of previous work on the same subject (*Abstr.*, 1911, ii, 632); it is found that potassium hexatantalate not only destroys the poisonous action of potassium antimonyltartrate on the trypanosomes of mice, but it also diminishes or even inhibits the general poisonous action of antimony compounds on the organism of the mouse.

Potassium hexatantalate alone does not destroy these organisms, although it appears to inhibit to some extent their power of transmission from one individual to another. F. M. G. M.

**Formation of Invertase in Yeasts.** HANS VON EULER and D. JOHANSSON (*Zeitsch. physiol. Chem.*, 1912, 76, 388—395. Compare Euler and Kullberg, *Abstr.*, 1911, ii, 320).—Previous treatment of yeast with sucrose and dextrose respectively does not produce any

differential increment in the amount of invertase. The treatment does, however, produce an increase in the amount of invertase; after seventy-one hours about four times as much is present as in the original yeast. The rate of formation of enzyme seems to follow the usual logarithmic law.

E. F. A.

**Destruction of Sugar and Formation of Carbon Dioxide in Alcoholic Fermentation.** HANS VON EULER and DAVID JOHANSSON (*Zeitsch. physiol. Chem.*, 1912, 76, 347—354).—Dextrose solutions were fermented with living yeast, and after a given time the carbon dioxide developed and the change in optical rotatory power were measured simultaneously and expressed as percentages of the total possible change. The alteration in rotatory power shows considerably more change than the carbon dioxide formed; this possibly indicates the formation of an inactive compound. The magnitude of the difference depends on the previous treatment of the yeast. The results are at present only of a preliminary character.

E. F. A.

**The Importance of Manganese in the Formation of Conidia of "Aspergillus niger."** GABRIEL BERTRAND (*Compt. rend.*, 1912, 154, 381—383. Compare Javillier and Sauton, this vol., ii, 192).—Taking the utmost precautions to avoid the presence of traces of manganese, it is found that the addition of minute amounts of iron and zinc to the culture medium does not induce sporulation in *Aspergillus niger*. The addition of a trace of a manganese salt, however, brings about profuse formation of conidia, and the mycelium acquires a velvety-black appearance. If insufficient manganese is introduced, development of mycelium takes place, but without sporulation.

For the latter to occur it is necessary for all three metals to be present. Javillier and Sauton's results are probably due to the presence of manganese in their ferrous sulphate, the purest commercial specimens of which contain 0.2—0.5 mg. of manganese per gram.

W. O. W.

**Extraordinary Sensitiveness of "Aspergillus niger" to Manganese.** GABRIEL BERTRAND (*Compt. rend.*, 1912, 154, 616—618. Compare preceding abstract).—By taking elaborate precautions to secure an artificial culture medium free from manganese, the author has been able to show that very minute doses of manganese (one part in 10,000,000,000) have an appreciable effect in increasing the yield of *Aspergillus niger*. To obtain material sufficiently free from manganese, repeated crystallisations were insufficient. The substances were treated in alkaline solutions with hydrogen peroxide and the trace of manganese dioxide carried down by precipitating magnesium ammonium phosphate in the liquid. Vessels of quartz were employed for growing the organism.

W. O. W.

**Effect of Withdrawing Zinc from the Culture Medium of "Aspergillus niger" on the Secretion of Sucrase [Invertase] by this Mould.** MAURICE JAVILLIER (*Compt. rend.*, 1912, 154, 383—386. Compare Abstr., 1908, ii, 124; 1911 ii, 222, 421, 644).—*Aspergillus*

*niger* grown in a zinc-free nutrient solution produces invertase, but this does not diffuse from the cells into distilled water, and does so only slightly in sodium phosphate solutions. When zinc is present, however, even in such small amounts as 1 : 100,000,000, the enzyme is readily diffusible when the culture liquid is replaced by dilute sodium phosphate solution. In the former case the enzymatic activity compared with the weight of dried organism is considerably less than when traces of zinc are present. The curves showing variation in activity with time are of the same form in each case, but the maximum is attained earlier, and is followed by a much more rapid fall when zinc is excluded during the experiment. W. O. W.

**The Respiration Calorimeter and Its Uses for the Study of Problems of Vegetable Physiology.** C. F. LANGWORTHY and R. D. MILNER (*Proc. Amer. Soc. Biol. Chem.*, 1911, xxxiii; *J. Biol. Chem.*, 11).—An Atwater respiration calorimeter with some improvements was utilised for investigating the heat elimination and gaseous interchanges which occur during the ripening of fruit, and so a fresh field of work is opened up. W. D. H.

**Measurement of the Oxydase Content of Plant Juices.** HERBERT H. BUNZEL (*J. Amer. Chem. Soc.*, 1912, 34, 303—315).—In connexion with investigations of certain pathological conditions of some important agricultural crops, it was desired to ascertain the oxidising power of the plant tissues and extracts. As sufficiently accurate quantitative methods for this purpose have not hitherto been described, a process has been devised which is based on the absorption of oxygen by pyrogallol solution under the influence of the oxydases in the plant-extract and its measurement by means of a manometer. The method has been tested with samples of potato-juice, and has given results in good agreement with one another.

It has been found that only a definite and limited quantity of oxygen is absorbed by pyrogallol in presence of a definite quantity of potato-juice within a space of two or three hours. The concentration of the pyrogallol does not affect the results, provided that an excess is employed. The amount of oxygen absorbed is directly proportional to the volume of potato-juice used, or, in other words, to the amount of oxydase present. This result does not harmonise with the usual conception of an enzyme as a catalytic agent, in accordance with which it would be expected that small quantities of the juice would continue to effect the oxidation of pyrogallol as long as this substance and oxygen are both present. It seems therefore that the oxydase in potato-juice is not an enzyme in the ordinary sense of the word, but rather a substance entering directly into the reaction and destroyed during its course.

The method has been applied to the study of the curly-top disease of sugar-beets, and has shown that the juice of the diseased leaves has a much higher oxydase content than that of the normal leaves.

E. G.

**Migration of Mineral Substances on the Death of Leaves in Autumn.** EMIL RAMANN (*Landw. Versuchs-Stat.*, 1912, 76, 157—164).—The results of analyses of leaves at different periods and

of dead leaves showed that under normal conditions a considerable portion of the nitrogen in the leaves of trees returns to the stems on the death of the leaves. The return of potassium and phosphorus seems to be influenced by the conditions of nutrition; as a rule, considerable amounts of phosphorus return to the stem. The amounts of calcium and silica generally increase in dying leaves, frequently to the extent of 100%. The migration occurs chiefly in the comparatively short period when the leaves become yellow and die off.

In the case of a beech tree, it was found that the leaves contain 16% of the total nitrogen of the tree. The retention of a quarter or half of this nitrogen, which is in an immediately available form, must be of considerable importance. The loss of green leaves owing to early frost cannot fail to have injurious effects. N. H. J. M.

#### Migration of Mineral Substances when Leaves are Frozen.

EMIL RAMANN (*Landw. Versuchs-Stat.*, 1912, 76, 165—167).—Pear leaves killed by a severe frost which occurred when the tree was in full vegetation were found to contain the same amount of nitrogen as uninjured leaves. The dead leaves contained, however, considerably less potassium and phosphoric acid than the uninjured leaves; and as there had been no rain, these substances must have migrated from the leaves to the stems in the course of a few hours. N. H. J. M.

#### Biochemical and Bacteriological Studies of the Banana.

E. MONROE BAILEY (*Proc. Amer. Soc. Biol. Chem.*, 1911, xlii—xliii; *J. Biol. Chem.*, 11).—In maturation of the banana, the following enzymes were detected: amylase, sucrase, raffinase, protease, lipase, and peroxydase. Tests for maltase, dextrinase, and lactase were doubtful or negative. In sound fruit, the inner portion of the pulp is sterile, but the inner coats of the peel are sparsely inhabited by bacteria. As ripening progresses, starch disappears, but dextrin and sugars soluble in alcohol increase. Maltose could not be detected. W. D. H.

#### Composition of *Bassia* Fats. RUSSELL G. PELLY (*J. Soc. Chem.*

*Ind.*, 1912, 31, 98—99).—The fats of three specimens of *Bassia* were examined, the fats being extracted from the seeds by means of light petroleum. From the results of the analysis of the fatty acids separated from the fats, the conclusion is drawn that the fats of *Bassia longifolia* and *B. latifolia* consist of glycerides of stearic, palmitic, and oleic acids, and in the case of *B. longifolia* of linoleic acid, whilst the fat of *B. butyracea* contains glycerides of palmitic and oleic acids only. W. P. S.

**Development of Active Principles in Some Medicinal Plants in 1911.** JAMES BURMANN (*Bull. Soc. chim.*, 1912, [iv], 11, 172—176).—The author has determined the quantities of active principles present in colchicum, digitalis (*D. ambigua* and *D. purpurea*), aconite, and belladonna plants, gathered under the same conditions each year since 1907. All these plants show a high content of active principles in 1907, less in 1908, still less in 1909, a slight increase on the previous year in 1910, and in 1911 a large increase, so that in

this year the percentages found were higher than in 1907, except as regards *Digitalis purpurea* and aconite, where they were a little less.

T. A. H.

**Enzymatic Activity of Different Organs of "*Ecballium elaterium*."** Physiological Rôle of the Pulp Surrounding the Seeds. ARMAND BERG (*Compt. rend.*, 1912, 154, 370—372. Compare Abstr., 1910, i, 499).—The juice from *Ecballium elaterium* contains three distinct hydrolytic enzymes, an amylase, a protease, and a third, elaterase, having a specific action on the glucoside elateridin. A tabular statement shows the relative distribution of these ferments in different organs of the plant. The pulp in which the seeds are embedded contains only a small amount of amylase, but has a much greater proportion of the other two enzymes than the other organs. The pulp is probably a nutritive medium in which the glucoside splitting enzyme plays an important part by producing sugars assimilated by the seeds.

W. O. W.

**Identification of the Glucoside from the Leaves of "*Kalmia latifolia*" with Asebotin.** ÉMILE BOURQUELOT and (Mlle.) A. FICHTENHOLZ (*Compt. rend.*, 1912, 154, 526—528\*).—The glucoside recently extracted from *Kalmia latifolia* (this vol., ii, 196) is identical in every respect with the compound asebotin isolated by Eykman from the leaves of *Andromeda japonica* (Abstr., 1883, 215, 348). The latter plant yields only 0.415% of the glucoside, whilst *K. latifolia* gives 2.66%.

W. O. W.

**Carbohydrates of the Shoots of *Sasa paniculata*.** K. MIYAKE and T. TADOKORO (*J. Coll. Agric. Tohoku Imp. Univ. Sapporo*, 1911, 4, 251—259).—The carbohydrates of bamboo shoots, which amount to about 50% of the dry matter, consist of xylan, araban, cellulose, glucose, and sucrose. Galactan, methylpentosan, and starch, are not present.

N. H. J. M.

**The Non protein Nitrogenous Constituents of the Shoots of *Sasa paniculata*.** K. MIYAKE (*J. Coll. Agric. Tohoku Imp. Univ. Sapporo*, 1911, 4, 261—267).—The amounts of the various nitrogenous substances found in the fresh shoots were as follows: xanthine, 3.2; hypoxanthine, 2.0; adenine, 3.0; guanine, 1.03; tryosine, 50.0, and asparagine, 33.0 mg. per kilogram.

N. H. J. M.

**The Tannin-Colloid Complexes of the Persimmon Fruit.** FRANCIS ERNEST LLOYD (*Biochem. Bulletin*, 1911, 1, 7—41).—Views are advanced concerning the fate of tannin during the ripening in the date and persimmon. The material called tannin-mass is a complex of tannin and a cellulose-mucilage or allied colloid. During ripening the latter substance increases, and at last enough is formed to engage all the tannin.

W. D. H.

**Chemical Composition of the Embryo of Rice.** LUIGI BERNARDINI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 283—289).—The

\* and *J. Pharm. Chim.*, 1912, [vii], 5, 296—300.

author's analyses show that the rice embryo is very rich in phosphorus as compared with the rest of the seed, and the phosphorus is stated to be present chiefly in the form of phytin. The ash of the embryo had the following composition (referred to the original dried material):  $\text{SiO}_2$  0.250%,  $\text{Fe}_2\text{O}_3$  0.060%,  $\text{MnO}$  traces,  $\text{CaO}$  0.279%,  $\text{MgO}$  1.389%,  $\text{K}_2\text{O}$  1.691%,  $\text{Na}_2\text{O}$  traces. The composition of the embryo resembles greatly that of the aleurone grains. R. V. S.

**Localisation and Distribution of the Essential Oil in *Seseli bocconi* and *Crithmum maritimum*.** I. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Gazzetta*, 1912, 42, i, 185—193. Compare this vol., i, 123).—*Seseli bocconi* does not contain much essential oil. It is not present in the epidermal cells, as in many other plants, and it is not very abundant in the green tissues. The plant possesses a circulatory system for the oil, in the form of certain vessels which run along the main axes of the plant.

*Crithmum maritimum* also contains no great quantity of essence, which occurs chiefly in the assimilating tissue, and is absent from the storage tissue. In this plant, too, there is a circulatory system of special vessels for the essential oil. R. V. S.

**Hydrolysis of the Protein of Potato.** BOUWE SJOLLEMA and I. J. RINKES (*Zeitsch. physiol. Chem.*, 1912, 76, 369—384).—The crude protein product investigated contained 15.9% of nitrogen. On hydrolysis the following amino-acids were obtained: Ammonia 1.8%, histidine 2.3, arginine 4.2, lysine 3.3, cystine 4.4, glutamic acid 4.6, proline 3.0, alanine 4.9, leucine 12.2, valine 1.1, valine + alanine 8.2, valine + leucine 1.9, phenylalanine 3.9, tyrosine 4.3%. Serine, oxyproline, and tryptophan were not sought for. E. F. A.

**Carbohydrate Group in Yam Mucin.** KINTARO OSHIMA and K. TADOKORO (*J. Coll. Agric. Tohoku Imp. Univ. Sapporo*, 1911, 4, 243—249. Compare Ishii, Abstr., 1895, ii, 128).—The mucilaginous substance of *Dioscorea Batatas* dissolves readily in 5% alkali hydroxide solutions and in strong acetic and mineral acids. It gives the xanthoprotein, biuret, Adamkiewicz, and Millon reactions, but not Liebermann's reaction, and is precipitated by tannin. The presence of glucosamine was ascertained by means of the oxidation method of Neuberg and Wolff (Abstr., 1905, i, 84). When the dried substance is hydrolysed with 25% sulphuric acid, tyrosine, leucine, and glutamine are obtained. N. H. J. M.

**Oxydases in Certain Fungi Pathogenic to Plants.** HOWARD S. REED and H. S. STAHL (*Proc. Amer. Soc. Biol. Chem.*, 1911, xli; *J. Biol. Chem.*, 11).—Extracts of apples invaded by *Sphaeropsis malorum* show no oxidising power at all; but apples attacked by *Glomerella ruformaculans* show increased oxidising powers. In pure cultures, the latter fungus produces oxydases in certain media. W. D. H.

**Action of Flowers of Sulphur on Vegetation.** E. BOULLANGER (*Compt. rend.*, 1912, 154, 369—370).—The addition of small quantities of flowers of sulphur to soil improves the yield of plants such as

carrots, haricots, potatoes, etc. As this improvement is much more marked with ordinary soil than in the case of sterilised material, it would seem that sulphur acts indirectly by modifying the development or activity of the bacterial flora. W. O. W.

**The Fertilising Action of Sulphur.** A. DEMOLON (*Compt. rend.*, 1912, 154, 524—526. Compare Boullanger, preceding abstract).—The amount of nitrogen and its state of combination in crude ammonium salt residues from gas works is insufficient to explain the beneficial effects of this material in agriculture. Its efficiency as a manure is attributed to the presence of free sulphur. Flowers of sulphur in the soil becomes partly oxidised to sulphuric acid.

W. O. W.

**Comparative Influence of Water and of Crude Spirit on the Composition of [Beetroot] Pulp in Sugar Works and Distilleries.** LOUIS AMMANN (*Compt. rend.*, 1912, 154, 366—369).—Results of analyses are given showing that beetroot pulp from sugar manufactories, which has undergone extraction with water, contains less protein, nitrogen, and phosphorus than distillery pulp which has been extracted by hot dilute alcohol. These observations explain the superiority of distillery pulp as a food for cattle. W. O. W.

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## Analytical Chemistry

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**The Use of Rods of Magnesia Instead of Platinum Wire in Analytical Work.** EDGAR WEDEKIND (*Ber.*, 1912, 45, 382—384).—Owing to the high cost of platinum, the author recommends the use of rods made of the same material as that used for the upright supports in incandescent burners for qualitative testing. The rods are about 1 mm. thick and 15 cm. long, and after each test it is necessary to break off the end which has been used. They cost about half a farthing each. T. S. P.

**Application of Ultrafiltration to Analytical Chemistry.** RICHARD ZSIGMONDY, ERNST WILKE-DÖRFURT, and A. VON GALECKI (*Ber.*, 1912, 45, 579—582).—Collodion films have been used for some time as filters for colloidal solutions, and the authors suggest their use in ordinary analytical chemistry. The perforated bottom of a porcelain funnel is covered with a wetted, ash-free filter paper, and the collodion film placed on this, being pressed gently against the walls of the funnel whilst the filter-pump is in action. Filtration can then be carried out as in ordinary cases.

The collodion film is best made by pouring dilute collodion (200 c.c. of 6% collodion, 200 c.c. of ether, and 500 c.c. of absolute alcohol) on to

a glass plate, taking care that no air bubbles are formed. When most of the ether has evaporated and the collodion is no longer sticky, the plate is immersed in water; after five to ten minutes the collodion film is easily detached from the plate.

Such filters possess the advantage that the ultramicros of many colloidal solutions, as, for example, those of gold, ferric hydroxide, stannic acid, are retained, so that such solutions can be directly filtered for analysis without previous precipitation. They are readily adapted for use in the methods of micro-analysis.

Satisfactory results were obtained in the estimation of gold and of ferric hydroxide in their colloidal solutions, of silver as chloride, and of barium as sulphate. It was found necessary to wait twenty-four hours before collecting the precipitate of barium sulphate in order to allow for complete precipitation from the supersaturated solution. The fact that this is necessary with collodion filters indicates that the usual precautions observed in the estimation of barium as sulphate are not alone due to allowing time for the particles of the precipitate to grow to such a size that they will not pass through the filter paper.

T. S. P.

**Use of a Mixture of Nitric Acid and Hydrogen Peroxide in Analytical Investigations.** PAUL JANNASCH (*Ber.*, 1912, 45, 605—607).—In forensic analyses, after the (supposed) destruction of the organic matter by means of potassium chlorate and hydrochloric acid, the passage of hydrogen sulphide to precipitate the metals of the second group gives rise to a copious precipitate of a yellow to dark brown colour, which is mainly organic in nature. The ordinary methods for finally destroying this organic matter are very tedious, and the author finds that the best method is as follows: the hydrogen sulphide precipitate is evaporated on the water-bath first with fuming nitric acid, and then once, or at most twice, more with a mixture of 65% nitric acid and 15—20% hydrogen peroxide. The residual oil thus obtained is, at the most, of wine-yellow colour.

Ammonium salts are best destroyed during the course of analysis as follows: ammonium chloride by evaporation with 65% nitric acid; ammonium nitrate by evaporation with concentrated hydrochloric acid; ammonium sulphate by repeated evaporation with concentrated hydrochloric and nitric acids, or with the above-mentioned mixture of nitric acid and hydrogen peroxide; ammonium phosphate by repeated evaporation with concentrated nitric acid and liquid bromine. In the estimation of magnesium in silicate analyses, after precipitation of the calcium as oxalate, the ammonium salts are best expelled by evaporation of the residue twice with 65% nitric acid. Any remaining traces can then be expelled by ignition. This method is more accurate and quicker than the usual one.

T. S. P.

**A Combined Extraction and Distillation Apparatus.** FRITZ TAURKE (*Chem. Zeit.*, 1912, 36, 214).—A three-way tap is placed on the siphon tube of an ordinary Soxhlet apparatus; in one position of the tap the apparatus acts in the usual way, and at the end of the extraction the tap may be turned so that the solvent is run off through a side-tube and collected in a separate vessel.

W. P. S.

**Application of the Electrometer to the Study of Chemical Reactions in Electrolytes.** MARCEL BOLL (*Compt. rend.*, 1912, 154, 349—351).—A Curie-Moulin electrometer has been used in the differential method for the quantitative study of reactions in which the amount of material undergoing change is too small to admit of the ordinary analytical methods being employed. The electrometer is specially useful for the investigation of photochemical reactions.

W. O. W.

**Fluorescein as an Indicator of Bromine.** A. LABAT (*Bull. Soc. chim.*, 1912, [iv], 11, 143—146).—In reply to Baubigny (this vol., ii, 200), the author explains why his modification of this test was introduced.

T. A. H.

**Detection of Fluorine.** A. SARTORI (*Chem. Zeit.*, 1912, 36, 229—230).—The author finds that the test described by Rupp (this vol., ii, 88) is less sensitive than the usual etching test which will detect 0.1 mg. of fluorine, whilst Rupp's test fails when the quantity of fluorine present is less than 0.5 mg. The method proposed by Kickton and Behncke (Abstr., 1910, ii, 889) was found to be capable of detecting 0.3 mg. of fluorine in 200 c.c. of raspberry juice.

W. P. S.

**The Estimation of Sulphur and of Halogens in Small Quantities of Organic Substances.** JULIUS DONAU (*Monatsh.*, 1912, 33, 169—176).—The method already described (Emich and Donau, Abstr., 1910, ii, 152) has been improved, and the author's new method of filtration (Donau, Abstr., 1911, ii, 199) introduced. The process is similar to that of Carius, but applied on a very small scale. The advantages are that only a few milligrams of substance are required, whilst the cost and danger are reduced to a minimum. The paper is illustrated with diagrams and tables of results actually obtained.

D. F. T.

**Rapid Volumetric Method for the Estimation of Free Sulphur.** C. DAVIS and J. LOUIS FOUCAR (*J. Soc. Chem. Ind.*, 1912, 31, 100).—For the estimation of free sulphur in spent oxide and in other materials containing substances other than sulphur soluble in carbon disulphide, the following method is proposed: it consists in the conversion of the sulphur into sodium thiocyanate by digestion with alcoholic sodium cyanide solution, the thiocyanate being then titrated in the usual way. The procedure is as follows: One gram of the finely powdered sample is dried in a water-oven for one hour, then transferred to a 250 c.c. flask, 1.5 grams of sodium cyanide and 50 c.c. of alcohol are added, and the mixture is boiled under a reflux apparatus for two hours. The alcohol is now evaporated, the residue is treated with 100 c.c. of hot water, and the solution, when cold, diluted to a volume of 250 c.c. To 25 c.c. of this solution are added 75 c.c. of water and 5 c.c. of a saturated iron alum solution; the mixture is heated to 95°, filtered, and the filter and insoluble portion are washed until free from thiocyanate. After cooling, the filtrate

is acidified with 5 c.c. of nitric acid, and titrated with  $N/20$ -silver nitrate solution. Should the sample contain thiocyanate (as is most likely in the case of spent oxide), this should be titrated separately in another portion of the sample, and an allowance made for its quantity.

W. P. S.

**Modification of the Modified Winkler Method for the Estimation of Sulphates in Water.** HOWARD W. BRUBAKER (*J. Amer. Chem. Soc.*, 1912, **34**, 284—285).—In order to obviate the trouble involved in neutralising the hydrochloric acid with sodium hydroxide, which is necessitated by the modified Winkler method for the estimation of sulphates in water, the addition of sodium acetate is recommended. The modified process is as follows:

To 150 c.c. of the sample are added 10 drops of concentrated hydrochloric acid and 0.1—0.2 gram of pure barium chromate. The liquid is heated until it boils, is then cooled, and 5 grams of sodium acetate added. After filtering, 100 c.c. of the filtrate are placed in a colorimeter cylinder and rendered alkaline with sodium hydroxide. The standard for comparison should be made slightly stronger than this solution, and should be diluted to 100 c.c. after making it alkaline with sodium hydroxide. A blank determination must be made, using distilled water, in order to ascertain the correction to be applied for the solubility of the barium chromate under the conditions of the experiment. The method gives accurate results.

E. G.

**An Apparatus for the Rapid, Quantitative Removal of Nitrogen from a Gaseous Mixture by means of Electric Sparks.** FERDINAND HENRICH and W. EICHORN (*Zeitsch. angew. Chem.*, 1912, **25**, 468—470).—The apparatus consists of an inverted, pear-shaped bulb of about 200 c.c. capacity. The electrodes are introduced through the neck at the bottom of the bulb and reach well up into the narrow part, being kept in position by a rubber stopper; they consist of platinum wire, 0.35 mm. in diameter, fused into a short tube of fusible glass, which is then fused on to ordinary glass tubing. The neck of the bulb is also connected with an adjustable reservoir containing sodium hydroxide. The narrow part of the pear opens into a capillary tube connecting with (1) the reservoir of gas to be analysed, and (2) a reservoir of sodium hydroxide solution at a higher level than the bulb; connexions with the gas or sodium hydroxide can be made by means of appropriate stopcocks. After the gas from which the nitrogen is to be removed has been introduced into the bulb, sparks are passed and connexion made from time to time with the head of sodium hydroxide solution, which is thus caused to flow down over the inside of the bulb and brings about rapid absorption of the oxides of nitrogen. At the same time a blast of cold air is caused to impinge continuously on the external part of the bulb in the neighbourhood of the electrodes, and thus prevent too great a rise in temperature.

With the above apparatus the removal of nitrogen takes place from two to three times as fast as in the apparatus described by Travers, and the sparking can be carried on continuously.

T. S. P.

**The Phenolsulphonic Acid Method of Estimating Nitrates in Sewage Effluents.** HARRY SILVESTER (*J. Soc. Chem. Ind.*, 1912, 31, 95).—This method is liable to yield untrustworthy results when applied to sewage effluents containing waste gas liquor, the thiocyanate which may be present reacting with the nitric acid with the formation of hydrocyanic acid and nitric oxide; the sulphur is also oxidised to sulphate. The zinc-copper couple method yields the most uniformly trustworthy results, and the diphenylamine reaction may be employed for ascertaining approximately the quantity of nitrate in a sample of water or sewage effluent. W. P. S.

**Lorenz's Method for the Estimation of Phosphoric Acid.** HUGO NEUBAUER and F. LÜCKER (*Zeitsch. anal. Chem.*, 1912, 51, 161—175).—A recapitulation of Lorenz's method of estimating phosphoric acid (direct weighing of the yellow precipitate: Abstr., 1901, ii, 278) and a slight modification thereof.

The yellow molybdic precipitate is collected in a Neubauer crucible and then washed free from ammonium nitrate by means of pure acetone, which can easily be recovered by placing it over dry potassium carbonate and subsequent distillation.

The crucible and contents are then dried at the ordinary temperature under reduced pressure (150 mm.) for half an hour. If it cannot be weighed immediately, it may be kept meanwhile in a desiccator over dilute sulphuric acid (equal vols. of acid and water). The compound, if the directions have been scrupulously followed, contains exactly 3.295% of phosphoric oxide. L. DE K.

**Method of Ashing Foods and Other Organic Substances for the Estimation of their Phosphorus Content.** AM. VOZÁRIK (*Zeitsch. physiol. Chem.*, 1912, 76, 426—432).—Phosphorus in foods is to some extent present in the form of phosphatides, which are more or less volatile below 100°. The following method of ashing is proposed: 1 to 3 grams of the finely-ground substance are carefully mixed with 0.2 gram of magnesia in a platinum crucible, and carbonised, the crucible being supported obliquely with the lid off until the flame goes out. The lid is then replaced, and the crucible strongly heated until completely ashed, which occupies from one-half to three hours according to the substance. The phosphoric acid is then estimated in the usual manner. The results obtained are considerably higher than by direct ashing. E. F. A.

**Titrimetric Estimation of Phosphorus in Foods and Other Organic Substances by the Uranium Method, and the Errors of the Process.** AM. VOZÁRIK (*Zeitsch. physiol. Chem.*, 1912, 76, 433—456).—The titrimetric estimation of phosphoric acid in preparations derived from organic substances is subject to errors caused by free and partly neutralised mineral acids, by acetic acid, by several dissolved salts, in particular, alkali and alkaline-earth phosphates and aluminium ferric phosphate.

The solution which is to be titrated must not contain any phosphate showing an acid reaction with phenolphthalein. The harmful influence of free acetic acid begins at a concentration of 0.36% when a cochineal

tincture is used as indicator, or 0.6% when potassium ferrocyanide is used. The interference by sodium, ammonium, and magnesium acetates respectively is noticed at concentrations of 4%, 2%, and 0.75%.

Acids act in the opposite sense on the end-points given by the cochineal and potassium ferrocyanide indicators. The divergence found when both indicators are used together may be used to give some idea of the magnitude of the experimental error.

When a considerable proportion of other mineral salts are present, their influence on the reaction has to be determined and allowed for.

E. F. A.

**Hydrogen Apparatus for Marsh's Test.** F. JADIN and A. ASTRUC (*J. Pharm. Chim.*, 1912, [vii], 5, 233—235).—The apparatus is essentially a Drechsel bottle of 75 to 80 c.c. capacity having sealed into the stopper carrying the two side-arms (inlet and outlet tubes) a stoppered funnel, *A*, the stem of which reaches almost to the bottom of the bottle. The stem of the funnel and the inner end of the inlet tube are bent on themselves slightly inside the bottle. In using the apparatus, zinc is placed in the bottle, and boiled distilled water is poured in through *A* until it fills the bottle and flows through the side-arms. Any bubbles of air that remain in the tubes are displaced by shaking the bottle. The outlet tube is then closed by a piece of rubber tubing and a spring clip, and dilute sulphuric acid containing platinic chloride is added through *A*. The gas generated drives the excess of water out through the other side-arm, and when the liquid is reduced to a suitable bulk the second side-arm is closed and the bottle is ready for attachment to the rest of the Marsh apparatus. The arsenical liquid can be introduced through *A* after the apparatus has been at work fifteen minutes.

T. A. H.

**The Loss of Carbon During Solution of Steel in Potassium Cupric Chloride.** HELEN ISHAM (*J. Ind. Eng. Chem.*, 1911, 3, 577—579).—A continuation of previous work by the author, also of Moore and Bain (*Abstr.*, 1908, ii, 898, 899), on the estimation of carbon in steels by direct combustion and by solution in potassium cupric chloride. The lower results obtained by the latter method are now considered to be due to experimental errors, and not to the loss of carbon from the steel in the form of gaseous hydrocarbons previously identified during the process, which are now found to be present as impurities in the potassium cupric chloride solutions.

A sketch of the apparatus, with a detailed account of the procedure now adopted, is described, whilst the author also states that the estimation of sulphur in steel by direct combustion to sulphur di- and tri-oxides has not been satisfactorily achieved.

F. M. G. M.

**A Simple Method for Determining the Carbon Dioxide Content of the Alveolar Air by means of Baryta** YANDELL HENDERSON and DONALD G. RUSSELL (*Amer. J. Physiol.*, 1912, 29, 436—441).—A modification of Haldane's apparatus, in which the alveolar air is received directly into baryta water. The results obtained are very accurate.

W. D. H.

**The U-V Filter-lamp as a Valuable Aid in Determining the Purity of Chemical Products.** OTTOMAR WOLFF (*Chem. Zeit.*, 1912, 22, 197—198).—When commercial potassium carbonate is exposed to ultraviolet light, certain particles are seen to fluoresce with a bright red light, a few with a light blue light, whilst the remainder are indifferent. The red fluorescence has been shown to be due to the presence of potassium sulphide. It is noteworthy that this impurity collects in particular portions of the potassium carbonate. Pure potassium carbonate shows no fluorescence, but all specimens exhibit a more or less permanent greenish-white phosphorescence after illumination with ultra-violet light. H. W.

**Estimation of [Calcined] Magnesia in Magnesium Carbonate and in Mixtures of Asbestos.** V. FORTINI (*Chem. Zeit.*, 1912, 36, 270—271).—The process is based on the fact that normal magnesium carbonate does not cause a rise in temperature when dissolved in hydrochloric acid, whereas with the oxide considerable heat is developed. Exactly 25 c.c. of dilute hydrochloric acid (1:1) are introduced in a Tortelli thermoleometer, and, after noticing the temperature, 1 gram of the sample is added. With constant shaking the maximum rise in the temperature is recorded, and by referring to an empirical table, the amount of magnesium oxide is found. L. DE K.

**Detection of Small Quantities of Zinc in Wine.** A. STRAUB (*Zeitsch. Nahr. Genussm.*, 1912, 23, 140).—The following method is described for the detection of the small quantities of zinc which may be introduced into a wine by the use of zinc salts and potassium ferrocyanide as clarifying agents: Two hundred c.c. of the wine are boiled for some length of time with the addition of sodium carbonate, the precipitate formed is collected on a filter, washed with hot water, and then dissolved in a small quantity of hydrochloric acid. The solution is oxidised with potassium chlorate, iron and aluminium hydroxides and calcium phosphate are precipitated by adding sodium acetate and boiling the mixture, and, after filtration, the solution is tested with hydrogen sulphide. W. P. S.

**A Reaction for Mercury Salts.** J. A. SIEMSEN (*Chem. Zeit.*, 1912, 36, 214).—When mixed with ethylenediamine, mercuric chloride solution yields a white, amorphous salt, which is soluble in acids, in alkali solutions, in an excess of ethylenediamine, and in potassium iodide solution. The salt is precipitated from dilute nitric or hydrochloric acid solutions, but not from dilute sulphuric acid. It differs from the uranium salt described previously by the author (*Abstr.*, 1911, ii, 230, 773), in that it is soluble in an excess of the reagent and in the solvents mentioned. W. P. S.

**The Quantitative Separation of Copper from Arsenic, Aluminium, Zinc, Tungsten, and Tin in Sodium Hydroxide Solutions containing Sucrose by means of Hydrogen Peroxide.** PAUL JANNASCH and OSKAR ROUTALA (*Ber.*, 1912, 45, 598—604).—When hydrogen peroxide is added to a solution of copper

sulphate containing sucrose and sodium hydroxide, the sucrose being present in such quantity that the alkali produces no precipitate, an emerald-green solution is formed; on gentle warming, the copper is deposited quantitatively as cuprous oxide. This reaction may be used for the estimation of copper, and for its separation from other metals. The collected cuprous oxide is ignited to cupric oxide in either a platinum or quartz crucible.

In the separation of copper and arsenic, after the cuprous oxide has been collected, the filtrate is evaporated to small bulk with excess of concentrated nitric acid; the resulting clear, light yellow solution is made alkaline with ammonia, and the arsenic precipitated with magnesium chloride and weighed as magnesium pyroarsenate. A double precipitation is necessary for accurate results.

In the separation of copper from aluminium, a special method is necessary to destroy all the organic matter in the filtrate from the cuprous oxide. After evaporation to dryness in a platinum dish with concentrated nitric acid, the residue is taken down several times with a mixture of 65% nitric acid and 15% hydrogen peroxide, and finally fused over the bunsen flame. The cold mass is then dissolved in hot water, the solution acidified with nitric acid, and the aluminium precipitated as hydroxide in the usual way.

The separation of copper from zinc and from tin is similar to that described for copper and aluminium as far as the destruction of the organic matter in the filtrate from the cuprous oxide is concerned. The zinc is precipitated as basic carbonate and weighed as oxide; the tin is weighed as dioxide.

The following quantities were found to give good results in the above separations. In each case from 0.28 to 0.40 gram of copper sulphate pentahydrate was contained in the mixture, and the hydrogen peroxide used for precipitation was 7%.

	Sodium hydr- sucrose, oxide, grams.		Water, c.c.	Hydrogen peroxide, c.c.
0.187—0.229 gram of arsenious oxide ...	5	5	100	10 + 5
0.23 —0.62 „ potassium alum ...	2.5	6	80	15 + 5
0.23 —0.36 „ zinc sulphate .....	2.5—5	3—6	80	20 + 10
0.36 —0.40 „ tin .....	2.5	3—6	80	20 + 10

The filtration of the cuprous oxide must proceed without a break, otherwise traces of copper are liable to go into solution, owing to oxidation.

The method can also be used for the separation of copper from tungstic acid, molybdic acid, vanadic acid, phosphoric acid, etc. Details will be given later.

T. S. P.

**Researches on Very Small Quantities of Matter by the Direct Electrometric Method.** ALBERT GRUMBACH (*Compt. rend.*, 1912, 154, 645—646. Compare Boll, this vol., ii, 384).—A vessel containing sulphuric acid is connected with one containing sulphuric acid to which a small amount of potassium dichromate has been added. Two platinum electrodes connect the vessels with a capillary electrometer, employed either as a zero instrument or with a condenser in series for compensation.

By operating in the manner described in a previous communication, it has been found possible to detect chromium trioxide in a concentration of  $0.45 \times 10^{-8}$ . The observed *E.M.F.* is sensitive to convection currents, and has a maximum value when the electrodes are in the centre of the vessels. W. O. W.

**Oxidation of Chromic Salts by means of Silver Oxide.** I. D. MENEGHINI (*Gazzetta*, 1912, 42, i, 134—138).—Chromic salts are oxidised to chromates by silver oxide, which is reduced to the black suboxide,  $\text{Ag}_2\text{O}$ . This reaction can be used for the detection and estimation of chromium. In the scheme of qualitative analysis the hydroxides of the third group are dissolved in nitric acid, the solution is treated with silver nitrate, and rendered slightly alkaline with alkali hydroxide. A black precipitate of silver suboxide is produced, and the supernatant liquid is yellow. Quantitatively, silver nitrate and alkali hydroxide are added to the chromium solution, and after filtration the chromate is determined iodometrically. The presence of iron salts does not affect the reaction. R. V. S.

**New Method for the Separation of Thorium.** T. O. SMITH and CHARLES JAMES (*J. Amer. Chem. Soc.*, 1912, 34, 281—284; *Chem. News*, 1912, 105, 109).—When sebacic acid is added to a neutral solution of a thorium salt, *thorium sebacate* is produced quantitatively as a voluminous, granular precipitate. It is shown that this reaction can be employed for the estimation of thorium in presence of cerium, lanthanum, praseodymium, neodymium, samarium, and gadolinium. It would also be of value for the separation and purification of thorium. Sebacic acid dissolves in water to the extent of 1 part per litre at  $17^\circ$ , 40 parts per litre at  $65^\circ$ , and is fairly soluble at  $100^\circ$ .

When pyrotartaric acid is added to a cold neutral solution of a thorium salt, a precipitate is not formed, but on boiling the solution thorium pyrotartrate is quantitatively precipitated. It therefore seems that pyrotartaric acid could also be used for estimating thorium.

Thorium is also precipitated, but not quantitatively, by phenoxy-acetic, malic, anisic, aspartic, and oxanilic acids. E. G.

**The Estimation of Vanadium in Vanadium and Chrome-vanadium Steels.** JOHN R. CAIN (*J. Ind. Eng. Chem.*, 1911, 3, 476—481).—A comprehensive account of experiments undertaken by the Bureau of Standards in conjunction with eleven other chemists to clear up the difficulty of accurately estimating vanadium in steel. The following classes of methods were investigated: (A) methods similar to that described by Campagne (*Abstr.*, 1903, ii, 761); (B) methods depending on the reduction of quinquivalent vanadium to the quadrivalent condition; (C) methods by which the vanadium is separated from iron and chromium, etc., by pouring a nitric acid solution of the metals into boiling sodium hydroxide, when the vanadium goes into the filtrate and is precipitated by means of mercurous or lead salts, the final estimation being either gravimetric or volumetric. The possible errors incident to each of these are fully discussed, and the following procedure described as appearing most satisfactory.

The steel (2 to 4 grams) is dissolved in 40—60 c.c. of 10% (by volume) sulphuric acid in a covered 300 c.c. flask, the insoluble matter separated, washed, ignited, fused with potassium hydrogen sulphate, and the aqueous solution of the fusion added to the previously obtained liquid. The solution is nearly neutralised with saturated sodium carbonate, and then treated with finely powdered cadmium carbonate at intervals of four to five minutes; boiling vigorously between each addition, and keeping the flask carefully covered, a gram or two of carbonate should remain undissolved at the end of the operation, which lasts fifteen to twenty minutes, or even less with vanadium steels containing little or no chromium.

The precipitate is rapidly collected, washed with hot water, redissolved in boiling 10% sulphuric acid, and refiltered into the flask; the solution cooled, and treated with ammonium hydroxide until only sufficient acid is left to prevent the precipitation of iron by hydrolysis when the liquid is boiled during the introduction of a rapid stream of hydrogen sulphide. The precipitate is separated, washed, the filtrate concentrated to about 60—70 c.c., and electrolysed with a current of 5 to 6 amperes at 6 to 7 volts, as described by Smith (*Electroanalysis*, 4 ed.). When the solution no longer answers to tests for iron or chromium, it is removed from the apparatus and the mercury washed several times while the current is still passing; 2 or 3 c.c. of sulphuric acid (1:1 by volume) are added, the temperature raised to 70—80°, followed by the addition of potassium permanganate until there is a strong pink colour. Sulphur dioxide is first passed into the boiling liquid, and then carbon dioxide until the excess of sulphur dioxide is removed, the solution filtered, and the filtrate titrated at 70—80° with *N*/10-potassium permanganate.

For extreme accuracy, repetition of the final reduction and titration is recommended, whilst the electrolysis can be rapidly carried out in a separating funnel with a tube inwardly projecting from the stem containing mercury, a fused-in platinum wire, and a rotating anode. The disturbing influence of other metals, if present, is discussed, and modifications of the method suggested to overcome the difficulties.

F. M. G. M.

**Estimation of Vanadium in Steel and Iron.** B. O. CRITES (*J. Ind. Eng. Chem.*, 1911, 3, 574—577).—The author describes a method based on the work of J. Kent Smith for estimating vanadium in steel and iron which gives satisfactory results when the vanadium content is below 0.3%. An improved process on similar lines was subsequently published by Blair (*Abstr.*, 1908, ii, 900) and another by C. M. Johnson (*Chemical Analysis of Special Steels, etc.*), by modifying which, results usually about 5% too low are obtained; but by simultaneously running two blanks on a steel of similar constitution to the sample, but in one case free from vanadium, and in the other containing a known amount of a standard vanadium solution, indications of the correction necessary to employ are obtained. The methods of Auchy, Slawik, and of Campbell and Woodham (*Abstr.*, 1908, ii, 901) are found to give less satisfactory results.

F. M. G. M.

**Estimation of Gold, Silver, and Platinum.** TRENNER (*Metallurgie*, 1912, 9, 103—105).—In assaying alloys containing gold and platinum, in which the error of the estimation by ordinary methods may amount to 1%, the following improved method is recommended. After a preliminary assay has been made to determine the approximate composition of the alloy, 0.5 gram is taken, and alloyed with sufficient silver to make the ratio Au+Pt:Ag about 1:10. The alloy is cupelled with lead, a check of similar composition being used to determine the loss of silver in cupellation. Lead is not retained by the bead under these conditions. The bead, without being hammered or rolled, is heated in a parting flask with 25 c.c. of concentrated sulphuric acid, without boiling. The silver is removed in twenty-five to thirty minutes, leaving a coherent residue. After cooling and washing, the residue is ignited and weighed. It is then dissolved in aqua regia, evaporated, diluted with water, and filtered from silver chloride. To the filtrate are added 15 c.c. of hydrochloric acid, D 1.19, and 1 gram of hydrazine hydrochloride. After an hour at 18—20°, with occasional stirring, the gold is precipitated, and may be filtered, ignited, and weighed. Platinum is precipitated from the filtrate by ammonia, the large excess of hydrochloric acid being previously removed by evaporation if the platinum content is low. The separation is quantitative, with an accuracy of 0.05%, as is shown by a number of test assays. The method may also be applied to ores. C. H. D.

**Detection of Methyl Alcohol.** WILHELM SAILER (*Pharm. Zeit.*, 1912, 57, 165. Compare this vol., ii, 301).—For the detection of methyl alcohol in ethyl alcohol, 5 c.c. of the alcohol are treated with 0.1 gram of chromic acid and ten drops of concentrated sulphuric acid. After the lapse of a few minutes, and when the mixture has become green in colour, six drops of the solution are mixed with twenty drops of concentrated sulphuric acid, and a small quantity of morphine is added. In the presence of a large proportion (50%) of methyl alcohol, a dark violet coloration is produced; with smaller quantities, the colour is red, and with traces, yellowish-brown. Pyrogallol may be used in place of morphine; the coloration obtained in this case is chocolate-brown. Ethyl alcohol gives a lemon-yellow coloration with the test, the colour changing gradually to orange and then brown. W. P. S.

**Detection of Methyl Alcohol in Alcoholic Preparations and Especially Tincture of Iodine.** E. VOISENET (*J. Pharm. Chim.*, 1912, [vii], 5, 240—245).—The tincture of iodine is decolorised by sodium thiosulphate solution, and the test already described (*Abstr.*, 1906, ii, 807) is applied. T. A. H.

**Analysis of Small Samples of Spirits.** XAVIER ROCQUES (*Ann. Chim. anal.*, 1912, 17, 86—88).—The process is devised for samples not exceeding 100—125 c.c. After taking, by way of a check, the density, the volume (*V*) of the sample is measured, and 10 c.c. are pipetted off and used for the free acidity test. The whole (including the 10 c.c. taken) is then submitted to distillation, collecting exactly nine-tenths of the volume (*V*). After determining the alcohol by means of the density as usual, one-tenth of the figure obtained is deducted; this gives the actual amount of alcohol.

The solid matter may be got by making up the residual liquid to the volume ( $V$ ), and then operating in the usual manner; allowance should be made for the alkali added.

From the distillate is taken a volume equal to exactly 33.35 c.c. of alcohol ( $V'$ ). After neutralising this with  $N/10$ -sodium hydroxide with a trace of solid phenolphthalein as indicator, the esters are determined in the usual way by the saponification process. After adding aniline phosphate and removing the aldehydes by boiling for an hour in a reflux apparatus, 50 c.c. are distilled off; this distillate is examined for the higher alcohols as usual.

If the sample amounts to 10 c.c., the above determinations may be carried out; if exceeding this by something like 25 c.c., there will be still enough left for the usual estimation of aldehydes and furfural-aldehyde.

L. DE K.

**New Method for the Estimation of the Reducing Sugars.** E. C. KENDALL (*J. Amer. Chem. Soc.*, 1912, 34, 317—341).—In a study of the velocity of amylolytic action, it was desired to estimate accurately the reducing sugars resulting from the digestion of starch. An investigation has therefore been made of some modifications of Fehling's solution with the object of ascertaining the best conditions for the gravimetric determination of reducing power. It has been found that more accurate results are obtained by replacing the sodium hydroxide of Fehling's solution by potassium carbonate, and the Rochelle salts by salicylic acid. The results of several estimations have shown that 15 grams of potassium carbonate, 5 grams of salicylic acid, and 2 grams of copper sulphate in a total volume of 140 c.c. give satisfactory conditions. The potassium carbonate and copper sulphate are dissolved in water and added separately to the sugar solution, whilst the salicylic acid is added in the dry state. The solution should be heated in a bath of boiling water rather than over a flame. After twenty minutes' heating in boiling water, the reaction is nearly complete in the case of dextrose and invert-sugar, somewhat less so in that of lactose and maltose. The reducing powers of these sugars have been determined and compared with those obtained by other methods. The relation has been calculated between each of the four sugars and copper for every mg. of copper from 30 mg. to 450 mg. and the results are tabulated.

E. G.

**Estimation of Sucrose in Cane Molasses by the Double Polarisation Method, using Invertase and Acid as Hydrolysts.** JAMES P. OGILVIE (*Int. Sugar J.*, 1912, 14, 89—93. Reprint).—The methods described previously for the examination of beet products (*Abstr.*, 1911, ii, 232) have been applied to cane molasses, the results found by the invertase method being compared with those given by acid hydrolysis when the sucrose is calculated (1) from the alkaline direct polarisation; (2) from the neutral direct polarisation; and (3) from the hydrochloric acid and sulphurous acid polarisations. The results found by the selective hydrolyst invertase as compared with the figures obtained by acid hydrolysis show that the quantity of sucrose found by the alkaline direct polarisation method are too high; the neutral direct polarisation method may also yield results which are too

high. On the other hand, the acid direct polarisation method yields results which agree closely with those obtained by means of invertase. In order to avoid the disturbing effect of the reducing sugars, both the direct and the inversion readings must be made under the same conditions of acidity; when this is done, the agreement between the invertase and the double polarisation methods is very close.

W. P. S.

**Occurrence of Boric Acid in Honey.** G. BÜTTNER (*Zeitsch. Nahr. Genussm.*, 1912, 23, 139—140).—Many samples of honey of various origins examined by the author were found to contain traces of boric acid; 25 grams of the honey yielded an ash which gave a distinct boric acid reaction when tested in the usual way with turmeric paper. A sample of artificial honey, also examined, was free from boric acid.

W. P. S.

**Inversion of Sucrose by Honey.** O. ACHERT (*Zeitsch. Nahr. Genussm.*, 1912, 23, 136—139).—Results of experiments carried out by the author show that natural honey which has not been heated to a temperature above 55° is capable of inverting sucrose; for instance, mixtures of honey and sucrose, containing from 22 to 42% of the latter, after remaining for four months at the ordinary temperature were found to contain from 2 to 11% of sucrose. Honey which has been heated to 100° does not invert sucrose. It is further shown that the acidity of the honey does not play any part in the inversion.

W. P. S.

**Constant Temperature Heating Apparatus for Explosives and Experiments on the Decomposition of Nitrocelluloses.** JOHN S. S. BRAME (*J. Soc. Chem. Ind.*, 1912, 31, 159—161).—A detailed description is given of a special form of apparatus designed for the study of the decomposition of nitrocelluloses when heated in a vacuum, by measuring the gases evolved. The nitrocellulose under investigation is contained in a decomposition tube, which is placed in a vessel maintained at a constant temperature by circulating through it the vapour of a suitable liquid, such as toluene.

W. H. G.

**Photolytic Decomposition of Smokeless Powders, of Picric Acid and Ammonium Picrate by Ultra-violet Light.** DANIEL BERTHELOT and HENRI GAUDECHON (*Compt. rend.*, 1912, 154, 514—517. Compare this vol., i, 163; ii, 210).—The volumes of gases formed when French powder *B* and other explosives are exposed to ultra-violet light are given, the substance being treated in atmospheres of oxygen, hydrogen, and carbon dioxide. In each case a portion of the atmospheric gas is absorbed, hence an atmosphere of nitrogen is best for such observations.

Picric acid underwent no alteration at 5 cms. from the quartz-mercury lamp. After three hours at 2 cms. it gave the following gas volumes: CO<sub>2</sub> (0.16 c.c.), CO (0.08 c.c.), N<sub>2</sub>O (0.03 c.c.), N<sub>2</sub> (0.43 c.c.). Ammonium picrate is more stable, and remains unchanged under these conditions.

W. O. W.

**Determination of Urinary Acidity.** LÉON GRIMBERT and J. MOREL (*Compt. rend.*, 1912, 154, 378—380).—The method recommended involves titration with sodium hydroxide, using phenolphthalein as indicator, calcium being removed by addition of solid potassium oxalate in order to avoid the disturbing effect of calcium phosphate. The retarding influence of ammonia on the end point is allowed for by carrying out a formaldehyde estimation of this substance and applying the necessary correction. The result is the "real acidity," corresponding with the conversion of  $\text{NaH}_2\text{PO}_4$  into  $\text{Na}_2\text{HPO}_4$  and neutralisation of organic acids. The amount of the latter may be calculated after estimating the total phosphoric acid. W. O. W.

**Estimation of the Molecular Weights of Small Quantities of Fatty Acids.** W. ARNOLD (*Zeitsch. Nahr. Genussm.*, 1912, 23, 129—135).—The method proposed consists in neutralising the fatty acid with  $N/2$ -alcoholic potassium hydroxide solution at the ordinary temperature, evaporating the solution, drying the residue of soap for two and a-half hours in the water-oven, and weighing the dry soap. It is essential to break up the soap residue into a fine powder before it is dried. Formulae are given for calculating the molecular weight of the fatty acid under examination from the weight of the soap and the quantity of potassium hydroxide used for the neutralisation, corrections being applied for the weight of the phenolphthalein introduced as indicator, and for impurities in the potassium hydroxide solution. Experiments with a series of fatty acids ranging from butyric acid to stearic and oleic acids show that the method yields trustworthy results; in over 90% of the experiments the results obtained differed by less than two units from those required by theory. W. P. S.

**Estimation of Tyrosine and Glutamic Acid.** EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1912, 77, 75—76).—Compare this vol., i, 261.

**The Detection of Salicylic Acid.** HENRY C. SHERMAN and ABRAHAM GROSS (*J. Ind. Eng. Chem.*, 1911, 3, 492—493).—The value of the Millon reaction or of ferric chloride for detecting the presence of salicylic acid is greatly impaired by the fact that numerous other substances react with these reagents in a similar manner, whilst the formation of the methyl ester, the nitro- or bromo-compounds are only suitable in the presence of comparatively large quantities of the acid.

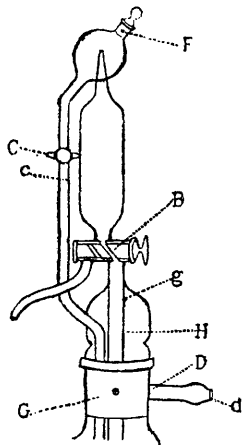
The Jorissen reaction (*Bull. Acad. roy. Belg.*, 3, 259) has been further studied by the author (compare *J. Ind. Eng. Chem.*, 1910, 2, 24), and found to give satisfactory results; it is applied as follows: The solution to be tested is treated with four to five drops of a 10% solution of sodium or potassium nitrite, the same quantity of 50% acetic acid and one drop of 1% copper sulphate solution, shaken after the addition of each reagent, and finally heated during forty-five minutes in boiling water, care being taken that the test liquid is completely immersed; after cooling, it is examined against a white background and compared with a blank test containing the same

amount of the reagents mixed with water; in this way the presence of 0.005—0.01 mg. of salicylic acid can be detected in aqueous solution. When larger quantities of salicylic acid are present, the concentration of the copper sulphate solution may be increased to 10%, when the red coloration develops much more rapidly, and this is quite permanent even at the greater dilution.

This test may be used in conjunction with ferric chloride and Millon's reagent, it being found that phenol and saligenin give the same colour as salicylic acid with Jorissen's reagent, but that the limits of delicacy are quite different; 2-hydroxyisophthalic acid gives the Jorissen reaction up to dilutions of 1:100,000, but is readily distinguished from salicylic acid by its colour with ferric chloride; methyl ethylacetoacetate gives a violet colour with ferric chloride in concentrated solution, but does not react with either Millon's or Jorissen's reagents at a dilution of 1:1000, whilst orcinol, arbutin, resorcinol, and phloridzin, which give colour reactions with ferric chloride, do not respond to the Jorissen test. F. M. G. M.

**New Method for the Estimation of Hippuric Acid in Urine.** OTTO FOLIN and FRED F. FLANDERS (*Proc. Amer. Soc. Biol. Chem.*, 1911, xxvii—xxviii; *J. Biol. Chem.*, 11).—The method is based on the hydrolysis of hippuric acid, the extraction of the benzoic acid with chloroform, and titration with sodium ethoxide. W. D. H.

**An Automatic Pipette for the Determination of Iodine- and Saponification-Numbers.** FRANZ MICHEL (*Chem. Zeit.*, 1912, 22, 198).—This pipette is specially designed to avoid alteration in concentration of iodine and alcoholic potash solutions during measurement.



The iodine solution is forced into the pipette by means of a rubber ball (fixed at *d*), any excess returning to the flask when *D*, *G*, and *C* are suitably placed. The contents of the pipette are discharged by opening the stopcock, *B*, and any residue blown out by gentle pressure of the rubber ball, the opening *F* having been closed.

For use with alcoholic potash, it is recommended that the stopcock be made of phosphor-bronze, or, better, of silver. H. W.

**The Quantitative Estimation of Ketones in Essential Oils.** E. K. NELSON (*J. Ind. Eng. Chem.*, 1911, 3, 588—589).—An attempt to find a general method for the estimation of aldehydes and ketones for

which in many cases the bisulphite method is useless; for this purpose the author has extended Walther's experiments (*Abstr.*, 1901, ii, 49) on citral and carvone to pulegone, camphor, thujone, menthone, benzaldehyde, and fenchone, obtaining (except with the last) fairly satisfactory results.

The procedure employed is as follows: A standard hydroxylamine solution is prepared by dissolving 20 grams of hydroxylamine hydrochloride in 30 c.c. of water and adding 125 c.c. of aldehyde-free alcohol; the purified substance (1—2 grams) is boiled under reflux with 35 c.c. of the reagent and sodium hydrogen carbonate (2 grams), cooled, 6 c.c. of hydrochloric acid added down the condenser, and the solution made up to 500 c.c. with water and filtered; the free acid in a measured volume is then neutralised with  $N/2$ -sodium hydroxide in the presence of methyl-orange, phenolphthalein added, and the hydroxylamine in excess of that required to form the oxime titrated with  $N/10$ -sodium hydroxide.

The application of this method to oils containing ketones is being proceeded with, the percentage of ketone found in the following oils being as follows: Wormwood oil, 33.15 and 31.24 (as thujone); pennyroyal oil, 81.87 (calculated at  $C_{10}H_{16}O$ ); rosemary oil, 30.33 and 30.24 (calculated as camphor).

F. M. G. M.

**Hübener's Method of Estimating Caoutchouc as its Bromide.** F. WILLY HINRICHSSEN and ERICH KINDSCHER (*Chem. Zeit.*, 1912, 36, 217—218, 230—232).—This method is stated to be untrustworthy for the direct estimation of caoutchouc in vulcanised materials, the results being much too high. The bromination is carried out with difficulty, and it is not possible to ascertain the end-point of the action of the aqueous bromine solution; the precipitated bromide always contains free bromine or bromine compounds, which are not removed by washing as described by Hübener, and there is also a risk of adding too little bromine. On the other hand, the decomposition of the bromide by nitric acid in the presence of silver nitrate is accompanied by loss of bromine, and in the estimation of the "free" sulphur in the filtrate from the bromide, considerable quantities of combined sulphur are oxidised and pass into solution (compare Abstr., 1911, ii, 445).

W. P. S.

**Some Colour Reactions.** NAZARENO TARUGI and F. LENCI (*Boll. Chim. Farm.*, 1911, 50, 907—910).—The paper deals with the action of hypochlorites on substances containing the groups  $-NH_2$  or  $:NH$ . When an aqueous suspension of *p*-benzoquinone is treated with a solution of ammonia, then with a solution of sodium hypochlorite, and finally with a little zinc chloride, and the whole heated for a quarter of an hour on the water-bath, a substance is produced which, after evaporation, may be extracted with alcohol. It is a yellow, crystalline compound, m. p.  $85^\circ$ , and on analysis gives figures agreeing with those required for *p*-benzoquinonechlorimide,  $C_6H_4O:NCl$ . 2:6-Dibromoquinone, when treated in the same way, yields 2:6-dibromo-*p*-benzoquinonechlorimide,  $C_6H_2Br_2O:NCl$ , a dark yellow, crystalline substance, m. p.  $78^\circ$ . Both chlorimides give a blue coloration with alkaline phenol solution. In the latter case the reaction product, after treatment with acetic acid, deposits 3:5-dibromo-1:4-benzoquinonehydroxyphenylimide,  $C_{12}H_7O_2NBr_2$ , which is a dark red, crystalline substance becoming blue when treated with alkalis.

The amino-acids, amino-aldehydes, and, in general, all substances containing the groups  $-\text{NH}_2$  or  $:\text{NH}$ , give an intense blue coloration when treated with phenol and hypochlorite, and the same substances react with quinone and hypochlorite, giving 1:4-benzoquinone-chlorimide. Some aliphatic primary and secondary amines (diisobutylamine and dipropylamine) do not give the reaction. It is probable that the coloration given by aniline with hypochlorites is due to a similar reaction.

Nitro-compounds give the same blue coloration when treated with phenol and hypochlorite; in all cases *p*-nitrosophenol is formed, which, reacting in its oximic form with the excess of phenol, gives *p*-benzoquinoneoxyphenylimide. An analogous reaction was effected with 3:5-dibromo-4-oximino- $\Delta^{2:5}$ -cyclohexadien-1-one (Fischer and Hepp, Abstr., 1888, 456; Kehrmann, Abstr., 1889, 244), which, when treated with phenol, yields 3:5-dibromo-1:4-benzoquinone-hydroxyphenylimide,  $\text{C}_{12}\text{H}_7\text{O}_2\text{NBr}_2$ , which is a dark red, crystalline substance giving a blue solution with alkalis.

Hydrocyanic acid, cyanides, carbylamines, thiocyanates, and thiocarbimides also give a blue coloration when treated with phenol and hypochlorite.

In using this reaction as a test, about 0.5 gram of substance is treated with an excess of phenol in crystals, and a solution of sodium hypochlorite (containing about 3% of active chlorine, and of an alkalinity equivalent to 4% of sodium hydroxide) is added drop by drop. Sometimes an excess of alkali prevents the appearance of the coloration.

The reaction is recommended for use in water-analysis, because it is much more sensitive than Nessler's reagent, and reacts with some nitrogenous substances which the latter does not reveal.

R. V. S.

**Extraction and Estimation of Alkaloids in Syrups and Saccharine Liquids.** ÉMILE KOHN-ABREST (*Bull. Soc. chim.*, 1912, [iv], 11, 73—75; *Ann. Chim. anal.*, 1912, 17, 85—86).—In principle the method depends on the fact that if potassium carbonate is added to diluted alcohol containing sugar, an aqueous solution of potassium carbonate, containing all or nearly all the sugar, forms, in which the alcohol is insoluble, and from which it separates as a distinct layer. If alkaloids are present, they remain dissolved in the alcohol and can be recovered in the usual manner.

T. A. H.

**Estimation of Nicotine in Tobacco and in Green Tobacco Leaves.** RICHARD KISSLING (*Chem. Zentr.*, 1911, ii, 1840; from *Schweiz. Woch. Chem. Pharm.*, 1911, 49, 537).—Mellet's process for the estimation of nicotine is open to the objection that loss of solvent may take place during the filtration of the ethereal solution. It is also pointed out that Mellet's modification of the older process proposed by the author is unnecessary, as the latter has described a new and simple method based on the precipitation of the nicotine with potassium mercuric iodide.

W. P. S.

**Reactions of Pyramidone.** A. MOULIN (*Ann. Chim. anal.*, 1912, 17, 13—14).—The blue coloration which is obtained when pyramidone is treated with nitric acid (compare Abstr., 1911, ii, 777) is due to the presence of nitrous oxides in the acid; the colour does not develop when pure nitric acid is employed. Silver nitrate and mercuric nitrate also yield a blue coloration with pyramidone, as do many other oxidising substances, but the reaction is best obtained with nitric acid containing nitrous oxides. W. P. S.

**The Formaldehyde Titration of Proteins.** I. FRIEDRICH OBERMAYER and ROBERT WILLHEIM (*Biochem. Zeitsch.*, 1911, 38, 331—343).—The authors give the details as to their method of determining the amino-nitrogen index by means of the Schiff-Sørensen method. They find that the amino-index of the various globulin fractions (euglobulin, pseudo-globulin) is invariably higher than that of the albumins (19.1—22.3 : 13.3—13.8). S. B. S.

**Oxydases.** IV. Cresol-Tyrosinase, a Reagent for Peptides, Polypeptides, Proteins, and Proteolysis by Micro-organisms. ROBERT CHODAT (*Arch. Sci. phys. nat.*, 1912, [iv], 33, 70—95. Compare Abstr., 1907, i, 574, 575).—Tyrosinase from potato peelings purified by precipitation with alcohol gives a yellow coloration with *p*-cresol in 1% solution, which finally becomes orange-yellow. Impure tyrosinase from *Russula delica* gives a cherry-red coloration with *p*-cresol. This is due to the presence of amino-acids; a mixture of purified tyrosinase, *p*-cresol, and glycine becomes red in a few minutes and cherry-red in the course of an hour. Occasionally the red colour changes to violet, and finally to an intense blue with a magenta-red dichromism; this necessitates the presence of a sufficient quantity of glycine, which is proved to take part in the reaction and not to act as a catalyst. Other amino-acids behave similarly to glycine, finally giving the blue coloration, alanine, however, gives a Congo-red shade without becoming blue; this behaviour is attributed to the fact that, unlike the other amino-acids tested, it belongs to the *d*-series.

Glycyl-*l*-tyrosine gives with tyrosinase only a madder-rose coloration changing to violet or blue. The addition of glycine retards the changes, the succession of colours, which are very characteristic, being red, rose, apricot, greenish, olive, emerald, emerald-bluish.

Proteins and peptones give a rose colour with the tyrosinase-cresol reagent which does not change to blue.

It is shown how the colour reactions described may be used to recognise first proteins, then peptones, which give a more pronounced colour, and finally the formation of amino-acids and polypeptides. The use of tyrosinase alone enables glycyl-*l*-tyrosine and tyrosine to be recognised. The tyrosinase-cresol reagent further identifies *d*-alanine when the fraction containing this has been isolated. The method is widely applicable to the study of the products of proteoclastic enzymes.

E. F. A.

**Test for Blood.** MAX REICH (*Chem. Zeit.*, 1912, 36, 138).—When dried blood, or commercial blood meal, or other blood prepara-

tion is dissolved in a 10% solution of hydrogen chloride in acetone by heating under reflux, a blood-red solution is obtained having a characteristic absorption spectrum. If the solution is made alkaline with ammonia and filtered, the filtrate shows a different absorption spectrum, which it retains for some time. After one or two weeks, however, the solution takes on a green fluorescence; in thick layers the whole spectrum is absorbed up to the red, whilst in thin layers there is a band in the green. Evaporation of this solution gives a reddish-brown, viscid mass, which is purified by solution in 96% alcohol, filtering from ammonium chloride, and precipitation with excess of ether. A non-fluorescent, white, flocculent precipitate is obtained but the filtrate shows a very strong, green fluorescence; after evaporation a residue is obtained, which is soluble in water, alcohol, or isobutyl alcohol to green fluorescent solutions, but insoluble in ether. The solutions show no spectrum, and the fluorescence is destroyed by alkalis or acids. Urobilin, which is soluble in ether, cannot be the cause of this fluorescence.

T. S. P.

**Detection of Blood by means of Pyridine.** FRANZ MICHEL (*Chem. Zeit.*, 1912, 36, 93—94, 105—106).—The author has investigated the test proposed by von Furth (*Abstr.*, 1911, ii, 947) and finds it to be trustworthy; he describes how certain interfering substances may be eliminated, and suggests a few modifications in the test in order to render it more sensitive. A quantity of about 0.5 c.c. of the pyridine blood solution should be placed in a small porcelain crucible, 0.5 c.c. of glacial acetic acid added, then 1 c.c. of the leucomalachite-green reagent, and, finally, 2 drops of a 1% hydrogen peroxide solution.

W. P. S.

**Detection of Biliary Pigments in Urine.** CROUZEL (*Ann. Chim. anal.*, 1912, 17, 58—59).—When urine containing biliary pigments is allowed to flow on the surface of a mixture consisting of 3 volumes of sulphuric acid and 1 volume of nitric acid, the urine becomes green in colour, and is separated from the acid layer by a red-coloured zone; the acid layer remains colourless. On shaking, the whole mixture develops a yellow coloration. In a similar test with a mixture of hydrochloric and nitric acids, the urine is at first coloured red and then yellow. Basic lead acetate and barium nitrate solutions yield a yellow precipitate with urines containing biliary pigments; with normal urines the precipitate is white. Mercuric nitrate yields a grey precipitate, and alum a yellow precipitate with these urines. The latter also give a yellow-coloured froth when shaken with granulated zinc; this colour is discharged on the addition of nitric acid, and the whole mixture becomes green.

W. P. S.

## General and Physical Chemistry.

**Recalculation of Atomic Refractions. II. The Constants for Nitrogen.** FRITZ EISENLOHR (*Zeitsch. physikal. Chem.*, 1912, **79**, 129—146).—In a previous paper (Abstr., 1911, ii, 81) the results of a recalculation of the atomic refractions for a number of elements have been given, the constants being free from the influence of conjugation. In the present paper the analogous data are given for nitrogen in aliphatic amines, tertiary imides and nitriles, the values for the latter two series including the increment for the double and triple linkings.

### *Atomic Refraction for Nitrogen.*

	$H_a$ .	D	$H_\beta$ .	$H_\gamma$ .	$H_\beta - H_a$ .	$H_\gamma - H_a$ .
Primary amines.....	2·309	2·322	2·368	2·397	0·059	0·086
Secondary amines .....	2·478	2·502	2·561	2·605	0·086	0·119
Tertiary amines.....	2·808	2·840	2·940	3·000	0·133	0·186
Tertiary imides .....	3·740	3·776	3·877	3·962	0·139	0·220
Nitriles .....	3·102	3·118	3·155	3·173	0·052	0·060

The values for nitrogen in aliphatic oximes are fairly constant and in close agreement with those for nitrogen in imides, quoted in the table. Further, the values for the  $\text{NO}_2$  group in aliphatic nitrites and nitro-compounds and aliphatic nitrates are fairly constant, the value of  $H_a$  for the  $\text{NO}_2$  group in the nitro-compounds being 6·605, in the nitrites 7·292, and for the  $\text{NO}_2$  group in nitrates 8·952.

In certain other series of compounds, more particularly those containing aromatic groups, the values for nitrogen are not even approximately constant. G. S.

**Spectrochemistry of Nitrogen. IX.\* Spectrochemical Constants of Nitrogen in Heterocyclic Unsaturated Systems.** JULIUS W. BRÜHL (*Zeitsch. physikal. Chem.*, 1912, **79**, 481—510. Compare this vol., ii, 311).—For pyridine and its homologues the mean atomic refractivity of nitrogen for the  $D$  line is 3·110, and the dispersion  $H_\gamma - H_a$  is 0·289. The value of the refractivity is smaller, and that of the dispersion greater, than the mean value in compounds of the type  $\text{C}-\text{N}=\text{C}$  and  $\text{O}-\text{N}=\text{C}$ . The nature of the different factors affecting the value of the constant is discussed. For  $\Delta'$ -tetrahydro- $\alpha$ -propylpyridine the value for the  $D$  line is 1·740, and the dispersion  $H_\gamma - H_a$  is -0·022.

For pyrazine the constant is 3·358, and the dispersion  $H_\gamma - H_a$  is 0·310; for the homologues of pyrazine the constant is 3·502, and the dispersion 0·397. In the case of pyridazine, the value of the constant for nitrogen depends on the formula assigned to the compound. It is shown that the nitrogen in pyridazine behaves spectrochemically like the carbim nitrogen in other compounds, hence the  $\text{C}=\text{N}-\text{N}=\text{C}$  complex must be present, and the only possible constitution for pyridazine is

\* The immediately preceding paper of this series (this vol., ii, 311), designated VII, by an oversight of the author, is really VIII.



In certain *heterocyclopentadienes*, including 1 : 2 : 5-triazole and dimethylfurazan, the mean value of  $N_D$  is 3.014, and the dispersion  $H_\gamma - H_\alpha$  is 0.143. In the case of pyrrole,  $N_D$  is 2.23, and  $H_\gamma - H_\alpha$  is 0.06. The values for the carbim nitrogen in glyoxalidines, benziminazoles, and phenyloxazolines are also given.

In quinoline, isoquinoline, and quinoxaline compounds the mean values of  $N_D$  are 5.415, 4.725, and 4.572 respectively, and the values for  $H_\gamma - H_\alpha$  1.341, 1.172, and 0.981 respectively. G. S.

**Refraction and Dispersion of Nitrates of Mercury.** PAUL T. MULLER and E. CARRIÈRE (*Compt. rend.*, 1912, 154, 695—698).—The refractive indices of mercurous and mercuric nitrates in nitric acid solution have been determined for the *D*-sodium and  $\alpha$ -,  $\beta$ -, and  $\gamma$ -hydrogen lines. The detailed results are given, and it is seen that the specific atomic refractive index and dispersion for the metal in the mercurous salt is greater than that in the mercuric if the acid radicle has the same optical value in the two compounds. The atomic refractive indices are approximately 13.1 and 7.4 respectively.

W. O. W.

**Ratio of the Intensities of the Series Lines of Hydrogen in the Canal Ray Spectrum.** F. LUNKENHEIMER (*Ann. Physik*, 1912, [iv], 37, 823—831. Compare Abstr., 1911, ii, 950).—Polemical against Stark (this vol., ii, 1). Further details of the conditions obtaining in the author's experiments are given, and the conclusion reiterated that, within the limits of the experimental error (about 20%), there is no variation of the relative intensities of the series lines when the velocity of the canal rays is altered.

H. M. D.

**Structure of Solar Bands Due to Oxygen.** R. FORTRAT (*Compt. rend.*, 1912, 154, 869—872).—A mathematical analysis of the solar bands *A*, *B*, and *a*, with the object of distinguishing those components due to absorption by terrestrial oxygen. W. O. W.

**A Peculiar Luminous Effect in the Bunsen Flame and the Flame Spectrum of Sulphur.** E. S. JOHANSEN (*Zeitsch. wiss. Photochem.*, 1912, 11, 20—26).—If a flat-bottomed flask containing water is brought in contact with the upper portion of a Bunsen flame, supplied with excess of air, a thin luminous layer having a bluish-violet colour is observed in immediate contact with the surface of the glass. The colour is quite distinct from that of the other portions of the flame, and the luminous layer in question is, moreover, separated from the flame itself by a dark zone, one to two mm. thick.

The bluish-violet luminosity has been traced to the presence of sulphur (hydrogen sulphide) in the coal gas, no such effect being obtained when sulphur is entirely absent from the gas.

The spectrum of the violet region, which is also observed when any other solid substance is introduced into the flame, has been examined. It consists essentially of a series of double bands and of another series

of simple bands, and the frequencies of these can be satisfactorily expressed by means of Deslandres' formulæ. Whether the spectrum is due to sulphur or sulphur compounds cannot be definitely decided on the basis of existing data.

H. M. D.

**Consequences of a Valence Hypothesis. I. Band Spectrum and Valence Energy.** JOHANNES STARK (*Jahrb. Radioactiv. Elektronik*, 1912, 9, 15—27).—In the further development of the author's valence theory (compare Abstr., 1908, ii, 138), it is pointed out that the character of a particular valence is determined by the geometric form and extension of the electrical field between the valence electron and the neighbouring positive atomic spheres. The difference between the positive and negative elements is largely due to differences of this kind.

The potential chemical energy is identical with the potential electrical energy, and can be measured in terms of the difference between the values of the electrical energy of a free electron and of that of the electron when associated with particular atoms in a molecule. The potential energy will have different values according to the nature and degree of approximation of the positive spheres of neighbouring atoms.

The view that band spectra are due to valence electrons is also examined in further detail. If any change occurs in the potential energy, there will be a corresponding change in the frequency of the valence electron, and the effect of this will be a displacement of the short-waved and also of the coupled long-waved bands. When, therefore, such displacement of the bands is observed, it may be inferred that the energy of the valence electrons has increased or diminished. The bands characteristic of oxygen and carbon in combination with oxygen, hydrogen, and carbon are examined from this point of view.

H. M. D.

**Relative Velocities of the Luminous Vapours of Different Elements in the Electric Spark.** GUSTAVE A. HEMSALECH (*Compt. rend.*, 1912, 154, 872—874).—The rate at which the vapour of 14 different elements is projected from the spark electrode has been measured, using self-induction and a rapid current of air across the spark to deviate the trajectory. In groups of elements chemically related, the relative velocities stand in the same order as the atomic weights. For a reason difficult to explain, the velocity of calcium derived from the enhanced lines in the spark is double that deduced from the arc spectrum. The velocities are not appreciably modified by varying the capacity, and are therefore probably independent of temperature. Probably the luminous vapour is produced by projection of molecules from causes other than thermal ones, the speed of projection being a function of the force necessary to overcome the resistance offered by cohesion between the molecules.

W. O. W.

**Spectroscopic Observations: Lithium and Cæsium.** PENRY V. BEVAN (*Proc. Roy. Soc.*, 1912, A, 86, 320—329. Compare Abstr., 1910, ii, 87, 370; 1911, ii, 350).—Further measurements of the wave-

lengths of the principal series lines in the absorption spectrum of lithium vapour have been made. The series has been extended considerably, fourteen new lines being recorded between  $\lambda = 2305.82$  and  $\lambda = 2302.15$ . The total number of lithium lines belonging to the principal series has thus been brought up to forty-one.

In the case of caesium, a convenient method of obtaining an absorbing layer of vapour was found in heating the anhydrous chloride with metallic lithium. By the use of this, it has been possible to photograph the principal series lines up to the thirty-first member of the series, the wave-length of this being  $\lambda = 3193.83$ . The two separate lines corresponding with each member of the series cannot be distinguished beyond the ninth member, and the actually observed lines of the later members are those belonging to the  $P_1$  series. The lines of the  $P_2$  series cannot be brought out by increase of density of the vapour, for this produces broadening of the  $P_1$  lines.

The broadening of the lines with increased density of the vapour has been examined in detail in the case of the pair  $\lambda = 4593.16$  and  $4555.26$ . The broadening takes place unsymmetrically, extending much further on the more refrangible side than on the other.

The wave-length data for both the lithium and caesium series are applied to the calculation of the constants of the Hicks formula.

H. M. D.

**Nature and Distribution of the Emission in the Arc Spectrum of Different Metals.** HEINRICH OELLERS (*Zeitsch. wiss. Photochem.*, 1912, 10, 374—392, 393—432).—The spectral emission from different parts of the arc passing between copper, silver, magnesium, calcium, zinc, cadmium, aluminium, thallium, and tin electrodes has been examined by means of both prism and grating spectrographs. As a general rule, the emissive power decreases from the electrodes towards the middle of the arc, and also from the axis to the periphery. For most metals the intensity of the emission is greater at one pole than at the other, but this may be either the positive or the negative pole.

The structure of the arc and the origin of the bands and different series of lines is discussed in reference to Lenard's theory. No evidence of the structure which this theory demands has been obtained in the investigation of any of the metal arcs submitted to examination.

H. M. D.

**Wave-length Normals from the Arc Spectrum of Iron in the International System.** I. F. GOOS (*Zeitsch. wiss. Photochem.*, 1912, 11, 1—12).—Measurements have been made of the wave-lengths of iron lines of the third order between  $\lambda = 4282$  and  $\lambda = 5324$ . Thirty-seven plates were employed in obtaining the photographic record of the lines in this region, the middle line corresponding with a displacement of about 35 Ångström units for successive plates in the series. By this arrangement, each of the lines investigated was recorded on seven or eight different plates, its position on each plate being different.

The wave-lengths of 184 lines are recorded, the relative intensity

and probable accuracy of the measurement being indicated in each case. H. M. D.

**Photochemical Studies. V. Measurements of Light Absorption in Solutions of Bromine and of Certain Dyes.** JOH. PLOTNIKOFF (*Zeitsch. physikal. Chem.*, 1912, 79, 357—376).—The absorption spectra of bromine and of cinnamic acid in benzene solution and the extinction coefficients of bromine in water, benzene, carbon tetrachloride, and chloroform for four lines of the mercury spectrum have been determined, and it is shown that bromine follows Beer's law. It is suggested that the bromine spectrum in the visible region consists of two superposed absorption bands.

The extinction coefficients of erythrosine, acid-green, guinea-green, and potassium dichromate in aqueous solution and of certain binary mixtures of dyes have been measured; in the case of the mixtures the extinction coefficients are a complicated function of the concentrations of the constituents. The absorption of iodine in carbon tetrachloride does not accurately follow Beer's law, and alters somewhat with time.

Sulphuric acid affects the absorption of quinine in the violet, and within certain limits of concentrations the absorption attains a minimum.

The preparation of quantitative light filters is discussed. G. S.

**Absorption Spectrum of Toluene in the Ultra-violet.** FRIEDRICH CREMER (*Zeitsch. wiss. Photochem.*, 1912, 10, 349—367).—The absorption spectrum of toluene has been examined in the form of vapour at different temperatures and in ethyl-alcoholic solutions of varying concentration. The spectrum of the vapour consists of a series of bands extending from  $\lambda = 235$  to  $\lambda = 273\mu\mu$ , which are shaded off towards the red. The position of the heads of the bands is independent of the thickness of the absorbing layer and of the temperature. For a given thickness of the vapour column, the bands broaden towards the red end as the temperature rises, and at the same time the middle portion of the region of absorption gradually changes and begins to show continuous absorption.

The solution spectrum is also banded, and the position of the heads of the bands is quite independent of the thickness of the absorbing layer and its concentration. The stronger bands in the vapour spectrum are nearly all present in the solution spectrum, but they are displaced towards the red end to the extent of 13 to 15 Ångström units.

The bands in the vapour spectrum fall into eleven series, which are characterised by the same constant difference between the vibration frequencies of the successive heads of the bands. The bands in the solution spectrum are such that the frequencies form an arithmetic series. H. M. D.

**Absorption of Light by Solid and Gaseous Substances.** JOHANNES KOENIGSBERGER and K. KÜPFERER (*Ann. Physik*, 1912, [iv], 37, 601—641).—The absorption of light by thin layers of solid indigotin, alizarin, and 1:5-dianilinoanthraquinone has been measured

for different wave-lengths, the layers of the two former being obtained by vaporisation in a vacuum and that of the last substance by evaporation of an alcoholic solution. The curves showing the variation of the absorption coefficient with the wave-length exhibit a maximum at about  $\lambda = 678$  in the case of indigotin and at  $\lambda = 533$  in the case of dianilinoanthraquinone. The corresponding maximum for alizarin appears to lie in the ultra-violet. With rise of temperature, the region of absorption broadens out towards the red end of the spectrum, and the maximum is also displaced to a small extent in this direction.

The absorption of visible light by the vapours of the above colouring matters was also examined, the absorption curves being similar to those for the solid substances, although the maxima are displaced to some extent. From the close agreement between the absorption by the solid and vapour, it appears that the absorption is an intra-molecular effect.

Other organic and a large number of inorganic substances (both elements and compounds) have also been investigated in vapour form. In so far as these do not undergo dissociation, the absorption in all cases is continuous. The authors consider therefore that the absorption and emission of gases and vapours in the normal state is of the continuous type.

Colouring matters, which exhibit fluorescence in solution, do not fluoresce in the form of vapour when subjected to the action of visible light.

H. M. D.

**Fluorescence of Sodium Vapour.** LOUIS DUNOYER (*Compt. rend.*, 1912, 154, 815—818. Compare Abstr., 1911, ii, 832).—Using pure sodium distilled into a glass vessel freed from occluded gas, in which a vacuum of 0.0001 mm. is maintained, the author has been able to show distinctly the yellow fluorescence of sodium vapour. This is very distinct at 210—220°, and increases in intensity when the temperature is raised, without changing colour, until about 290°, when it becomes green. The yellow fluorescence showing the *D* line is supposed to be due to single atoms, and the green one with the canal spectrum to arise from the vibration of more complex systems. The presence of occluded gas from the tube or the metal is capable of causing the *D* line to persist during the green fluorescence. If this is induced by an arc with the carbons sufficiently separated, two regions of fluorescence can be distinguished, corresponding with the positive and negative craters. These regions are yellow with the pure sodium vapour, but on adjusting the proportion of foreign gas the positive one becomes green, whilst the other remains yellow.

W. O. W.

**Fluorescence [of the Minerals] of the Sodalite and Willemite Group in Ultra-violet Light.** THEODOR LIEBISCH (*Sitzungsber. K. Akad. Wiss. Berlin*, 1912, 229—240).—It has been found that many minerals belonging to the sodalite and willemite groups become fluorescent when acted on by the ultra-violet light which is transmitted by a Wood's filter. Observations are also recorded which show the influence of the wave-length of the incident light on the fluores-

cence of the minerals. Certain of the minerals belonging to these groups also exhibit phosphorescence to a limited extent.

Tables are appended showing the elements present in the minerals of the sodalite group, in troostite and tephroite, as indicated by observations of the arc spectra.

H. M. D.

**Rotation Dispersion. IV. Influence of the Solvent on the Light Absorption and Rotation Dispersion of Coloured Compounds.** LEO A. TSCHUGAEFF and A. OGORODNIKOFF (*Zeitsch. physikal. Chem.*, 1912, 79, 471—480. Compare Abstr., 1911, ii, 450, 787).—The light absorption and rotation dispersion curves for six coloured optically active substances (iminoxanthides, Abstr., 1902, i, 604) in toluene and acetone as solvents have been measured, and the results are tabulated in full. It is shown that the toluene curves are throughout displaced towards the red end of the spectrum in comparison to the corresponding acetone curves, so that the solvents have a parallel influence on the light absorption and rotation dispersion.

G. S.

**Pulverisation of Metals by Ultra-violet Light.** F. SCHULZE (*Ber. Deut. physikal. Ges.*, 1912, 14, 246—257).—The question as to whether or not ultra-violet light has a pulverising action on metals has been examined by three different methods involving the measurement of (a) the transparency of gold leaves; (b) the activity of a thin layer of a polonium preparation, and (c) the electrical resistance of thin sheets of silver, platinum, and gold. All three methods gave a negative result for the ultra-violet light from a quartz-mercury lamp, and it appears, therefore, that the pulverisation effect, if it exists, is very much smaller than has been assumed to be the case.

H. M. D.

**Photochemical Kinetics of the Hydrochloroplatinic Acids in very Dilute Solution.** MARCEL BOLL and PAUL JOB (*Compt. rend.*, 1912, 154, 881—883).—Variations in the electrical conductivity of aqueous solutions of the acids (0.0001*N*) on exposure to light were followed by the electrometer in the manner previously described (this vol., ii, 384). The results were very concordant, and in the case of the acids  $\text{H}_2\text{PtCl}_6$ ,  $\text{H}_2\text{Pt}(\text{OH})\text{Cl}_5$ ,  $\text{H}_2\text{Pt}(\text{OH})_2\text{Cl}_4$ , and  $\text{H}_2\text{Pt}(\text{OH})_4\text{Cl}_2$ , appear to show that the reactions taking place are bimolecular.

W. O. W.

**Heliochromic Decoloration Process. Stable Positives with Methylene-blue.** S. RAMÓN Y CAJAL (*Anal. Fis. Quim.*, 1912, 10, 26—30).—Methylene-blue is fixed and made stable to light by means of ammonium molybdate (as in Ehrlich's histological technique). A bath containing 3% of ammonium molybdate and 2% of copper sulphate is used to fix methylene-blue and erythrosine. A fixing agent for yellow is still wanting.

G. D. L.

**Biochemical Reactions in Light. I.** HANS VON EULER and E. LINDBERG (*Biochem. Zeitsch.*, 1912, 39, 410—421).—There is formed from dextrose in ultra-violet light an acid, which on the further action of

light evolves a gaseous mixture containing 15% carbon dioxide, 40% carbon monoxide, and 40% hydrogen. This gas is formed from the primary products of the action of light on the sugar. The scission of lactic acid in pure aqueous solution into alcohol and carbon dioxide which takes place in light is a special case of the evolution of carbon dioxide from vegetable acids. The condensation of acetaldehyde, a process so important in the formation of plant acids, is a light reaction. The rate of change of lactic acid into alcohol and carbon dioxide is, within certain limits, independent of the concentration.

S. B. S.

**The Ranges of the  $\alpha$ -Particles from Uranium.** HANS GEIGER and J. M. NUTTALL (*Phil. Mag.*, 1912, [vi], 23, 439—445).—The ionisation-range curve of the  $\alpha$ -rays of uranium was compared by a special method with those given by polonium and ionium under identical conditions. In the first case the active surface consisted of a circular ground glass plate over which uranium oxide had been uniformly distributed as a very thin layer (0.4 mg. per sq. cm.) by rubbing in the powder with the finger. In the other two cases mixtures of minute traces of the active materials with relatively large quantities of uranium oxide were employed, the activity due to the uranium being only 2 or 3% of the total. In this way absorption of the  $\alpha$ -rays in the material, if any, was the same for all three substances. These films were placed in a bell-jar filled with hydrogen at various pressures, below a grid formed of a thick metal plate perforated with a large number of holes to which a very thin uniform film of mica was fixed. Above the grid was another bell-jar containing an electroscope. The ionisation-range curve was determined by varying the pressure of the hydrogen in the lower bell-jar. The ionium and polonium curves were identical in form, but the uranium curve gave a maximum less sharply defined, and showed a much slower fall of ionisation towards the end of the range. The uranium curve could be compounded out of two ionium or two polonium curves shifted relatively to one another by 4 mm. of range. The conclusion was drawn that uranium gives two sets of  $\alpha$ -rays of ranges respectively 2.9 and 2.5 cm. of air at atmospheric pressure and 15°. The connexion between the logarithms of the ranges and periods agrees much better when uranium I of half-period  $5 \times 10^9$  years is given the range 2.5 cm. The half-period of the product of uranium, called uranium II, giving rays of range 2.9 cm., can be deduced from this connexion to be about  $2 \times 10^6$  years. Hence in a gram of uranium there should be a quantity of the chemically similar element of atomic weight 4 units less of the order of a milligram. This can only affect the chemically determined atomic weight of uranium in the third decimal place. The period of ionium calculated from the new values of the periods and ranges of uranium I and II is 200,000 years.

F. S.

**The Numbers and Ranges of the  $\alpha$ -Particles Emitted by the Emanation and Active Deposit of Thorium.** T. BARRATT (*Proc. Physical Soc.*, 1912, 24, 112—119).—Experiments have been

made to determine the relative number of  $\alpha$ -particles from each of the four products, thorium emanation, thorium *A*, thorium *C*<sub>1</sub>, and thorium *C*<sub>2</sub>, together with the ranges of the particles. Emanation from a mesothorium preparation was drawn through a box provided with a thin mica window, and a microscope with a zinc sulphide screen in focus was arranged to slide, so as to bring the screen to different distances from the window. The number of  $\alpha$ -particles reaching the screen was counted, and this number multiplied by the square of the distance from the window represents the number emitted which travel over the distance in question. Measurements were made with the thorium emanation alone and with the active deposit alone giving  $\alpha$ -rays. It was found that for each 100  $\alpha$ -particles given by the emanation, 100 were given by thorium *A*, 35 by thorium *C*<sub>1</sub>, and 65 by thorium *C*<sub>2</sub>, the ranges of these four  $\alpha$ -particles being respectively 5.0, 5.4, 4.8, and 8.6 cm. of air at 76 cm. of mercury pressure and 0°. F. S.

**The Magnetic Spectrum of  $\beta$ -Rays of Thorium.** OTTO VON BAEYER, OTTO HAHN, and LISE MEITNER. (*Physikal. Zeitsch.*, 1912, 13, 264—266).—New determinations of the  $\beta$ -rays of mesothorium-2 with a preparation deposited electrolytically on a silver wire, recently prepared from mesothorium-1, free from radio-thorium, and having the  $\gamma$ -activity equivalent to 6 mg. of radium, showed in addition to the  $\alpha$ -rays five sets of strong  $\beta$ -rays instead of four as previously announced. The velocities of these rays in terms of that of light are 0.57, 0.50, 0.43, 0.39, 0.37. In a stronger field two other sets of feeble  $\beta$ -rays of velocities 0.66 and 0.60 were observed. The spectrum of the faster  $\beta$ -rays of mesothorium-2 showed no clear discontinuities, but is a broad band with variations in the intensity. This may be due to there being a large number of different types of fast  $\beta$ -rays. With the same wire as the mesothorium-2 decayed, the rays of thorium-*X* made their appearance. Two sets of  $\beta$ -rays of velocities 0.51 and 0.47 were measured.

New observations with the thorium active deposit have succeeded in assigning the various types of  $\beta$ -rays to the various products. Thorium-*B* (new nomenclature) gives two sets of  $\beta$ -rays of velocities 0.73 (very weak) and 0.63 (very strong). Thorium-*C* and -*D* give in addition to fast  $\beta$ -rays of velocity over 0.72, a weak set of velocity 0.36 and a strong set of velocity 0.29. For these experiments thorium-*C* was separated from the other products of the active deposit on nickel, and its radiation measured separately. F. S.

**Structure of the  $\gamma$ -Rays.** II. EDGAR MEYER (*Ann. Physik*, 1912, [iv], 37, 700—720. Compare Abstr., 1910, ii, 673).—Experiments are described when seem to show that the ionisation which is brought about by a bundle of  $\gamma$ -rays exhibits variations along the line of propagation of the rays, and also in a direction at right angles to this. The apparatus employed was similar to that described previously. The results indicate that a single  $\gamma$ -ray is capable of participating in more than one ionisation process, or, in other words that more than one secondary  $\beta$ -ray may be liberated by one and the same  $\gamma$ -ray. This does not appear to be consistent with Bragg's

theory, according to which a  $\gamma$ -ray can only give rise to a single electron. The observed longitudinal and transverse effects can, however, be explained, at any rate qualitatively, by Sommerfeld's theory.

The view put forward in the previous paper, that the  $\gamma$ -rays are anisotropic, is now modified to the extent that the anisotropy is not complete, but only partial.

H. M. D.

**Ionisation by Moving Electrified Particles.** SIR JOSEPH J. THOMSON (*Phil. Mag.*, 1912, [vi], 23, 449—457).—The theory developed assumes that kinetic energy is imparted to electrons in an atom by the passage of cathode or positive rays through the atom, and that when this energy exceeds a definite value (that required to ionise the atom) the electron escapes from the atom, leaving the latter positively charged. The first consequence is that for  $\beta$ -rays and cathode rays, or similarly rapidly moving electrons, the number of ions produced per cm. of path in a gas should vary inversely as the kinetic energy of the  $\beta$ -ray or cathode ray particle, which Glasson has found to be approximately confirmed by experiment with cathode-rays. For a velocity of  $4.7 \times 10^9$  cm./sec., 1.5 pairs of ions result per cm. in air at 1 mm. pressure, or 1140 pairs at atmospheric pressure. These results, on the assumption throughout the paper that the energy required to ionise an atom corresponds with that acquired by an electron moving through a difference of potential of 10 volts, gives the consequence that the number of electrons in an atom is not greater than two or three times the atomic weight. Eve's results on the number of ions (48) per cm. produced in air by  $\beta$ -rays of radium are in agreement with Glasson's for cathode rays on this theory. The ionisation produced in a gas under defined conditions should vary as the density of the gas divided by the energy necessary to ionise an atom of the gas, a result which makes it appear that hydrogen is much more easily ionised than any other atom. With regard to positive rays, moving at high velocity, the number of ions produced should vary as the square of the number of atomic charges carried by the positive ray particle, and for  $\alpha$ -rays is four times that produced by a  $\beta$ -ray of the same velocity. Geiger's number for the  $\alpha$ -particle, 22,500 per cm. for an  $\alpha$ -ray of velocity  $2.06 \times 10^9$  cm./sec., agrees with that calculated (23,940) from Glasson's results with cathode-rays on this theory. Only the lighter atoms and molecules in a vacuum-tube in ordinary circumstances will produce ionisation as positive rays, the minimum potential necessary for an atom of oxygen being, for example, 58,000 volts. The original direction of motion of the electron expelled from an atom is at right angles to the path of the ionising ray. In the re-combination of ions, the electron as the less massive of the two ions will acquire practically all the kinetic energy, which must be dispersed by radiation before the atom resulting returns to its normal condition. This radiation should have a maximum of energy in the vicinity of wave-length  $3.8 \times 10^{-6}$  cm., which corresponds with that of light very far in the ultra-violet. By assuming that, in addition to electrons capable of being dislodged from an atom by energy corresponding with 10 volts, others exist requiring an

amount of energy corresponding to thousands of volts, radiation, of energy maximum in the vicinity of  $10^{-8}$  cm. wave-length, would result. This would be  $X$ -radiation, corresponding in all its characteristics with the characteristic secondary  $X$ -radiation of Barkla, produced by matter when the atomic weight is above 39, and the exciting rays possess more than a certain minimum degree of penetrating power. Finally, an expression for the diminution of specific heat with fall of temperature, of the same form as that given by Einstein and obtained experimentally at very low temperature by Nernst and his pupils, is obtained by assuming the existence of corpuscles, the thermal kinetic energy of which at one temperature exceeds, and at a lower temperature is less than, that necessary to produce ionisation, and by giving to the thermal energy among the electrons the distribution required by Maxwell's law.

F. S.

**Ionisation by Collision.** NORMAN CAMPBELL (*Phil. Mag.*, 1912 [vi], 23, 400—412).—Townsend's theory of ionisation by collision assumes that the negative ion is not changed by collision, whether or not ionisation results, but remains an electron throughout its history, and does not collect round it a cluster of neutral molecules. This assumption is discussed in the paper following. In the present paper a correction is made in the theory to allow for the fact that the layer of ions within the minimum distance from the positive electrode necessary for the ions to acquire the velocity requisite to ionise by collision do not contribute to the ionisation. More approximate formulæ, taking this into account, applied to Townsend's results agree better than those he used, and confirm the main physical basis of his theory.

F. S.

**Ionisation by  $\alpha$ -Rays.** NORMAN CAMPBELL (*Phil. Mag.*, 1912, [vi], 23, 462—483).—The  $\alpha$ -rays from a polonium preparation traverse two parallel electrodes of different materials separated by a layer of gas, forming  $\delta$ -rays at the surface of the electrodes. The difference of potential between the electrodes is sufficient to cause the  $\delta$ -rays to ionise by collision, the  $\delta$ -rays from the negative electrode alone escaping into the gas. Reversal of the direction of the field will then show whether the  $\delta$ -rays from the two electrodes are the same in number and in initial velocity. The results with gold and aluminium electrodes showed no differences between the two sets of  $\delta$ -rays, and with electrodes of the same metal, between the incident and emergent  $\delta$ -rays. A detailed series of accurate measurements based on the theory of ionisation by collision (see previous abstract) afford considerable support of the theory on the view that in dry air the electron remains an electron, and that the formation from it of complex ions occurs rarely, if at all. The conclusions are drawn that the initial velocity of the  $\delta$ -ray is very small and may be zero, and that no important part of the energy spent in ionisation appears as energy of the ejected electron. The experiments are consistent with the view that none of the energy spent appears as energy of ionisation, but is utilised in producing changes in the atom of which ionisation is a by-product. In this case the energy of ionisation would be derived from

that of the external electric field. The fact that a metal emitting  $\delta$ -rays raises itself to a finite positive potential is against this view, and this phenomenon is being further investigated. F. S.

**Determination of the Number of Ions Produced by an  $\alpha$ -Particle from Polonium.** THOMAS S. TAYLOR (*Phil. Mag.*, 1912, [vi], 23, 670—676).—The determination involved three measurements: (1) the saturation current produced by a limited beam of  $\alpha$ -rays from polonium; (2) the capacity of the measuring system; (3) the number of  $\alpha$ -particles producing the ionisation current, by counting the number of scintillations produced on a zinc sulphide screen. This number was taken to be 85% of the number expelled, the screen having been calibrated by counting the  $\alpha$ -particles from some radium active deposit for which the  $\alpha$ -activity was calculated from the  $\gamma$ -activity. The mean of five closely agreeing determinations gave the number 164,000 for the ions produced by the single  $\alpha$ -particle of polonium, assuming the value of  $e$  to be  $4.67 \times 10^{-10}$  E.S.U. The energy required to produce an ion in air, calculated by dividing the kinetic energy of the  $\alpha$ -particle at the beginning of its path by the above number, works out at  $5.3 \times 10^{-11}$  erg. F. S.

**The Charges on Ions.** JOHN S. TOWNSEND (*Phil. Mag.*, 1912, [vi], 23, 677—679).—The value of the charges on ions produced by a hot wire in air and hydrogen at atmospheric pressure recently published by J. C. Pomeroy (this vol., ii, 114), in which the principle of the author's method is stated to have been employed, is vitiated by neglect of a fundamental condition on which the success of this method depends, namely, that such experiments must be conducted at low pressures. The reasons for this are discussed in detail. Not only does the diffusion of the ions enter into the method, but also their self-repulsion, and in order that the first may be the predominating effect, low pressure of the gas is essential. F. S.

**The Direct or Indirect Nature of the Ionisation by  $X$ -rays.** WILLIAM H. BRAGG (*Phil. Mag.*, 1912, [vi], 23, 647—650).—Some criticisms of Barkla with reference to the author's conclusion, that the ionisation by  $X$ -rays is an indirect process due to the secondary cathode-rays generated, are replied to. It is pointed out that Barkla's experiments do not reveal the large proportion of indirect ionisation which is known to exist, and therefore cannot be held to prove anything definite as to the relative amounts of direct and indirect ionisation. Further, the arguments assume the applicability of Lenard's density law of absorption, and it is unknown whether this applies. F. S.

**Liberation of Electrically Charged Particles from an Incandescent Platinum Wire during the Catalysis of Electrolytic Gas (Hydrogen and Oxygen).** LEON WEISSMANN (*Zeitsch. physikal. Chem.*, 1912, 79, 257—278).—In continuation of the experiments of Haber and Just (*Abstr.*, 1911, ii, 954), the effect of the composition of the surrounding gas on the discharge of electrically charged particles from platinum at 800° and 850° has been investigated. As regards

the escape of positively charged particles, when the effect has ceased in air it is restored by the action of a gas containing hydrogen, and conversely, when the positive charge has ceased in hydrogen, it is restored by surrounding the wire with air or oxygen. The presence of a mixture of hydrogen and oxygen also lengthens the period during which positive particles escape from the platinum, and as quite different effects are obtained when one of the gases is displaced by the indifferent nitrogen, it is suggested that the liberation of the positive particles is connected with the chemical combination of the gases. The matter is not fully explained, however, since the discharge of positive particles in electrolytic gas continuously diminishes in intensity, although the rate of combination of the gases remains constant.

In gaseous mixtures poor in hydrogen there is practically no liberation of negatively charged particles, but in mixtures rich in hydrogen the discharge of positive and negative particles is of the same order. In such mixtures the presence of oxygen along with hydrogen greatly diminishes the intensity of the negative discharge. G. S.

**Liberation of Electrically Charged Particles from an Incandescent Platinum Wire during the Catalysis of Mixtures of Oxygen with Hydrogen and with Carbon Monoxide.** C. GRIEB (*Zeitsch. physikal. Chem.*, 1912, 79, 377—381).—After the work of Weissmann on this subject was concluded (compare previous abstract), a paper by H. A. Wilson appeared (*Abstr.*, 1911, ii, 572), in which it is stated that a platinum wire previously dipped in water or potassium sulphate solution gives a strong positive effect when heated. The author confirms Wilson's observation for potassium sulphate, but finds that water has no effect, and suggests that the wire used by Wilson for his observations with water was not free from potassium. It follows that Weissmann's results with electrolytic gas are not due to the formation of water vapour. Further, there is no restoring effect on the positive discharge when carbon monoxide and oxygen combine in contact with hot platinum, so that the results already described are connected in some way with the presence of the hydrogen. G. S.

**Atomic Weight of Radium.** ROBERT WHYTLAW-GRAY and SIR WILLIAM RAMSAY (*Proc. Roy. Soc.*, 1912, A, 86, 270—290).—The method employed consisted in the conversion of radium chloride into radium bromide and vice versa by heating in a current of hydrogen bromide or hydrogen chloride respectively, and possessed the advantages that there were no transferences of the material from the vessel containing it, and that only gaseous reagents were employed. The raw material consisted of 0.33 gram of 70% radium bromide from Cornish pitchblende, which was fractionally crystallised from water or dilute hydrobromic acid. The products used to determine the atomic weight consisted usually of between 2 and 3 mg. of radium bromide, which was weighed in silica capsules on a modified form of the micro-balance described by Steele and Grant, and used in connexion with the determination of the density of the radium emanation. The value of the atomic weight adopted is 226.36 (Cl = 35.46, Br = 79.92), which confirms Mme. Curie's and is at variance with Hönigschmid's results.

The value calculated by subtracting the weight of three atoms of helium expelled from the atomic weight of uranium is either 226.52 or 226.43, according to the value adopted for uranium. On the other hand, the atomic weight of lead calculated by the subtraction of eight atoms of helium should be 206.5 to 206.6, which is about 0.5 unit lower than the accepted number. Various possibilities are discussed, including one that the atomic weights of uranium and radium may both be 0.5 unit too low, and that the value found for radium is really a minimum value. In an appendix details are given of the precautions adopted in the weighings with the micro-balance, and full data of the weighings in the various experiments. The atomic weight of barium found by converting 3.5 mg. of barium bromide into the chloride gave a value practically identical with the International atomic weight.

F. S.

**Experiments with Weak Radium Solutions.** HEINRICH W. SCHMIDT and H. NICK (*Physikal. Zeitsch.*, 1912, 13, 199—207).—The preparation of standard solutions containing  $2.19 \times 10^{-9}$  gram radium per c.c. was carried out by diluting a solution containing 0.055 mg. of radium. The latter figure was derived from  $\gamma$ -ray comparisons with a preparation of Stefan Meyer giving 118 gram-calories per hour per gram of radium. The emanation from the standard solutions was measured in two electroscopes provided with separate ionisation chambers, the larger being 25.2 cm. high and 7.10 cm. diameter, the smaller 6.5 cm. high and 7.10 cm. diameter. The emanation was removed from the solutions by boiling out under reduced pressure. Measurements were taken from three to five hours after introducing the emanation into the electroscope. The single observations varied several %, which is ascribed to variations in the emission of  $\alpha$ -rays from these small quantities of radioactive material. A series of measurements in which the emanation was in equilibrium with the radium and in which it had accumulated only two days gave the same result, the variations observed by Mme. Curie in this connexion not being confirmed. The capacity of the larger apparatus was 6.33 and of the smaller 4.34, and the value of the ionisation current per 1 curie of emanation was for the smaller  $3.19 \times 10^6$ , and for the larger,  $3.84 \times 10^6$  E.S.U. The values calculated from Duane and Laborde's empirical formula from Mme. Curie's results were for the sizes of cylinders employed, 3.16 and 3.99 ( $\times 10^6$  E.S.U.).

F. S.

**Electrochemistry of Radioactive Substances.** GEORG VON HEVESY (*Phil. Mag.*, 1912, [vi], 23, 628—646).—Since in the electrochemistry of radioactive substances quantities may be detected far below those that can be detected in the case of other substances, the deposition of radioactive substances by electrolysis in detectable amount should occur with differences of potential below the decomposition voltage of the system, and it is to be expected that every metal immersed in a neutral solution should be capable of depositing a radioactive substance to greater or less degree. This has been found to be the case for fifteen radio-elements and for all metals, not

excepting gold and silver. The paper deals chiefly with the influence of the difference of potential between the metal and the solution on the deposition of the three active deposits. Various known potentials were employed by simply dipping the metal into a solution of one of its salts of known concentration, to which the solution of active deposit was added. The concentration of the radium-*C* employed varied from 8 to 4, and of thorium-*C* from 1 to 0.5 ( $\times 10^{-16}$  gram per c.c.). When the metal is positive to the solution, as, for example, silver in silver nitrate, the deposit consists of the *C*-member practically pure, but as the potential difference is reduced, the relative quantity of the *B*-member depositing increases, and when negative potentials, like zinc in zinc sulphate, are used, the *B*-member is deposited in excess of the equilibrium amount. The relative quantities of the two members in terms of the equilibrium proportion was readily determined by the decay curve of the active material deposited. The three *B*-members and the three *C*-members (radium, thorium, actinium) are respectively identical in their electro-chemical behaviour. The potential at which the *B*- and *C*-members are deposited in equilibrium proportions is 0.63 volt, the metal being negative to the solution. By making use of the graph connecting the relative proportion of the *B*- and *C*-members deposited with the single electrode potential, it was easy to determine single electrode potentials not capable of being measured by ordinary methods; thus Cu/H<sub>2</sub>O, in which the copper was immersed one minute, was found to be the same as Cd/CdSO<sub>4</sub>, or 0.7 volt more negative than Cu/CuSO<sub>4</sub>. The potential of a copper plate immersed in water containing radium-*B* and -*C* in equilibrium for 0.2 second was found to be 2 volts negative to the liquid from the relative amount of the *B*- and *C*-members deposited. Actinium-*B* and -*C* form the quickest indicator to employ for this purpose, as from  $\alpha$ -ray measurements for a few minutes after the deposition, the *P.D.* can be accurately found. The determination with thorium-*B* and -*C* takes longer, but is more accurate, whilst radium-*B* and -*C* is not suitable, partly on account of the relative persistence of the *A*-product, partly because of the similarity of the two periods. The *P.D.*'s tantalum/KCl (normal) and Ta/Ta<sub>2</sub>O<sub>5</sub> found by radioactive and electrochemical methods were in agreement.

Electrolysis of an acid solution containing *B*- and *C*-members in equilibrium (1) with very small current density and voltage far below the decomposition voltage of water, gives very pure radium-*C*; (2) with voltage equal to the decomposition voltage of water, gives a mixture of *B* and *C* corresponding with a potential of metal to solution of -0.4 volt. In an alkaline solution the mixture corresponded with -0.7 volt, whilst with a large current density, so that the decomposition of water is exceeded, the mixture of *B* and *C* corresponded to -1.1 volt. Von Lerch's original method of depositing pure radium-*C* on nickel in an acid solution is discussed and explained by the abnormal negative potential of nickel in an electrolyte and the passivity of the electrode in consequence, and to the selective solution of the radium-*B* deposited at the same time by the acid liquid. In neutral solution pure radium-*C* is never obtained.

Per molecule of the *C*-members, the calculated equilibrium amounts

of the *B*-members are for radium 1.4, for thorium 10.6, and for actinium 17 molecules. Radium-*C* is much more easily separated pure than either actinium-*C* or thorium-*C*, but actinium-*C* is more easy to separate pure than thorium-*C*. This anomaly receives an explanation if the thorium-*C* member corresponding to the other *C*-members is that one of the branch series found by Marsden and Barratt to give only 35% of the total  $\alpha$ -radiation, for in this case the ratio of *B* to *C* would be, for thorium, 30 instead of 10.6. F. S.

**The Penetrating Radiation Present in the Atmosphere.**  
ALBERT GÖCKEL (*Jahrb. Radioaktiv. Elektronik.*, 1912, 9, 1—15).—The mass of observations bearing on the questions as to origin of the penetrating radiation in the atmosphere and the cause of its changes is discussed in detail. Some of these favour the view that the rays have their origin in the radioactive matter in the earth's crust, whilst others point to the active deposit in the atmosphere as the chief source of the rays. New observations are recorded, in which the intensity of the penetrating rays on successive days, which differed entirely in their meteorological character, did not differ within the error of measurement. In the immediate neighbourhood of the ground, however, the effect of active deposit on the surface was marked. The lowest value recorded was in the ice grotto of the Grindelwald glacier, where the value corresponded with the production of three ions per c.c. per second. A great number of other isolated observations are recorded. F. S.

**Effect of Temperature on Radioactive Disintegration.**  
ALEXANDER S. RUSSELL (*Proc. Roy. Soc.*, 1912, A, 86, 240—253).—The experiments of other workers on the changes of magnitude of the penetrating radiation from the radium emanation and its products in sealed quartz tubes when the temperature is varied have been repeated, and a complete explanation arrived at. In the first place it was shown that pure radium-*C* and also the whole active deposit from the emanation are not affected as regards the intensity of their  $\beta$ - or  $\gamma$ -rays, nor the rate of decay of their activity when heated in quartz tubes. It was found with the radium emanation in a sealed quartz tube that, when differences of temperature occur between different parts of the tube, above 320° the radium-*C* shifts its position to the cooler part of the tube, and may so be localised in a very small part. From 650° upward volatilisation of radium-*C* is complete, whilst from 450° to 600° the effect is important. Radium-*B* commences to volatilise at room temperature. Using spherical and conical shaped quartz vessels containing the emanation, changes of intensity of the  $\beta$ -rays occurred, as found by other investigators, which could be explained, in the first place, by differences of temperature at different parts of the tube and consequent change of position of radium-*C*, and in the second place by differences in the absorption of the  $\beta$ -rays by the quartz walls according as they originated from matter deposited on the walls or distributed through the gas-phase. The absorption in the first case is greater than in the second, rays coming from near the centre of the tube of necessity having a shorter average path through

the quartz than those originating at the inside surface of the walls. There is no real effect of temperature on the radioactive changes.

F. S.

**Decomposition of Uric Acid by the Action of Radium Emanation.** P. MESERITSKY (*Compt. rend.*, 1912, 154, 770—772).—Monosodium urate suspended in a saturated aqueous solution of the salt is decomposed by the  $\alpha$ -rays from radium emanation, the substance going into solution with formation of ammonia. The intermediate products of decomposition could not be identified. Oxygen is without effect on the change, which occurs equally readily in an inert atmosphere. Radium bromide sealed in glass tubes produces only slight decomposition of the urate.

W. O. W.

**A Negative Result Connected with Radioactivity.** JOSEPH H. VINCENT and A. BURSILL (*Proc. Physical Soc.*, 1912, 24, 71—74).—Bismuth, antimony, and iron were subjected to a high-frequency alternating magnetic field to see whether instability could be produced in them accompanied by radioactive effects. The specimens were contained inside a gold-leaf electroscope, and surrounded by a coil traversed by the oscillatory discharge from a condenser, but no radioactivity was produced.

F. S.

**The Common Instruments for the Determination of the Radio-activity of Springs.** SIMON LOEWENTHAL (*Zeitsch. angew. Chem.*, 1912, 25, 670).—Henrich and Glaser (*ibid.*, 16), in their remarks on the Engler-Sieveling Fontaktoscope and on the modification of it by the author, omitted to correct their results for the difference in the size of the measuring cylinders, which can easily be done by Duane's formula. The indications of the two instruments then become alike.

F. S.

**The Mineral Waters of Bath.** SIR WILLIAM RAMSAY (*Chem. News*, 1912, 105, 133—135).—The estimated volume of gas per twenty-four hours coming from the King's Well is 4927 litres, and it consists of nitrogen and carbon dioxide, without hydrogen, oxygen, or methane. The nitrogen contains rare gases in the proportion 73·63% argon, 23·34% neon, and 2·97% helium, the total volume per twenty-four hours emitted being 39, 12·5, and 1·5 litres for the three gases respectively. There is 188 times as much neon in the gas from the King's Spring as in the atmosphere. The water of the King's Well contains  $0\cdot1387 \times 10^{-9}$  gram of radium per litre, and  $1\cdot73 \times 10^{-9}$  curie of emanation, whereas the gas from the King's Well contains  $33\cdot65 \times 10^{-9}$  curie. The water is about twice, and the gas about four times, as rich in emanation as the Buxton waters and gas. About 0·17 of a millicurie per twenty-four hours is contained in the natural gas from the King's Spring.

F. S.

**Action of Röntgen Rays on Gold Hydrosol.** ANT. GALECKI (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 149—150).—It is shown by ultramicroscopic observations that Röntgen rays have a coagulating

effect on the particles in gold hydrosols; the change of colour with increase in the size of the particles is very slight. G. S.

**Electron Theory of Metals.** GEORGE JAFFÉ (*Physikal. Zeitsch.*, 1912, 13, 284—287).—A theoretical paper in which the author examines the relationship between the thermal and electrical conductivities of the metals and the variation of the conductivity ratio with temperature from the point of view of the electron theory. The conclusion is drawn that the metals not only contain free electrons and positive ions, but also negative ions, these resulting from the combination of electrons with neutral molecules.

H. M. D.

**Relationship between Electrical Resistance, Fusion Temperature, and Atomic Volume of the Metals.** A. STEIN (*Physikal. Zeitsch.*, 1912, 13, 287—288).—Since the electrical resistance of a metal is proportional to the absolute temperature and therefore to the square of the amplitude of the atomic vibrations, it can be shown on the basis of Lindemann's theory that the atomic electrical resistance at temperature  $T$  should be proportional to  $v^{2/3}T/T_s$ , where  $v$  is the atomic volume and  $T_s$  the melting point of the metal. If  $k$  is the specific resistance, the atomic resistance is given by  $k/v^{1/3}$ , and therefore  $k.T_s/v.T$  should be constant.

The experimental data for different metals do not give the same value, although copper, gold, aluminium, magnesium, cadmium, and tin furnish a group for which this quantity is equal to  $1.1 \times 10^{-6}$ . Lead and thallium give a value twice, platinum and palladium a value six times, as large as that characteristic of the first group. H. M. D.

**Electrical Conductivity of Metals and Alloys from the Standpoint of Dispersoid Chemistry.** P. P. VON WEIMARN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, *Phys. Part*, 74—82).—Theoretical considerations lead to the conclusion that, with increase in the degree of dispersion, the resistance of chemically pure metals should increase and its temperature-coefficient decrease, whilst the supplementary resistance should be approximately independent of the temperature. The influence of the degree of dispersion on the conductivity of alloys is also discussed. T. H. P.

**Electrical Conductivity of Sulphur.** M. FIGULEWSKY (*J. Russ. Phys. Chem. Soc.*, 1912, 44, *Phys. Part*, 105—122).—The manner in which the electrical conductivity of sulphur changes with the temperature varies according as the sulphur is crystalline or amorphous. The conductivity of crystalline sulphur increases with rise of temperature to a maximum at about  $140$ — $150^\circ$ , and afterwards continues to fall until the boiling point is reached. With amorphous sulphur the conductivity falls as far as  $140$ — $150^\circ$ , then increases up to  $160$ — $170^\circ$ , after which temperature it falls continuously to the boiling point. With amorphous, but not with crystalline, sulphur the conductivity is increased by the action of light, this effect being caused more especially by rays of shorter wave-length than  $280 \mu\mu$ .

This phenomenon is conditioned by changes occurring in the sulphur, and by phenomena such as that of Hallwachs. T. H. P.

**Influence of Temperature and Light on the Conductivity of a Phosphorescent Substance (Calcium Sulphide).** PIERRE VAILLANT (*Compt. rend.*, 1912, 154, 867—869).—The electrical conductivity of a thin plate of calcium sulphide increases when it is exposed to light, until a maximum is reached, when it rapidly diminishes. In darkness the diminution is continuous, and is so considerable after five days that the conductivity is not measurable. These results are not due to changes in temperature, since the curves showing variation of conductivity with temperature during illumination have at their rectilinear portions an angular coefficient which varies with the source of light and its distance, and is modified by the interposition of a cell of water. When the light is withdrawn the temperature and concentration both diminish, but the curve is of a different nature from the preceding ones, even when the illumination is of short duration. W. O. W.

**Electrical Behaviour of Certain Sulphides and Oxides and the Continuity and Reversibility of Physical Properties in Different Modifications of Solid Substances.** JOHANNES KOENIGSBERGER (*Physikal. Zeitsch.*, 1912, 13, 281—284).—The author discusses the changes in the physical properties which are observed when the stable forms of certain minerals (iron pyrites, magnetite, quartz) are transformed at certain definite temperatures into other modifications. Whereas the magnetic properties change continuously in passing through the transition temperature, this is not the case with the electrical conductivity. Corresponding with this difference, the change in the paramagnetism is found to be reversible, whereas the alteration in the electrical properties represents an irreversible transformation.

Those properties which depend on the structure of the molecules may be expected to exhibit continuity and reversibility at the transition temperature, whereas those which depend partly or entirely on the relative positions of the molecules will show a more or less sharp change when the one form is transformed into the other.

H. M. D.

**Electrolytic Dissociation.** SVANTE ARRHENIUS (*J. Amer. Chem. Soc.*, 1912, 34, 353—364).—The Willard Gibbs Address, delivered before the Chicago Section of the American Chemical Society, and giving a historical account of the development and progress of the theory of electrolytic dissociation. E. G.

**Influence of Electrolytes on Electric Endosmosis.** G. von ELISSAFOFF (*Zeitsch. physikal. Chem.*, 1912, 79, 385—420).—The method used was as follows: A capillary tube partly filled with water or an electrolyte was supported in a horizontal position between two discharge points, one of which was connected with one of the poles of an influence machine, the other earthed. When the machine is in

action, water is slowly transferred to the end of the capillary turned towards the negative pole. In this way the electro-endosmose of water and of aqueous solutions of a number of salts, dyes, acids, and alkalis were investigated in quartz and glass capillary tubes.

Both in glass and quartz, water is transferred to the negative pole. All electrolytes, with the exception of the alkalis, diminish the endosmosis. Alkalis in small concentration have very little effect on the osmosis in glass, but increase it considerably in quartz tubes. The diminution in the amount of liquid transferred is connected with the concentration in dilute solution by the formula  $\partial v = k \log c + \gamma$ , where  $k$  and  $\gamma$  are constants. As regards the nature of the electrolytes, the cations are more effective than the anions, and for cations of the light metals the effect increases markedly with the valency, whilst cations of the same valency have equal effect in equivalent concentration.  $H^+$  ions, the cations of the heavy metals, of the organic bases, and especially of the basic dyes have a much greater effect than corresponds with their valency.

With solutions of thorium nitrate in glass and quartz and with solutions of crystal-violet in glass, the liquid moves towards the positive pole.

The lowering effect of electrolytes on osmosis is shown in extremely small concentration; in the case of a solution of thorium nitrate containing 0.2 mg. per litre, the amount of liquid transferred is about 50% less than in water.

There is a close parallelism between the effect of electrolytes on osmosis and on the precipitation of suspension colloids.

The phenomena can be accounted for on the basis of adsorption if it is assumed that the electric properties of the walls depend on the nature of the material, and are only indirectly influenced by adsorption.

G. S.

**Electric Osmosis and Concentration of Electrolytes.** J. O. WAKELIN BARRATT and ALBERT B. HARRIS (*Zeitsch. Elektrochem.*, 1912, 18, 221—225).—The method of investigation was to measure the rate of passage of the solution through a diaphragm under the influence of a potential gradient. As diaphragms parchment paper and gels of gelatin (10%) and agar-agar (1.5%) were used, and the effect of hydrochloric acid, sodium hydroxide, and certain salts was investigated. The potential gradient in the diaphragms, the strength of the current, and the relationship between the amount of transport and the concentration of the electrolyte are given in tabular form.

With diaphragms of agar-agar and of parchment, the liquid was in all cases transported from anode to cathode. With gelatin diaphragms, on the other hand, the direction of transport was from anode to cathode in the case of solutions of sodium sulphate, sodium nitrate, and potassium hydroxide, but in the reverse direction for solutions of nitric acid and of copper and aluminium nitrates. In gelatin the amount of osmosis increases regularly with the concentration of the electrolyte, but in agar-agar maxima are observed with most electrolytes in 0.01 molar concentration, but in aluminium chloride solution in 0.002 molar concentration. With parchment paper maxima were observed only with two salts, cupric chloride and aluminium chloride.

As regards the dependence of osmosis on the nature and valency of the ions, the effect is greater for tervalent and bivalent anions than for univalent anions in equivalent concentration, and the amount of liquid transported is still further diminished when bivalent and tervalent cations are present.

G. S.

**Dielectric Constants of Dissolved Salts. I. PAUL WALDEN** (*Bull. Acad. Sci. St. Pétersbourg*, 1912, [vi], 305—332).—The determination of the effect of addition of small quantities of salts to water on the dielectric constant of the solvent has given greatly divergent results (compare Cohn, *Ann. Phys. Chem.*, 1892, [iii], 45, 370; Nernst, *Abstr.*, 1894, ii, 437; Drude, *Abstr.*, 1897, ii, 438; Smale, *Abstr.*, 1897, ii, 357; Palmer, *Zeitsch. physikal. Chem.*, 1902, 41, 501), but it seems that in dilute aqueous solutions inorganic salts are almost without influence on the dielectric constant of water. Such a result is, however, by no means applicable to other solvents. Water exhibits a very high dielectric constant, and aqueous salt solutions are considerably dissociated, and consequently good conductors. Hence, in order that the dielectric constants of these solutions may be measured, their conductivities must be low, so that only very dilute solutions can be dealt with. Any influence of the salt on the dielectric constant of the water is therefore masked.

The author's measurements of the dielectric constants were made on chloroform solutions by Drude's second method (*loc. cit.*). The salts employed, with the values of  $D_4^{25}$  (vac.), were as follows:  $\text{NEt}_4\text{Br}$ , 1.3880;  $\text{NEt}_4\text{NO}_3$ , 1.1622;  $\text{NEt}_3\text{HNO}_3$ , 1.0890;  $\text{NHEt}_2\text{HNO}_3$ , 1.1561;  $\text{NEt}_4\text{Cl}$ , 1.1115;  $\text{NPr}_4\text{NO}_3$ , 1.0568;  $\text{NPr}_4\text{I}$ , 1.3138; also mono-, di-, and tri-ethylamine hydrochlorides and tetraethylammonium chloride (compare Schiff and Monsacchi, *Abstr.*, 1898, ii, 110), and  $\text{NPhMe}_2\text{HBr}$ ,  $\text{NHPhMeHBr}$ ,  $\text{NH}(\text{C}_5\text{H}_{11})_2\text{HCl}$ , and  $\text{NH}_2\cdot\text{C}_5\text{H}_{11}\text{HCl}$ . The dielectric constants were calculated according to the formulæ given by Philip (*Abstr.*, 1898, ii, 9; compare Philip and Haynes, *Trans.*, 1905, 87, 998), Bouty (*Compt. rend.*, 1892, 114, 1421), and Silberstein (*Ann. Phys. Chem.*, 1895, [iii], 56, 661).

The numerical results show that, under the experimental conditions employed, the addition of small quantities ( $V=10-20$ ) of binary salts produces considerable increases in the value of the dielectric constant of the chloroform. The type of the binary electrolyte has a marked influence on the magnitude of this increase, the smallest effects being due to salts of primary amines, and the largest to tetra-alkylammonium salts. With salts of the same type, radicles of different character (complexity) produce different effects; thus, in the disubstituted salts, replacement of ethyl by amyl or phenyl lowers the dielectric constant of the solution, and in tetrasubstituted salts, propyl has a less effect than ethyl.

The three formulæ mentioned above give divergent numbers for the dielectric constants of the salts, Philip's formula, in general, giving higher results than that of Bouty, and the latter higher ones than that of Silberstein. The accuracy of Philip's formula is less than that of the other simpler ones. The constitutive character of the dielectric constants of salts is brought out most clearly by Philip's formula,

which gives the value 5 for amylamine hydrochloride and 970 for tetraethylammonium chloride.

The dielectric constant must therefore be regarded as a highly characteristic physical property of salts, which may be divided into the two kinds, strong and weak, the former being those which exhibit high dielectric constants and are largely dissociated even in solvents with low ionising powers. In general, there is a parallelism and a causal connexion between the ability of a salt to dissociate and its dielectric constant.

T. H. P.

**Temperature-coefficients of Conductivity of Certain Electrolytes in Non-aqueous Solvents.** EBERHARD RIMBACH and K. WEITZEL (*Zeitsch. physikal. Chem.*, 1912, 79, 279—302).—The electrical conductivities of nickel, cobalt, and manganese chlorides in methyl alcohol, ethyl alcohol, and acetone have been measured for a series of dilutions at temperatures from 0° to 45°, and the temperature-coefficients of conductivity are calculated for all the dilutions by means of the usual quadratic formula  $\lambda_t = \lambda_0[1c(t - t_0) + c'(t - t_0)^2]$ . The coefficients are lower than for aqueous solutions, being about 0.01 for methyl alcohol, rather higher for ethyl alcohol, and considerably lower for acetone in the neighbourhood of 10°. The value of  $c'$  is negative practically throughout.

In general, the conductivity increases regularly with the temperature, but solutions of cobalt chloride in ethyl alcohol and in acetone show negative temperature-coefficients. In alcohol the conductivity maximum occurs at 30° for  $v = 32$ , and at 40° for  $v = 323$ ; in acetone the maximum occurs about 24° for  $v = 6$ , about 12° for  $v = 24.6$ , and for  $v > 50$  below 0°. The significance of these maxima is discussed.

G. S.

**Abnormal Conductivity Changes. II.** AL. N. SACHANOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 324—339. Compare Abstr., 1911, ii, 689, 691).—Solvents in which diminution of the molecular conductivity on dilution is observed are divided sharply into two classes: (1) those in which all solutes, independently of their nature, exhibit such diminution, and (2) those few in which the molecular conductivity as a rule increases with dilution, but with certain dissolved substances diminishes. In what follows, solvents of class (1) are dealt with.

Considering the series of ammonia and the amines and that of the aliphatic saturated acids, the following results are obtained, the numbers in brackets representing the dielectric constants. Solutions in liquid ammonia (22 at -34°) and methylamine (about 10) show increase of the molecular conductivity with dilution; those in aniline (6.85), ethylamine (6.17), methylaniline (5.93), dimethylaniline (4.48), amylamine (4.5) show decrease; those in hydrocyanic (96), formic (57), or thioacetic (12.8—17.3) acid show increase, and those in acetic (6.46) or propionic (3.15) acid diminution.

Thus, for solvents with low dielectric constants, diminution of the conductivity on dilution is as characteristic a property as is increase of the conductivity with dilution for solvents with high dielectric

constants. In general, too, solvents with low dielectric constants are characterised by divergence from the Nernst-Thomson law.

The electrolytic dissociation is conditioned, not only by the dielectric constant, but also by the formation of complex ions from the original ions with increased electro-affinity. Further, in solvents with low dielectric constants, it is only complex compounds (polymerised molecules of solute combined with molecules of the solvent) forming complex ions with considerably increased electro-affinity that undergo electrolytic dissociation; the decomposition of these compounds on dilution explains the diminution of the molecular conductivity then occurring. The formation of such complex ions is the cause of the inapplicability of the Nernst-Thomson law.

Abnormally high conductivity and also abnormal variation of the conductivity are observed most frequently in concentrated solutions. With aniline solutions of ammonium iodide, for instance, the molecular conductivity is very high at high concentrations. On continued dilution, the conductivity at first diminishes very rapidly, but ultimately increases in the normal manner. T. H. P.

**Electrical Conductivity of Solutions of Platinum Tetraiodide and of Iodine in Alcohol.** EBENEZER H. ARCHIBALD and W. A. PATRICK (*J. Amer. Chem. Soc.*, 1912, **34**, 369—375).—Determinations of the conductivity of solutions of platinum tetraiodide in ethyl alcohol at 25° have shown that the molecular conductivity increases with the dilution and becomes constant at dilutions of one equivalent ( $\frac{1}{4}\text{PtI}_4$ ) in about 600 litres.

In connexion with these experiments it was considered of interest to study the conductivity of alcoholic solutions of iodine. Determinations have therefore been made of 0.1*N*- and 0.01*N*-solutions at 25°, and have yielded the following results. The initial specific conductivity of the 0.1*N*-solution is  $2.4 \times 10^{-6}$  reciprocal ohms. The conductivity increases with the time, and attains a maximum value in about twenty-five hours. The velocity of the reaction to which this increase is probably due is greatly accelerated by platinum-black. The conductivity of alcoholic iodine solutions at 0° is very small, and increases with the dilution. The conductivity decreases as the temperature is lowered from 0° to -78°. It is suggested that the brown colour of alcoholic solutions of iodine is due to the interaction of the iodine and alcohol with formation of a compound which is probably slightly dissociated and gives rise to the low initial conductivity observed.

Solutions of iodine in methyl alcohol have a somewhat greater conductivity than those in ethyl alcohol, and show a similar variation between the conductivity and concentration. E. G.

**Solubility of Silver Thiocyanate.** AAGE KIRSCHNER (*Zeitsch. physikal. Chem.*, 1912, **79**, 245—247).—The solubility product of silver thiocyanate, determined by measurement of the *E.M.F.* of the cell  $\text{Ag} | \text{AgNO}_3 | \text{NH}_4\text{NO}_3 | \text{KONS} | \text{AgCNS}(\text{solid}) | \text{Ag}$  amounts to 0.49 and  $1.16 \times 10^{-12}$  mols. per litre at 18° and 25° respectively, in good agreement with the results of previous observers. G. S.

**Chlorides of Zinc and Mercury in Aqueous Solution.** KARL DRUCKER (*Zeitsch. Elektrochem.*, 1912, 79, 236—249. Compare Luther, Abstr., 1901, ii, 301).—From measurements of the *P.D.* at a mercury electrode in mercurous nitrate and the known position of equilibrium between mercurous and mercuric salts the difference of potential for the half-cell  $\text{Hg}-\text{Hg}^{++}$  is 0.859 volt at 25° for *N/1*  $\text{Hg}^{++}$  ion concentration, taking the value for the normal calomel electrode as 0.285 volt. The difference of potential between mercury and mercurous nitrate solutions depends greatly on the nitric acid concentration.

On the basis of the recalculated constant  $[\text{HgCl}_3']/([\text{HgCl}_2] \times [\text{Cl}']) = 13.5$ , the dissociation constant for mercuric chloride  $[\text{Cl}']^2[\text{Hg}^{++}]/\text{HgCl}_2 = 0.94 \times 10^{-14}$  at 25°, in agreement with the value  $0.95 \times 10^{-14}$  given by Morse (Abstr., 1903, ii, 12).

It is shown by conductivity, transport, and *E.M.F.* measurements that even in concentrations less than 0.1 molar the aqueous solution of zinc chloride contains a complex anion, probably  $\text{ZnCl}_4$ , in considerable concentration. On the basis of *E.M.F.* cryoscopic and distribution experiments, it is shown that solutions 0.05 molar with reference to zinc chloride and mercuric chloride contain a mixed complex, which in the non-ionised condition contains four chlorine atoms, and is probably represented by the formula  $\text{ZnHgCl}_4$ . G. S.

**Passivity.** G. GRUBE (*Zeitsch. Elektrochem.*, 1912, 18, 189—211).—It is shown that both the formation of a thin film of oxide and the absorption of oxygen can produce passivity, which of the two factors are mainly concerned depending on the experimental conditions.

Since anodes of platinum, gold, nickel, cobalt, and copper do not become polarised when a ferrocyanide undergoes electrolytic oxidation in alkaline solution, the process is practically instantaneous and probably consists in the loss of a negative charge,  $\text{Fe}(\text{CN})_6^{4-} \rightarrow \text{Fe}(\text{CN})_6^{3-} + \ominus$ . Anodes of iron, nickel, cobalt, copper, lead, and silver, become polarised in a neutral solution of potassium ferrocyanide and ferricyanide, and anodes of iron, lead, silver, and zinc become polarised also in alkaline solutions of these substances. In all these cases there is evidence of the formation of a surface film of oxide, and it must be assumed that in these cases the oxidation of the ferrocyanide is effected by the intermediate formation of peroxides. These peroxides in the case of nickel, silver, and lead have the respective formulæ  $\text{NiO}_2$ ,  $\text{Ag}_2\text{O}_2$ , and  $\text{PbO}_2$ .

Since at electrodes of gold and platinum in neutral and alkaline solution, at electrodes of nickel, cobalt, and copper only in alkaline solution, of potassium ferrocyanide and ferricyanide oxidation of the former salt takes place at the same potential and with the same velocity, it is improbable that the passivity of these metals is due to a layer of oxide; it is probably due to the effect of the oxygen charge of the electrode in retarding the liberation of cations from the metal. It is shown that an electrode immersed in alkaline ferrocyanide-ferricyanide solution becomes more fully charged with oxygen than in neutral solution, and this explains the greater passivity in alkaline solution. In the case of iron the oxygen charge does not completely

hinder the liberation of  $\text{Fe}^{++}$  ions from the metal, and therefore there is the possibility of the formation of a surface film of oxide on the anode.

No explanation has been found for the assumed retardation of the liberation of cations from the metal by the oxygen charge. G. S.

**Electrolytic Corrosion of Iron by Direct Current.** J. L. R. HAYDEN (*J. Franklin Inst.*, 1911, 172, 295—308).—A study of the corrosion of iron produced by stray direct currents in the ground as illustrated in electric railways when the rails are used as return conductors, under which conditions the leakage of current causes serious corrosion of rails, gas and water pipes. The experiments were carried out under varying conditions as comparable with the above as possible, and the results summarised as follows.

(1) No conclusion can be drawn on the electrolytic corrosion of iron from the amount of current which passes from the iron as anode, since iron may assume a passive state in which electrolytic corrosion is entirely absent, or an active state in which the corrosion follows Faraday's law.

(2) The conditions which produce the active or the passive state are not yet fully understood, as under apparently identical conditions either state may occur.

(3) An alkaline reaction of the electrolyte, the presence of nitrates or dichromates tend to produce a passive state; sulphates and especially chlorides induce the active state of electrolytic corrosion.

(4) High current density, even if only momentary, tends to produce the passive state; absence of current favours the active.

(5) The products of corrosion in the active state are initially ferrous compounds, in the passive state ferric compounds; the passive state occurs in those electrolytes in which ferrous compounds cannot exist or are chemically unstable.

(6) The potential difference at the electrodes in the passive state is much higher than it is in the active state. F. M. G. M.

**Magneto-chemical Investigations. Thermo-magnetic Properties of the Elements. II.** MORRIS OWEN (*Ann. Physik*, 1912, [iv], 37, 657—699).—A full account of work of which a preliminary notice has appeared (this vol., ii, 227). Fifty-eight elements have now been examined in reference to their magnetic susceptibility. These are arranged in six groups, according to whether they are paramagnetic or diamagnetic, and according to whether a rise of temperature increases, decreases, or has no effect on the susceptibility. H. M. D.

**Magnetic Researches. V. The Initial Susceptibility of Nickel at Very Low Temperatures.** ALBERT PERRIER and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 14, 1004—1007. Compare this vol., ii, 228).—The magnetic susceptibility of nickel has been measured for fields of low intensity ranging from 0.017 to 0.090 gauss at liquid oxygen and hydrogen temperatures. At these temperatures the susceptibility appears to be

quite independent of the strength of the field over the range investigated, and within the limits of experimental error, the diminution of the susceptibility with falling temperature is in agreement with the relationship established by Radovanovitch from observations ranging from the ordinary temperature to the Curie point. The temperature-coefficient of the susceptibility can therefore be represented as a function of the saturation magnetisation at the temperature under observation and that at absolute zero. H. M. D.

**Magneto-chemical Researches.** PAUL PASCAL (*Ann. Chim. Phys.*, 1912, [viii], 25, 289—377).—A résumé of work already published in Abstr., 1909, ii, 788, 859; 1910, ii, 100, 179, 483, 580; 1911, ii, 91, 183, 251, 252, 464, 679, 850, 1058, and this vol., ii, 326. T. A. H.

**Magnetic Double Refraction and Chemical Constitution.** A. COTTON and HENRI MOUTON (*Compt. rend.*, 1912, 154, 818—821. Compare Abstr., 1910, ii, 368; 1911, ii, 4).—The author defines specific magnetic double refraction,  $b_m$ , as the ratio of the double refraction of the liquid studied to that of nitrobenzene, multiplied by 100 and divided by the density. Toluene has  $b_m$  28.2; benzyl chloride, 21.8; benzylidene chloride, 19.0, and tri- $\omega$ -chlorophenylmethane, 18.4.

All benzene and naphthalene derivatives showed positive double refraction. Saturated ring compounds showed lower double refraction than the corresponding unsaturated derivatives. By substituting the groups  $\cdot\text{NO}_2$ ,  $\cdot\text{CH:CHR}$ ,  $\cdot\text{CR:O}$ ,  $\cdot\text{CN}$  in the benzene or naphthalene rings the index was increased, whilst the radicles  $\text{NH}_2$ , I, Br, Cl had an opposite effect. The position of substituents, and the distance of the ethylenic linking from the ring have some influence on the double refraction. W. O. W.

**New Substances Showing Magnetic Double Refraction. Molecular and Atomic Anisotropism.** A. COTTON and HENRI MOUTON (*Compt. rend.*, 1912, 154, 930—933. Compare Abstr., 1911, ii, 4).—The magnetic double refraction of aromatic compounds may be considered as due to the tendency of optically anisotropic molecules to orient themselves in a magnetic field. Those substituting atoms or groups which in a recent communication (preceding abstract) were shown to increase or diminish the double refraction in a regular way, act additively owing to their specific optical and magnetic anisotropism. The groups which are most active in this respect are now found to act similarly when substituted in aliphatic hydrocarbons which are inactive in the magnetic field; thus nitromethane has  $b_m$  + 3.5, acetone + 2, methyl iodide - 1.3, di-iodomethane - 3.7, chloroform - 1.9. The values for the specific magnetic double refraction in the aliphatic series are always very small as compared with aromatic compounds containing the same groups, but they are measurable in a sufficiently powerful field, even when the substance contains no carbon; thus, nitric acid gave a double refraction of +7', when nitrobenzene under the same conditions gave 281'. W. O. W.

**A Relation between Coefficients of Expansion of Liquids and their Critical Temperatures.** H. DAVIES (*Phil. Mag.*, 1912, [vi], 23, 657—659).—By making use of the relationship between the

densities at absolute zero and the critical temperature,  $D_0/D_c = 4$ , it is shown that the law of the "rectilinear diameter,"  $D_l + D_v = a - bT$ , may be written in the form  $D_l + D_v = 4D_c - 2D_c T/T_c$ , in which  $T_c$  and  $D_c$  represent the critical temperature and critical density.

If  $V$  is the specific volume of the liquid at any temperature sufficiently removed from the critical temperature, then from the above equation it is found that the coefficient of expansion  $\alpha = 1/(2T_c - T)$ . This may be written in the form  $\alpha = 1/2T_c + T/(2T_c)^2 + T^2/(2T_c)^3 + \dots$ . The coefficients of expansion calculated from this equation are shown to agree fairly well with the observed values for a number of liquid substances chosen at random.

The relationship  $\alpha = 1/(2T_c - T)$  is shown to be equivalent to that deduced by Thorpe and Rücker (Trans., 1884, 45, 135), in which the densities  $s_1$  and  $s_2$  at temperatures  $T_1$  and  $T_2$  are connected by the formula  $s_1 - s_2 = (T_2 s_1 - T_1 s_2)/AT_c$ , in which  $A$  is a constant.

H. M. D.

**Thermal Expansion of Aqueous Salt Solutions.** ALFONS DAVIDTS (*Zeitsch. physikal. Chem.*, 1912, 79, 303—356).—The thermal expansion of aqueous solutions of calcium, barium, and copper chlorides, copper sulphate and calcium bromide have been measured for each 1/100 degree between 15° and 65° by means of a very sensitive dilatometer and the results are tabulated in great detail and represented graphically. The expansion does not vary regularly with the temperature; at certain "abnormal points" the expansion is greater than the normal value. The nature of the results will be evident from the data for the abnormal points for calcium bromide solution between 17·9° and 64°: 26·7—26·8°; 30·6—30·7°; 33·2—33·3°; 40·9—41·0°; 44·7—44·9°; 50·9—51·0°. The concentration has only a very slight effect on the position of the abnormal points and the magnitude of the deviations. The expansion of water has been measured in the same apparatus and found to be regular. The results are ascribed to the existence of complexes in solution, and can only be adequately explained when both electrolytic dissociation and hydration are assumed.

A bibliography of the subject is given.

G. S.

**The Share of the Free Electrons in the Specific Heat.** JOHANNES KOENIGSBERGER (*Ber. Deut. physikal. Ges.*, 1912, 14, 275—281).—The part played by the free electrons in connexion with the specific heat of the metals is examined. If it is assumed that the free electrons are not concerned in the absorption of heat, the maximum value of the atomic heat at constant volume should not exceed six. From the data for the specific heat of platinum up to 900°, the author has calculated the atomic heat at constant volume, and finds that this increases from 6·34 at 200° to 6·78 at 900°. In a similar way, the data for silver give  $C_v = 5·93$  at 100° and 6·32 at 700°. From these relationships the author draws the conclusion that the free electrons play an active part in connexion with the specific heat of the metals.

H. M. D.

**The Variation of the Specific Heat of Water, with Experiments by a New Method.** HUGH L. CALLENDAR (*Proc. Roy. Soc.*, 1912, A, 86, 254—257\*).—The lack of agreement between the results obtained by previous observers for the variation of the specific heat of water with the temperature suggests that the discrepancy may be due to some fundamental difference between the calorimetric and thermometric methods. Measurements have accordingly been made by an independent continuous mixture method, in which continuous currents of water at different, accurately measured temperatures are passed through an arrangement of concentric tubes, known as a "heat exchanger," in which thermal interchange is effected by conduction without actual mixture. The results of about 150 experiments by this method, in which the conditions as to rate of flow of current and heat loss were varied as widely as possible, are such as to confirm the data obtained by the continuous electric method for the ratio of the mean specific heat from 70—100° to the mean specific heat from 30—60°, to less than 1 in 5000.

The previous formulæ covering different ranges of temperature have now been combined into a single formula of a slightly different type, the specific heat  $s$  at any temperature  $t$  between 0° and 100° being given by  $s = 0.98536 + 0.504/(t + 20) + 0.0084(t/100) + 0.0090(t/100)^2$ .

H. M. D.

**Specific Heat of Binary Mixtures. II.** ALFRED SCHULZE (*Ber. Deut. physikal. Ges.*, 1912, 14, 258—274. Compare this vol., ii, 327).—In continuation of experiments on the specific heats of binary liquid mixtures, measurements have been made for mixtures of benzene and carbon tetrachloride, benzene and nitrobenzene, and ethyl ether and nitrobenzene.

In all three cases the specific heat of mixtures is less than that corresponding with the mixture rule, the deviation increasing as the temperature falls. The deviation from the mixture rule is attributed to the association of one of the components of the mixture (carbon tetrachloride or nitrobenzene), the diminution of the association with rise of temperature causing the various mixtures to approximate to the ideal limiting condition in which the specific heat would be accurately represented by the equation for the mixture rule.

The influence of association on the specific heat has also been examined in the case of pure nitrobenzene. The specific heat diminishes gradually from 0.3582 at 10° to 0.3286 at 60°, and then increases up to 0.3939 at 120°, the increase with rise of temperature corresponding with the normal effect of a non-associated liquid.

Similar minima in the specific heat values are also found in the case of methyl alcohol and ethyl bromide between 10° and 15°.

H. M. D.

**Variations in the Coefficient of Pressure with Temperature and their Connexion with the Internal Pressure of Liquids.** EMILE H. AMAGAT (*Compt. rend.*, 1912, 154, 909—914. Compare Abstr., 1911, ii, 1061).—The experimental fact which appears most distinctly to require the existence of variations of the

\* and *Phil. Trans.*, 1912, [A], 212, 1—32.

pressure coefficient in gases with temperature is the known variation in the specific heat at constant volume with this volume, in accordance with the relation  $dc/dv = AT.d^2p/dt^2$ , where  $c$  is the specific heat and  $d$  the absolute density. Hydrogen, helium, and argon show slight diminution of the pressure coefficient as the temperature rises, but whilst in the case of the two former this is exceedingly small, in the case of argon (private communication from Kamerlingh Onnes) it amounts to about 1% of the coefficient, for a rise of over  $300^\circ$ . The variations in specific heat with diminishing volume calculated from these numbers are much greater than the experimental values. The discrepancy is traced to systematic errors from condensation effects on the walls of vessels used in pressure determinations.

The remainder of the paper is of a mathematical character.

W. O. W.

**Phosphoryl Chloride as a Cryoscopic Solvent.** PAUL WALDEN (*Zeitsch. anorg. Chem.*, 1912, **74**, 310—314).—Polemical against Oddo and Manessier (Abstr., 1911, ii, 1060). The more highly purified the solvent, the higher is the cryoscopic constant. The author's value  $76.8$  (Abstr., 1910, ii, 1036) is thus more likely to be correct, using phosphoryl chloride of m. p.  $+1.25^\circ$  than  $72.1$ , found by Oddo with a solvent of m. p.  $+0.4-0.9^\circ$ .

C. H. D.

**Cryoscopic and Viscometric Behaviour of Some Solutions of Quinoline.** GIUSEPPE KERNOT and UMBERTO POMILIO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iii], **17**, 359—372).—The authors have executed cryoscopic measurements with mixtures of quinoline with benzene and with acetic acid, and have determined the viscosity at  $25^\circ$  of binary mixtures of quinoline with alcohol, benzene, and acetic acid. In freezing benzene the molecular weight of quinoline increases from 121, when 0.980 gram of quinoline is dissolved per 100 grams of solvent, to 129.7, when 15.460 grams are dissolved per 100 grams of solvent, and continues to increase as the concentration is raised further. In freezing acetic acid, quinoline acetate is practically undissociated.

The measurements of viscosity were made with Scarpa's viscometer (Abstr., 1911, ii, 17). For the viscosity of quinoline the authors obtained the value  $\eta^{25} 0.033610$ . The curve of the viscosities of mixtures of quinoline and benzene is a parabola. The maximum divergence from the curve calculated from the law of mixtures lies at 62% of quinoline, and corresponds with the composition  $C_9H_7N, C_6H_6$ . The curve exhibits also other peculiarities. The curve of the viscosities of mixtures of ethyl alcohol and quinoline is also parabolic, the maximum divergence between it and that calculated from the law of mixtures lying at 58.3% of quinoline, corresponding with the composition  $C_9H_7N, 2EtOH$ . In the case of mixtures of quinoline and acetic acid, the curve shows a maximum viscosity for a particular mixture. The greatest divergence from the law of mixtures lies at about 40% of quinoline, and corresponds with the molecular complex  $C_9H_8N \cdot OAc, 2AcOH$ , whilst from the cryoscopic measurements above recorded the maximum would be expected to correspond with the composition  $C_9H_8N \cdot OAc, AcOH$ .

R. V. S.

**Vapour Pressure of the Alkali Metals between 250° and 400°.** LOUIS HACKSPILL (*Compt. rend.*, 1912, 154, 877—880).—The measurements of vapour pressure for sodium, potassium, caesium, and rubidium were made by a method similar to that used by Dulong and Petit for mercury. The results for twenty-seven different temperatures are given in a tabular statement and in the form of curves. If the logarithms of the pressures are plotted against the temperatures, the curves are practically rectilinear and nearly parallel to one another. W. O. W.

**The Liquid State. III. Mechanism of Vaporisation.** WILLIAM C. McC. LEWIS (*Zeitsch. physikal. Chem.*, 1912, 79, 196—222).—The object of the paper is to test the relative applicability of the two expressions  $\int K dv$  (Bakker, *Zeitsch. physikal. Chem.*, 1893, 12, 670) and  $\sqrt{vdK}$  (Milner, *Abstr.*, 1897, ii, 439) for the internal heat of vaporisation of a liquid ( $K$  is the internal pressure). The formulæ are first tested in the case of mercury, and it is shown that Bakker's formula is the correct one. The expression  $\int K dv$  can be integrated in terms of  $b$  by making use of van der Waals' equation  $(p + K)(v - b) = RT$ , and the resulting expression,  $L = RT/m \times \log(v_1 - b)/(v_0 - b)$ , where  $b$  is a constant, gives numerical values for  $L$  in good agreement with the experimental values. Much less satisfactory results are obtained when the expression is integrated in terms of  $a$ . The advantage of Bakker's expression over that of Milner is also shown by means of the data for argon and xenon.

When the thermal data for ether are considered, however, it is found that the expression  $\int K dv$  does not include the complete mechanism of evaporation in the case of polyatomic liquids, nor does the assumption that  $b$  varies continuously with the volume lead to agreement between the observed and calculated values of  $L$ . A "correction factor" is introduced for the change of energy when gasogen particles change to liquidogen particles according to Traube's theory. An expression embodying the latter correction and the assumption that  $b$  varies continuously with  $v$  gives 82 calories as the latent heat of evaporation of ether at 5°, as compared with the experimental value, 92 calories. G. S.

**A New Method for the Separation of Mixtures of Liquids with Boiling Points very close together and of Mixtures of Constant Boiling Point.** A. GOLODETZ (*Chem. Zeit.*, 1912, 36, 273—274, 297—298, 302—304. Compare this vol., ii, 234).—The principle of the method used by the author is as follows: Supposing that a mixture of two liquids,  $A$  and  $B$ , is to be separated, a third liquid,  $C$ , is added which will give a mixture of constant boiling point with  $A$ . This constant boiling point must be such that it is lower than the boiling points of all the other components of the mixture, or of any other combinations, for example, ternary combinations, which may be produced. On distilling the mixture, the binary mixture of  $A$  and  $C$  will then distil over, leaving a residue of pure  $B$ . It is, of course, necessary to add  $C$  in such quantity that complete formation of the binary mixture of  $A$  and  $C$  with constant boiling point takes place.

Using the above principle, the following mixtures have been separated (the residual pure liquid is printed in *italics*): *toluene* and acetic acid by the addition of benzene; *toluene* and *acetic acid* by the addition of water; benzene and *toluene* by the addition of methyl alcohol; benzene and methyl alcohol by the addition of carbon disulphide; amyl bromide and *ethyl butyrate* by the addition of *n*-propyl alcohol.

These results also lead to other separations; for example, water and acetic acid can be separated by the addition of toluene, and in this way anhydrous acetic acid readily obtained. T. S. P.

**Ebullioscopic Constant of Carbon Tetrachloride.** ENRIQUE MOLES (*Anal. Fis. Quim.*, 1912, 10, 30--33).—The corrected boiling point of carbon tetrachloride is determined as 76.65°/760, and the freezing point as -22.7°, agreeing with the results of other authors.

The depression constant is found (using camphor and ethyl benzoate as solute) to be 47, as against 48, determined by Beckmann.

G. D. L.

**Ebullioscopic Determinations at Low Temperatures from -35.7° to -82.9°.** ERNST BECKMANN [and W. WEBER] (*Zeitsch. anorg. Chem.*, 1912, 74, 297—309. Compare Beckmann, Waentig, and Niescher, Abstr., 1910, ii, 581; McIntosh and Archibald, Abstr., 1904, ii, 534).—Hydrogen sulphide, b. p. -60.2°, may be used as an ebullioscopic solvent in an electrically heated vessel, enclosed in an air-bath cooled by solid carbon dioxide and alcohol. The same mixture is used for cooling the condenser. The constant, determined with toluene, is 6.3.

This apparatus is not successful with the hydrogen halides, and it is necessary to immerse the whole boiling vessel in a cooling-bath. The condenser is also immersed in a cooling-bath, with the connecting tube completely in the liquid. For hydrogen chloride, a bath of light petroleum is used, cooled by liquid air. The constants found are, using toluene as solute, hydrogen iodide, b. p. -35.7°, 28.3; hydrogen bromide, b. p. -68.7°, 15.0; hydrogen chloride, b. p. -82.9°, 6.4. The last value is about one-third of that found by McIntosh and Archibald. The theoretical values calculated from the heats of volatilisation found by Estreicher and Schnerr (Abstr., 1911, ii, 16) are: H<sub>2</sub>S 6.8, HI 32.8, HBr 16.9, HCl 7.2.

C. H. D.

**Ebullioscopic Determinations with Heating by Alternating Current.** ERNST BECKMANN [with KURT HARING] (*Zeitsch. physikal. Chem.*, 1912, 79, 177—184).—It is shown that good results by the boiling-point method can be obtained both with electrolytes and non-electrolytes when the solution is electrically heated by means of a rapidly alternating current (60,000 per minute). As solvents for non-electrolytes, carbon disulphide, chloroform, benzene, etc., were used, and as electrolytes, aqueous solutions of potassium chloride, iodide, nitrate, and sulphate. The experiments were not successful with concentrated sulphuric acid as solvent, mainly because it attacked both platinum and palladium spirals.

G. S.

**Mechanical Phenomena of Gaseous Combustion. Spiral Flame.** JEAN MEUNIER (*Compt. rend.*, 1912, 154, 698—700).—The flat burner employed has a large orifice, so that the gas may burn under a low pressure, not exceeding a few millimetres of water. Against the wide flame a narrow one is projected obliquely from a tube supplied with gas under a pressure of 8—10 c.c. of water. The "spiral flame" produced at the junction of the two owes its characteristic appearance to numerous luminous lines, arising from the movement of glowing particles. Attention is drawn to the resemblance between such flames and certain stellar nebulae.

W. O. W.

**Modified Jacket for a Victor Meyer Vapour Density Apparatus.** W. E. HENDERSON (*J. Amer. Chem. Soc.*, 1912, 34, 553—554).—An arrangement is described which has been devised to avoid the expense involved by the breakage of the outer tubes of the Victor Meyer vapour density apparatus.

The bulb is replaced by a beaker provided with a copper cover with a collar in the centre of such a size that the smallest tube to be used as a jacket will readily slip over it. There is a deep groove round the collar which serves as a water-seal for connecting the jacket-tube. The liquid condensing on the walls of the tube automatically fills the seal, and the collar is provided with several small holes just below the level of the flat cover to allow for drainage, and thus prevent the liquid from overflowing. It is not necessary to connect the cover with the beaker, since if the cover is flat and the rim of the beaker fairly true, the surface-tension of the film of liquid at the joint prevents any appreciable leakage. The jacket-tube can be made from tubing of a suitable width; it is cut level at each end, and its length is readily adapted to that of any inner tube.

E. G.

**Dependence of the Density and Surface Tension of Liquids on the Temperature.** RICHARD SWINNE (*Zeitsch. physikal. Chem.*, 1912, 79, 461—470. Compare Walden, *Abstr.*, 1909, ii, 122).—It is shown that Walden's rule that the product of the "expansion modulus" of a liquid and its critical temperature is constant can be deduced by means of the rule of the rectilineal diameter (Mathias) and the ratio of the critical density to that at the absolute temperature deduced by Guldberg. Further, Walden's rule as to the relationship between the temperature-coefficient of the surface tension,  $\beta$ , and the critical temperature can be deduced from the exponential temperature function of the surface tension obtained by van der Waals.

G. S.

**The Liquid State. II. Compressibility of Mercury.** WILLIAM C. MCC. LEWIS (*Zeitsch. physikal. Chem.*, 1912, 79, 185—195).—In a recent paper (*Abstr.*, 1911, ii, 855) the formula  $\beta = -T\alpha_1/L\rho$  has been deduced, where  $\beta$  is the compressibility,  $\alpha$  the thermal expansion of the liquid,  $L$  the latent heat of vaporisation per gram, and  $\rho$  the density of the liquid at the absolute temperature  $T$ . This formula is now tested for mercury by comparing the calculated value of  $\beta$  at 20° with the value obtained by Bridgman (*Proc. Amer. Acad.*, 1909,

44, 255). In the calculation  $L$  is obtained by means of the Clausius-Clapeyron equation ( $70\cdot47$  cal. at  $20^\circ$ ), and  $\alpha$  from the recent observations of Callendar and Moss (*Proc. Roy. Soc.*, 1911, A, 84, 595). The observed and calculated values are  $3\cdot70\cdot10^{-6}$  and  $(1\cdot30 \pm 0\cdot02)\cdot10^{-6}$  per kg./cm.<sup>2</sup>. This very considerable discrepancy is ascribed to inaccuracy in the experimental determination of  $\beta$ , and different sources of error are suggested.

Certain points in the recent paper of Parsons and Cook (*Abstr.*, 1911, ii, 699) are discussed, more particularly the fact that these observers find a lower value of the internal pressure for water than for ether and paraffin oil.

G. S.

### Connexion between the Physical Properties of Solutions.

III. The Ionic Moduli of the Density in Water. ADOLF HEYDWEILLER (*Ann. Physik*, 1912, [iv], 37, 739—771. Compare *Abstr.*, 1910, ii, 106, 398).—The densities of a further series of solutions of electrolytes have been measured in order to obtain further information relating to the density moduli of the ions.

The new results show that the relationship  $\Delta = A + (A - B)i$ , in which  $\Delta$  is the percentage change of density per gram-equivalent of the dissolved electrolyte,  $i$  the ratio of the equivalent conductivity at the concentration under measurement to that at infinite dilution, and  $A$  and  $B$  are constants, is satisfied with very considerable accuracy by all electrolytes containing two univalent ions and the majority of electrolytes which contain a bivalent and a univalent ion. On the other hand, considerable discrepancies are exhibited by electrolytes containing two bivalent ions.

The ionic moduli, which are calculated from the differences in the values of  $A$ , form integral multiples of  $0\cdot35$  in the case of univalent monatomic ions, and this is approximately the case for the moduli of the bivalent monatomic ions.

Substances which combine with water in the solid state appear to unite with it in solution to at least the same extent. The contraction which accompanies the combination of the ions with water is due to the contraction of both the ions and the combined water. From the magnitude of the contraction, it appears that the average number of molecules of water in combination with the ions is three to four.

H. M. D.

Specific Volume of Solutions of Tetrapropylammonium Chloride. J. W. McDAVID (*Proc. Roy. Soc. Edin.*, 1910, 30, 515).—The densities of aqueous solutions of tetrapropylammonium chloride of different concentrations have been determined at  $0^\circ$ ,  $25^\circ$ ,  $35^\circ$ , and  $56^\circ$ . At all temperatures the density of dilute solutions is less than that of water; with increasing concentration the density attains a minimum and then slowly increases. The concentration of the solution of minimum density at  $0^\circ$  is about 7%, at  $25^\circ$  about 16·5%, at  $35^\circ$  19%, and at  $56^\circ$  about 22·5%.

In order that the expansion on solution might be obtained, the density of the salt has been determined by the floating method;  $D^3$  is  $1\cdot0334$  and  $D^{13}$   $1\cdot0296$ . The expansion on solution in different con-

centrations at 0° and 25° is given in tabular form. At 0° a solution of 18.5%, at 25° a solution of 26%, concentration show maximum expansion. The expansion increases considerably as the temperature is raised. G. S.

**Alteration of Viscosity on Solution.** CARL SCHALL (*Zeitsch. Elektrochem.*, 1912, 18, 225—232. Compare Bingham, Abstr., 1906, ii, 218).—On the basis of the available experimental data it is shown that in the case of binary mixtures of liquids, the proportionality of the temperature-coefficient of the alteration of viscosity and fluidity with the concentration is a limiting law, which is the more nearly true the greater the difference in the properties of the two components, but it is not valid when there is reciprocal action between the components. Further, in the neighbourhood of the freezing point of the solvent, the temperature-coefficient of the viscosity of the solvent is under certain conditions proportional to the freezing-point depression. G. S.

**Viscosity of Liquids.** ALFRED W. PORTER (*Phil. Mag.*, 1912, [vi], 23, 458—462).—If any liquid at temperature  $T$  has the same viscosity as a standard liquid at temperature  $T_0$  and the ratio  $T/T_0$  is plotted as a function of  $T$ , the curve obtained is very nearly a straight line. This has been found to be the case for mercury and water, bromine and water, oil of turpentine and water, ethyl ether and benzene, and ethyl acetate and benzene. From the above relationship, it follows that the viscosity ( $\mu$ ) or the mobility ( $M = 1/\mu$ ) can be represented by the formula  $F(M) = f(\mu) = A + B/T$ . This equation is of the same form as that connecting the vapour pressure and the temperature.

Corresponding with this similarity in the forms of the vapour pressure and mobility equations, it is found that if the logarithm of the mobility is plotted against the logarithm of the vapour pressure, a curve differing very little from a straight line is obtained both in the case of water and of mercury. For carbon dioxide, the curve is concave upwards, and if the values are combined with that for the gas at ordinary pressure, a (conjectural) curve is obtained, which is very approximately a parabola with its axis horizontal.

It is further pointed out that liquids of small viscosity at ordinary temperatures have, in general, a large vapour pressure. H. M. D.

**Influence of Substances, Soluble in Fats, on the Viscosity and the Surface Tension of Olive Oil.** FRANZ BUBANOVIĆ (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 178—181).—The effect of the addition of small quantities of chloroform, ethyl alcohol, and camphor on the viscosity and surface tension of olive oil has been examined. In all cases the influence of the added substance is very small, and if it may be inferred that the corresponding effects on the lipid membranes of the phagocytes are of the same order, the conclusion may be drawn that the increased activity of the phagocytes, which is observed on the addition of very small quantities of certain substances, is not due to changes in the viscosity or surface tension resulting in an increased rapidity of movement of the phagocytes. H. M. D.

**Relations between Viscosity and Other Physical Properties.**  
**II. Influence of Contiguous Unsaturated Groups.** ALBERT E. DUNSTAN and THOMAS P. HILDITCH (*Zeitsch. Elektrochem.*, 1912, 18, 185—189. Compare *Proc.*, 1911, 27, 93).—The influence of contiguous unsaturated groups of the following four types: (a)  $-\text{CH}:\text{CH}-\text{CO}-$ ; (b)  $\text{C}_6\text{H}_5$  with  $-\text{CH}:\text{CH}-$ ; (c)  $\text{C}_6\text{H}_5$  with  $-\text{CO}-$ ; (d)  $\text{C}_6\text{H}_5$ ,  $-\text{CH}:\text{CH}-$  and  $\text{CO}$  on the viscosity has been determined. In this connexion the viscosities of a large number of substances containing the groups in question have been determined in the pure state or in amyl alcohol solution. The results are discussed in connexion with the accumulation of unsaturated groups and of the effect of symmetry, and it is shown that the effect on the viscosity is, in general, parallel to the effect on other physical properties G. S.

**Dependence of Absorption on Surface Tension.** A. CHRISTOFF (*Zeitsch. physikal. Chem.*, 1912, 79, 456—460).—In previous papers (compare *Abstr.*, 1905, ii, 806; 1906, ii, 525) the author has advanced evidence to support the rule that the greater the surface tension of a liquid the smaller is its absorptive power for gases. The absorption coefficients of a number of gases in ethyl ether, a liquid of small surface tension, have now been determined at  $0^\circ$  and  $15^\circ$ ; the values at  $0^\circ$  are as follows: hydrogen 0.115, nitrogen 0.2580, carbon monoxide 0.3618, oxygen 0.4235, methane 1.066, carbon dioxide 7.330. As these results are higher than the solubilities in water and in alcohol, liquids of fairly high surface tension, they are in accord with the above rule. G. S.

**Adsorption Experiments with Varying Degree of Dispersity of the Adsorbent.** KNUD ESTRUP and E. BUCH ANDERSEN (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 161—169. Compare *Abstr.*, 1911, ii, 20).—Further experiments have been made on the adsorption of potassium permanganate by precipitated barium sulphate. When a given quantity of barium sulphate is precipitated from a series of solutions, in which the concentration of the permanganate is kept constant, but the total volume of the solution is gradually diminished, the quantity of absorbed permanganate decreases, passes through a minimum, and in still more concentrated solution through a maximum.

Experiments with strontium sulphate also show that the adsorbed permanganate passes through a minimum as the volume of the solution is diminished, but corresponding with the larger size of the crystals, the adsorbed quantities are considerably smaller than in the case of barium sulphate. Potassium permanganate is also removed from solution in the precipitation of aluminium hydroxide, and the phenomenon in this case appears to be one of simple adsorption.

Other experiments were made in which the influence of the volume of the solution on the removal of iodine and ferric chloride by precipitated barium sulphate was examined. The data obtained show that the nature of the process differs, however, from that in which potassium permanganate is adsorbed. H. M. D.

**Removal of Tannin from its Solutions by Cotton Wool.** A. SANIN (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 82—88).—It is shown

that within certain limits of concentration the adsorption of tannic acid from aqueous solution by cotton wool follows exactly the exponential formula  $x/m = \beta c^{1/p}$ , where  $x/m$  is the quantity of tannin taken up by one gram of the wool,  $c$  is the concentration in the solution after adsorption, and  $\beta$  and  $p$  are constants. The formula  $\sqrt{C_{\text{water}}/C_{\text{wool}}} = 0.11$  suggested by von Georgievics (Abstr., 1895, ii, 255) is not valid. Tannin is not adsorbed by wool from alkaline solution. The effect of the addition of hydrochloric acid is slightly to increase the amount of adsorption from dilute solutions of tannic acid, and to decrease it from concentrated solutions.

G. S.

**Peculiarities in Certain Verifications in Physical Chemistry.** ALBERT COLSON (*Compt. rend.*, 1912, 154, 933—935. Compare this vol., ii, 238, 334.).—A reply to Langevin (this vol., ii, 334), in which the author again draws attention to the discrepancies between the experimental and calculated results in the classical observations, such as those on the dissociation of hydrogen iodide, on which the law of mass action was based.

W. O. W.

**Dissociation of Gaseous Acetic Acid and Phosphorus Pentachloride.** CARL HOLLAND (*Zeitsch. Elektrochem.*, 1912, 18, 234—236).—The measurements were made by a method depending on the use of the Ladenburg-Lehmann manometer. The dissociation of acetic acid vapour according to the equation  $(\text{CH}_3\cdot\text{CO}_2\text{H})_2 \rightleftharpoons 2\text{CH}_3\cdot\text{CO}_2\text{H}$  is represented by the equation  $\log p_1/p_2^2 = (16480/4.571T) - 11.05$ , where  $p_1$  is the partial pressure of the double molecules,  $p_2$  that of the double molecules, in cm. of mercury; that of phosphorus pentachloride by the equation  $\log p_1/p_2p_3 = (21798/4.571T) - 11.50$ , where  $p_1$  represents the partial pressure of the pentachloride,  $p_2$  and  $p_3$  those of trichloride and chlorine respectively. The heat of dissociation of bimolecular acetic acid at constant pressure is 16,480 calories, that of phosphorus pentachloride under the same conditions 21,800 calories.

G. S.

**Osmotic Measurements of Salt Solutions and Arrhenius' Theory.** EUGÈNE FOUARD (*Bull. Soc. chim.*, 1912, [iv], 11, 249—261. Compare Abstr., 1911, ii, 267, 1071; this vol., ii, 141).—The author has shown previously (*loc. cit.*) that determinations of osmotic pressures of saline solutions by his differential method give results which are not in harmony with those required by the ionic hypothesis. He now explains these results by supposing that the variations in osmotic pressure shown by solutions of certain salts on dilution are due, not to dissociation into ions, but to (1) the breaking-down of physical aggregates, or (2) to combination of the salts with water. Examples of the first case are afforded by potassium chloride and cupric sulphate, which at infinite dilution show osmotic pressures corresponding with their true molecular weights, namely, 74.5 and 159, whilst in solutions containing 1 gram-mol. per litre the osmotic pressures correspond with mol. weights of 240 and 274 respectively. In the case of barium chloride, a solution containing 1 gram-mol. per litre has an osmotic pressure corresponding with a mol. weight of 226, whilst at

infinite dilution it corresponds with a mol. weight of 320, affording an example of the second class. Potassium sulphate, on the other hand, behaves in accordance with the ionic hypothesis, the osmotic pressure at infinite dilution corresponding with a mol. weight of 58, and to explain this without having recourse to the ionic hypothesis it is tentatively suggested that the molecule of sucrose which is measured in osmotic pressure experiments may be  $(C_{12}H_{22}O_{11})_3$ , in which case the value found for potassium sulphate at infinite dilution would correspond with the true molecular weight of the salt, namely, 174. It is pointed out that similar objections to the ionic hypothesis have been brought forward recently by Colson (this vol., ii, 25). T. A. H.

**Application of the Theory of Chemical Potential to the Thermodynamical Theory of Solutions. II. Effect of Pressure on Vapour Pressure. Vapour Pressure Theory of Osmotic Pressure. The Freezing of Solutions.** SYDNEY A. SHORTER (*Phil. Mag.*, 1912, [vi], 23, 483—494. Compare this vol., ii, 24).—It is shown by reference to the theory of chemical potential that two solutions, which are in osmotic equilibrium, have the same generalised vapour pressure. Although the difference of osmotic pressure may be regarded as the increase of pressure which must be applied to the stronger solution to make its generalised vapour pressure equal to that of the weaker solution, this does not afford a satisfactory definition of osmotic pressure. The so-called vapour pressure theory of osmotic pressure is merely a particular statement of the general thermodynamical truism that the conditions of co-existence of two parts of a system are independent of the precise nature of the mechanism of the co-existence, and depend only on the "constraints" of the mechanism.

The thermodynamical theory of the equilibrium between solution and solid solvent is also considered, and formulæ are deduced connecting the lowering of the freezing point with the lowering of the potential of the solvent, the osmotic pressure, and the vapour pressure.

H. M. D.

**Concentration of Hydrogen Ion in Sulphuric Acid.** RICHARD C. TOLMAN and LUCIEN H. GREATHOUSE (*J. Amer. Chem. Soc.*, 1912, 34, 364—369).—Since the manner in which sulphuric acid dissociates is not known, it is impossible to calculate the degree of dissociation or the concentration of any of the ions from conductivity measurements alone. A study of the concentration of the hydrogen ion in sulphuric acid has therefore been made by means of indicators. The method consists in finding a solution of hydrochloric or nitric acid which will produce the same colour in a solution of an indicator of a definite concentration as does the sulphuric acid solution under examination. The indicators employed were malachite-green, methyl-violet, tropæolin, and methyl-green. The experiments were carried out at 24°.

The results show that hydrochloric and nitric acids and the different indicators lead to approximately the same values for the hydrogen ion concentration in sulphuric acid solutions. The hydrogen ion concentrations of sulphuric acid were found to be as follows: in 0.2*N*-solution, 0.108—0.111; in 0.1*N*-solution, 0.0597—0.0620, and in 0.05*N*-

solution 0.0315—0.0356. These values agree fairly well with those obtained by Noyes and Stewart (Abstr., 1910, ii, 937) by determining the relative concentrations of hydrochloric and sulphuric acids which drive back the ionisation of picric acid to the same extent. E. G.

**Physico-mechanical Conception of Solutions.** J. I. MICHAILENKO (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 373—378).—If, in an equilibrated system consisting of liquid and vapour, a force be applied to the surface of separation, the vapour pressure will increase or diminish, according as the force is directed towards or away from the liquid. The relation between the applied force and the vapour pressure is expressed by Schiller's equation (compare Abstr., 1899, ii, 357):  $RT \log(p_1/p_0) = (P - p_0)[1 - k(P - p_0)/2]/s$ , where  $p_0$  and  $p_1$  are the original and modified vapour pressures respectively,  $1/s$  is the specific volume of the liquid,  $P$  the pressure applied to the limiting surface,  $k$  the coefficient of compression,  $T$  the absolute temperature, and  $R$  the constant of the gas laws.

On the basis of this relation the author develops a theory of solutions which he terms the physico-mechanical theory, and which represents the properties of solutions as the results of the mechanical action on the solvent of forces applied to the surface of separation of liquid from vapour and of liquid and ice. T. H. P.

**Diminution of Crystallisation. Velocity as Adsorption Phenomenon.** HERBERT FREUNDLICH and E. POSNJAK (*Zeitsch. physikal. Chem.*, 1912, 79, 168—176).—It has been shown by von Pickardt that a number of organic compounds in equivalent concentration diminish the rate of crystallisation of benzophenone to the same extent. Freundlich has suggested that this effect may be due to adsorption of solute at the surface of the crystals, and in order to test this view indirectly the adsorption of a number of substances from acetone solutions by blood charcoal has been measured. It is found that a number of substances are adsorbed to an equivalent extent in equimolar solution, and this result is regarded as to some extent a confirmation of the theory.

There are, however, certain exceptions to the above rule regarding adsorption, more particularly as regards catechol and resorcinol, and similar deviations are shown in the case of velocity of crystallisation. In this connexion the freezing-point curves of the systems benzophenone—catechol and benzophenone—resorcinol have been determined. The curves are very similar, and both show maxima which appear to indicate the existence of compounds containing 2 mols. of benzophenone to 1 mol. of catechol and resorcinol respectively. G. S.

**Ternary Mixed Crystals.** R. SAHMEN (*Zeitsch. physikal. Chem.*, 1912, 79, 421—455).—A theoretical paper in which by means of the thermodynamic potential the temperature-concentration diagrams of two types of ternary system with breaks in the miscibility in the crystalline state are deduced. G. S.

**A More Exact Definition of Colloidal Systems and the Classification of Colloids in General.** P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 197—198).—Polemical against Bottazzi (this vol., ii, 337). H. M. D.

**Ultra-microscopic Structure of Gelatinous Precipitates and of Jellies.** P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 131—132).—In connexion with recent papers by Zsigmondy and by Bachmann (this vol., ii, 145), the author cites his numerous publications on the subject indicated in the title. G. S.

**Theory of Liesegang's Layers.** EMIL HATSCHKE (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 124—126).—The discovery of Liesegang that when reactions take place in organic gels the precipitate often forms in layers has been ascribed by Ostwald to supersaturation phenomena. The author has tested this explanation in the case of lead iodide by adding a little of this substance in crystalline form along with potassium iodide to agar-agar gel, and then pouring over the latter a solution of lead nitrate. It was found that the lead iodide still separates in layers, although supersaturation must be prevented by the presence of crystalline lead iodide throughout the mass, so that Ostwald's explanation is not valid. G. S.

**The Formation of Colloidal Solutions.** NICOLA PAPPADÀ (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 181—182).—In general, hydroxides of the type  $M(OH)_3$  and  $M(OH)_2$  are soluble in ferric chloride solutions. The corresponding metals can, however, be removed by dialysis, ferric hydroxide being the only hydroxide which is present in colloidal form.

Substances containing hydroxyl groups (alcohols, acids, carbohydrates) facilitate the formation of colloidal solutions of Prussian-blue in water. The action is attributed to the formation of unstable compounds by combination of the active substances with the colloid. H. M. D.

**Colloidal Chemistry of Indicators.** WOLFGANG OSTWALD (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 97—104, 132—146).—The experiments described in the paper were undertaken to test the suggestion of the author that changes in molecular complexity may play a part in the changes of colour of indicators. Fifty of the commoner indicators were examined with the ultramicroscope in neutral, acid, and alkaline solutions, and it was found that of these about forty are colloidal in neutral aqueous solution, and that alterations in the degree of dispersion take place when the solutions are made acid or alkaline. In the case of more than forty indicators the particles become more complex both on the addition of acid and of alkali. In the great majority of cases the change of colour of an indicator is accompanied by a change in the degree of dispersion, but the converse does not hold. There is a close connexion between the intensity of fluorescence and the size of the colloidal particles; thus at the same intermediate concentration of alkali, Magdala-red shows a maximum fluorescence and a maximum degree of dispersion.

The rule previously suggested by the author, that the absorption maximum is displaced in the direction of shorter wave-length with increasing degree of dispersion is tested for seventy-six cases of change in colour, the results being tabulated in full. The rule holds in fifty-six cases, does not apply in eight cases, and in twelve cases the results are doubtful. Harrison (this vol., ii, 240) mainly on theoretical grounds has recently thrown doubt on the validity of the above rule, but the author shows experimentally that all the special cases mentioned by Harrison conform to the rule. G. S.

**The Agglutination Optimum in Mixtures of Colloids.** LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1912, 39, 496—506).—From mixtures of amphoteric colloids, it is possible to precipitate a compound, the agglutination optimum for the mixture lying between that of the two components. Within certain limits, this optimal point is independent of the relative amounts of the two colloids present; in the presence of a large excess, however, of one or the other, the optimal agglutination point lies near the isoelectric point of the component, which is in excess. The observation of the optimal agglutination point of the compound is, however, often interfered with if either of the components can be precipitated separately in the neighbourhood of their isoelectric points. The experiments were carried out with mixtures of nucleic acid and various proteins, and of caseinogen and albumin. S. B. S.

**Colloidal Chemistry and the Phase Rule.** II. W. P. A. JONKER (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 126—131. Compare Abstr., 1911, ii, 103).—The phase rule is now applied to colloidal systems of different degrees of complexity. A unitary system can only occur in the case of a substance which exists in two forms, one of which is a colloid, and this form must be capable of existing in stable equilibrium with the other form, the dispersing medium. No such system has yet been discovered; the suggestion of Wo. Ostwald (*Grundriss der Kolloid. Chemie* I, 128) that styrene and metastyrene form such a system is shown to be untenable.

As regards binary systems, the phase rule does not apply to suspensions, which are not true equilibria, but may apply to emulsoids, which form a micro-heterogeneous equilibrium; experimental investigations, however, are still wanting.

A ternary system, water-ether-tannin, in which only one of the components is a colloid, has been investigated. In certain circumstances the system forms three layers, the compositions of which have been investigated at 25°. When the proportion of ether is successively reduced, two layers are first obtained; the composition of the lower one does not alter much as the ether is further reduced, but the upper layer approximates in composition to the lower, and finally the system becomes homogeneous. This behaviour corresponds with the deductions of Schreinemakers on the basis of the phase rule (compare Abstr., 1898, ii, 285).

As the temperature falls, the region of the three-phase equilibrium extends; on the other hand, the region of the two-phase system containing less ether is restricted by lowering the temperature.

The system tannin-water-lithium chloride has also been investigated at 25°; it behaves very similarly to that just described. G. S.

**Principle of the Change of an Equilibrated System under the Influence of an External Agent.** E. VOLCHONSKY (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 305—310).—A theoretical discussion of this question. T. H. P.

**Equilibrium in Heterogeneous Systems at Variable Pressure.** RUDOLF WEGSCHEIDER (*Zeitsch. physikal. Chem.*, 1912, 79, 239—244).—A mathematical paper in which the conditions of equilibrium are deduced in a heterogeneous system where the pressure is uniform in any one phase, but varies from one phase to another. G. S.

**Equilibrium of the System Cadmium Sulphate-Gaseous Hydrogen Chloride.** CAMILLE MATIGNON (*Compt. rend.*, 1912, 154, 772—775. Compare Abstr., 1905, ii, 235; 1908, ii, 465).—Attention has been drawn previously to the approximate constancy of the ratio  $Q/T$ , where  $Q$  is the heat developed in a univariant system during direct reaction between a gas and solid at the absolute temperature  $T$ , when the dissociation pressure is 760 mm. Conclusions may be drawn from this as to the reversibility or otherwise of such systems, and if  $Q$  is known, the dissociation temperature may be calculated approximately. Application to the reaction  $(n+1)\text{CdSO}_4 \text{ sol.} + 2\text{HCl gas} = \text{H}_2\text{SO}_4, n\text{CdSO}_4 \text{ sol.} + \text{CdCl}_2 \text{ sol.}$ , shows that the system is reversible, and that the dissociation temperature should be between 84° and 146°. Experiments have verified these predictions, and given 121° for the dissociation temperature at 760 mm. W. O. W.

**Equilibrium in the Ternary System: Barium Nitrate, Sodium Nitrate, and Water.** ANGELO COPPADORO (*Gazzetta*, 1912, 42, i, 233—242).—The author has investigated the system  $\text{H}_2\text{O}-\text{Ba}(\text{NO}_3)_2-\text{NaNO}_3$ , which is one of the four ternary systems constituting the quaternary system involved in the commercial preparation of barium nitrate from barium chloride and sodium nitrate. The other three systems have been studied by other workers. The results of the author's measurements of the solubility at 0° of the nitrates of barium and sodium in presence of one another, and of the analyses of the respective residues, are given in a table and exhibited on a diagram, from which it appears that the two nitrates do not form a double salt. The diagram further shows that when saturated solutions of barium nitrate and sodium nitrate are mixed, no separation of solid sodium nitrate occurs, no matter how the mixture be effected. R. V. S.

**The System: Water, Alcohol, Manganous Sulphate.** FRANS A. H. SCHREINEMAKERS and J. J. B. DEUSS (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 14, 924—927\*).—The equilibria occurring in the ternary system water, alcohol, and manganous sulphate are

\* and *Zeitsch. physikal. Chem.*, 1912, 79, 554—564.

shown by a diagram, the necessary data having been obtained by measurements at  $0^{\circ}$ ,  $25^{\circ}$ ,  $30^{\circ}$ ,  $35^{\circ}$ , and  $50^{\circ}$ . The diagram is characterised by the occurrence of a binodal surface representing the conditions of co-existence of two liquid layers. On the temperature axis, this region extends from  $5.3^{\circ}$  to  $43.5^{\circ}$ . Whereas, in general, ternary systems of the type—water, alcohol, and a salt—only exhibit a minimum critical mixing temperature, the behaviour of the system containing manganous sulphate shows that both a minimum and a maximum critical temperature may occur in certain cases.

H. M. D.

**Work Done in Chemical Changes.** RUDOLF WEGSCHEIDER (*Zeitsch. physikal. Chem.*, 1912, 79, 223—238).—The work done in an isothermal change against an external pressure has only the value  $RT$  per mol. of gas when the change takes place at constant pressure. The change can only be carried out reversibly at constant pressure in certain special cases.

The maximum work obtainable in a change is made up of a part which can only be obtained by working against an internal pressure and is zero only at constant volume, and a part which can also be obtained in other ways (for example, as *E.M.F.*). Under suitable conditions the latter can also be obtained by working against an external pressure.

Formulae are deduced for the maximum work obtainable in all forms and the maximum work obtainable electrically, and also for the *E.M.F.* of chemical changes, and are applied to the dissociation of a gas and to the reversible oxygen-hydrogen cell.

G. S.

**Theory of Dyeing. Dyeing with Basic Dyes with Subsequent Re-solution.** WILLIAM P. DREAPER and A. WILSON (*J. Soc. Dyers*, 1912, 28, 137—140).—In continuation of previous work on this subject (Dreaper and Wilson, *J. Soc. Chem. Ind.*, 1909, 28, 57; 1910, 29, 1432), the authors have investigated the effect of the addition of a third substance on the amount of dye taken up by the fibre during dyeing, and on the behaviour of the dyed fibre thus obtained towards alcohol and soap solution, the dye employed throughout the investigation being methylene-blue.

It is found that the proportion of dye required in the dye-bath to give a standard shade under standard conditions is not appreciably affected by the addition of sodium carbonate; acid, however, has a marked inhibiting effect; the amount of dye required to give the standard shade increases from about 1% to about 25% as the concentration of the sulphuric acid is increased until the strength of the solution is decinormal, after which the requisite amount of dye decreases on further addition of acid, being about 12% in normal sulphuric acid. Neutral salts, such as sodium chloride and sodium sulphate, also exert an inhibiting effect when added to the dye-bath.

Subsequent treatment of the dyed fibre with a 1% soap solution does not remove so much of the dye as treatment with alcohol when sodium carbonate has been added to the dye-bath, but if acid was present then the soap solution removes a far greater proportion of the dye than the alcohol.

W. H. G.

**Catalysis by Cations.** I. BROR HOLMBERG (*Zeitsch. physikal. Chem.*, 1912, 79, 147—167).—The rate of reaction between sodium dibromosuccinate (the racemic compound) and sodium hydroxide has been investigated in dilute solutions at 25°. Under the conditions of the experiments, the main product of the reaction is sodium bromofumarate. The reaction is bimolecular, but the velocity coefficient is the greater the greater the initial concentration, and it is shown by systematic variation of the concentrations of salt and alkali that this effect is due to a catalytic effect of the cation on the rate of reaction. The acceleration is proportional to the cube-root of the concentration of the cation. Similar experiments have been made with potassium, calcium, and barium salts, with results closely analogous to those obtained with sodium salts. The order of the catalytic activity of the cations is as follows:  $\text{Ca}^{++} > \text{Ba}^{++} > \text{Na}^+ > \text{K}^+$ .

The temperature-coefficients of the reactions have also been measured; the results are not satisfactorily represented by the Arrhenius formula. The catalytic effect of mixtures of salts has also been measured. With sodium and potassium salts the effect is the sum of the separate effects, but sodium with calcium, sodium with barium, and calcium with barium salts have in each case smaller values than the sum of the separate effects.

Corresponding experiments have been made with the sodium and barium salts of isodichlorosuccinic acid, with analogous results.

G. S.

**Law of Molecular Attraction.** RICHARD D. KLEEMAN (*Phil. Mag.*, 1912, [vi], 23, 656).—The conclusion, arrived at by Tyrer (this vol., ii, 136), that the attraction between two molecules is independent of the temperature, is shown to be involved as an assumption in the reasoning which leads up to the conclusion.

H. M. D.

**Determination of the Absolute Value of the Mass of Molecules of Liquids and Particularly of the Mercury Molecule.** ALFRED HENRY (*Compt. rend.*, 1912, 154, 880. Compare Perrin, *Abstr.*, 1908, ii, 927; 1911, ii, 480, 594).—Assuming the absence of friction between molecules, and that the energy absorbed by a molecule passing from the interior to the exterior of a liquid, measured by its internal heat of vaporisation, is twice the energy absorbed by a molecule in passing from the interior to the surface, measured by the surface energy of the molecule, the author calculates  $d$  and  $p$ , the diameter and weight of a molecule of different liquids. For mercury  $d \times 10^8 = 3.48$  cms.,  $p \times 10^{24} = 300$  grams, and the number of molecules in a gram-molecule is  $66.6 \times 10^{22}$ . These numbers agree with those of Perrin, but the following values of  $d \times 10^8$  differ considerably from this author's: chloroform 2.2, ether 2.1, acetone 1.7, water 1.0, and carbon disulphide 0.9 grams.

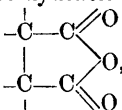
W. O. W.

**Affinity and Valency.** JACOB BÖESEKEN (*Rec. trav. chim.*, 1912, 31, 76—79).—A theoretical paper in which the author puts forward his views as to the spacial arrangement of atoms in molecules. He explains the stereoisomerism of nitrogen and phosphorus compounds on an electrical basis.

W. G.

**The Configuration of Ring Systems. II. Annular Tension.** JACOB BÖESEKEN (*Rec. trav. chim.*, 1912, 31, 80—85. Compare previous abstract).—A theoretical paper in which the author extends his theory to explain the stability of ring systems. W. G.

**The Configuration of Ring Systems. III. The Velocity of Hydration of Some Cyclic Acid Anhydrides.** JACOB BÖESEKEN, A. SCHWEIZER, and G. F. VAN DER WANT (*Rec. trav. chim.*, 1912, 31, 86—100. Compare this vol., ii, 243, and the two previous abstracts).—Rivett and Sidgwick (*Trans.*, 1910, 97, 132, 1677) have measured the rate of hydration of a series of anhydrides all containing the five-atom

ring, , and explain their results on Baeyer's strain theory.

They found, however, anomalous results from the introduction of a methyl group into maleic and succinic anhydrides. The authors have extended this work to other such anhydrides, and explain their results, and also those of Rivett and Sidgwick, on Böesecken's annular tension hypothesis (previous abstract). W. G.

**New Apparatus for Vacuum Sublimation.** GEORGE W. MOREY (*J. Amer. Chem. Soc.*, 1912, 34, 550—552).—Apparatus is described for the sublimation of large quantities of organic substances. It consists of a large bell-jar, 26 cm. in diameter, ground to fit closely on to a glass plate. A large, shallow, crystallising dish, of such a size as just to fit inside the bell-jar, stands on the glass plate, and on it is placed a glass cylinder 10.5 cm. in diameter and 20 cm. high. This cylinder serves as a support for the electrical heater, which is of the ordinary type with an iron top and enamel bottom. The top of the cylinder is ground loosely into the enamel bottom of the hot plate. The wires conveying the current are led in through rubber stoppers which fit into perforations in the glass plate and are inserted far enough to pass into holes in the bottom of the crystallising dish, thus holding the latter in position. The substance to be sublimed is placed in a flat-bottomed platinum or glass dish resting directly on the hot plate. A deep crystallising dish with a hole cut through the bottom to receive the flat-bottomed dish is inverted over the heater in order to prevent the sublimate coming into contact with the hot plate. The bell-jar is connected with the pump through a perforation in the glass plate. The whole is mounted on a wooden base.

The advantages of the apparatus are its convenient form, and the fact that most of the sublimate falls into the crystallising dish and does not come into contact with anything but glass and platinum. The apparatus can be readily calibrated, so that the approximate temperature can be determined by having an ammeter in the circuit.

E. G.

**Barbet Laboratory Rectifying Apparatus.** W. Y. KRSHIS-CHANOWSKY (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 384—395).—Two laboratory spirit rectifiers on the Barbet system were tested. T. H. P.

**Safety Apparatus for Preventing Undue Evaporation or Distillation, also for Automatically Shutting off the Gas Supply at a Given Time.** ERIK SCHIRM (*Zeitsch. anal. Chem.*, 1912, 51, 300—302).—A simplification of the elaborate forms of apparatus for this purpose devised by Geyer (*ibid.*, 1875, 14, 166) and Süss (*ibid.*, 1880, 19, 312).

L. DE K.

**Simple Constant Level Water-bath.** PIERRE MOREL (*Chem. Zentr.*, 1912, i, 457—458; from *Bull. Sci. Pharmacol.*, 1912, 18, 222—223).—A syphon and water reservoir are described, by means of which an ordinary water-bath may be converted into a constant level bath without any permanent attachment, only glass tubes and a glass cylinder being used.

C. H. D.

**Water-bath with Constant Level.** ERIK SCHIRM (*Chem. Zeit.*, 1912, 36, 348).—A modified Mariotte's bottle is employed.

L. DE K.

**A New Drying Apparatus.** CARL WOYTAČECK (*Chem. Zeit.*, 1912, 36, 316).—The apparatus consists of a two-necked Woulfe's bottle, into each neck of which is ground a glass cylinder, which may be filled with calcium chloride, soda lime, or other absorbing agent. The cylinder through which the gas passes into the bottle is prolonged into a tube reaching to the bottom of the bottle. Each cylinder is fitted with a rubber bung through which passes a right-angled tube containing a stopcock.

T. S. P.

**Improved Extraction Apparatus.** THOMAS B. FORD (*J. Amer. Chem. Soc.*, 1912, 34, 552—553).—Apparatus is described which combines the advantages of the Wiley and Soxhlet extractors, consists entirely of glass, is compact, convenient, free from stoppers, seals or ground connexions, and consists of separate parts which are readily accessible for cleaning or repair.

It consists of a straight outer tube into which is fitted a bulb-shaped condenser bearing a small glass hook on its lower end. The extraction tube for holding the material to be extracted is suspended on this hook by means of a semi-circular loop of wire, and is provided with a syphon for intermittent drainage. The solvent is boiled in the outer tube, and the condensed liquid falls into the extraction tube. By this means, the contents of the extraction tube are maintained at a temperature only slightly below the b. p. of the solvent. This is usually an advantage, but it renders the apparatus unsuitable for use with non-homogeneous solvents, such as light petroleum, since the more volatile constituents collect and boil in the extraction tube, whilst the syphon is superheated by the vapours of the higher boiling components and thus becomes inoperative.

E. G.

**Simple Apparatus for Preparing Emulsions.** EMIL HATSCHKE (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 79—80).—A tall graduated glass cylinder is closed by a rubber cork provided with two holes; through one passes a glass tube 3—4 mm. wide and reaching within

2—3 mm. of the bottom of the cylinder, and in the other is inserted the lower end of a wide tube provided with several bulbs. The top of the narrow tube is widened into a small funnel, and a pipette is suspended in such a way that its lower opening touches the inner wall of the funnel. The water and emulsifying substance (soap, etc.) are placed in the cylinder, the wide tube is connected with a filter pump, so regulated that a rapid stream of air is drawn through the liquid, and the oil to be emulsified then slowly added through the pipette.

G. S.

**Some New Forms of Projection Apparatus.** LOUIS M. DENNIS (*J. Amer. Chem. Soc.*, 1912, 34, 418—421).—Some small forms of lecture apparatus are described which enable experiments to be projected on to a screen by means of the lantern, and thus become clearly visible in all parts of the room. The glass tubes employed have the sides flattened and as nearly as possible parallel to one another. Apparatus has been devised for the demonstration of (1) the re-combination of the gases produced by the electrolysis of water and of the fact that there is no residue of gas except when hydrogen or oxygen is present in excess of the relative amount produced by electrolysis; (2) the relative volumes of hydrogen and oxygen, or hydrogen and chlorine, liberated by the electrolysis of water or hydrochloric acid, and (3) the formation of nitric oxide by the decomposition of sodium nitrate by sulphuric acid in presence of mercury.

A method has been devised for projecting the image, by means of a mirror, on to a screen behind the lecturer. An ingenious arrangement is also described for showing to a class Mayer's experiment in which small magnetised steel needles, thrust through disks of cork and floated on water, assume in the magnetic field configurations which vary as the number of needles is changed.

Diagrams are given of the various forms of apparatus described.

E. G.

**Simple Method of Illustrating the Relative Conductivity of Salts and Acids in Dilute Solutions.** WILLIAM M. BLANCHARD (*J. Amer. Chem. Soc.*, 1912, 34, 490—491).—Apparatus is described for lecture demonstration of the relative conductivity of salts in dilute solutions. An ordinary conductivity cell is employed with electrodes consisting of movable platinum disks, and has etched on the exterior a scale from 0 to 50 mm. Two lamps, one of 8-candle and the other of 16-candle power, are fixed one at each end of a block, 25 cm. long, and are connected by wires. The lamps are connected with an ordinary lighting system, and the solutions, of 0.01*N*-strength, are introduced into the cell. One electrode is fixed at the zero mark and the other is raised nearly to the top of the cell. The cell is now brought into the circuit and the upper electrode lowered until the filament of the smaller lamp is faintly but distinctly luminous. The distances between the electrodes for a series of solutions represent the relative conductivities. Some results obtained by this method are appended.

E. G.

## Inorganic Chemistry.

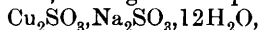
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**Quantitative Composition of the Earth's Crust in Percentage Numbers of Atoms.** ALEX. E. FERSMANN (*Bull. Acad. Sci. St. Pétersbourg*, 1912, [vi], 367—372).—The author has recalculated the tables given by Clarke (*Phil. Soc. Wash.*, 1889; *Bull. Geol. Survey*, 1891, 78, 34, and 1897, 148, 13) and by Vogt (*Zeits. prakt. Geol.*, 1898, 225, 314, 377, 413; *ibid.*, 1899, 10, 274; *ibid.*, 1906, 223) so as to show the percentage numbers of atoms of different elements in the earth's crust. Some of the figures obtained, which bring out more clearly the preponderance of elements of low atomic weights and the small proportions of those of high atomic weights, are as follows: O, 53·81; H, 17·18; Si, 15·85; Al, 4·76; Na, 1·80; Mg, 1·67; K, 1·44, etc. T. H. P.

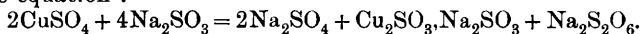
**Synthesis of Hydrogen Peroxide.** FRANZ FISCHER and MAX WOLF (*Ber.*, 1912, 45, 851—852).—Polemical, a reply to de Hemptinne (this vol., ii, 247). D. F. T.

**The Solubility of Ozone in Water.** ED. MOUFANG (*Woch. Brauerei*, 1911, 28, 434—436).—The tabulated results, with description of experiments for determining the solubility of ozone in water. The author draws the conclusion that the solubility is essentially a function of temperature, pressure, and the chemical nature of the water. One litre of water dissolves about 10 mg. of ozone at 2°, but only about 1·5 mg. at 28°. The effect of acids, alkalis, and neutral salts at different temperatures is also discussed, and the results tabulated in the original. F. M. G. M.

**Formation of Dithionic Acid in the Action of Alkali Sulphites on Copper Salts.** HENRI BAUBIGNY (*Compt. rend.*, 1912, 154, 701—703. Compare this vol., ii, 357).—Aqueous solutions of copper sulphate (4 grams) and sodium sulphite (13 grams) were mixed in a sealed tube at the ordinary temperature. After some hours, colourless crystals separated, having the composition



and the solution contained 57·9% of the amount of dithionate required by the equation:



The double sulphite is unstable, and undergoes oxidation with loss of water on exposure to air; it is the precursor of the red substance formed when the two salts are mixed in hot solution. W. O. W.

**Chemically Active Modification of Nitrogen Produced by the Electric Discharge.** III. (Hon.) ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1912, A, 86, 262—269. Compare *Abstr.*, 1911, ii, 482, 678; this vol., ii, 153).—The glow, which accompanies the conversion

of the chemically active modification into ordinary nitrogen, is intensified if the active nitrogen is strongly cooled. The transformation affords, therefore, an example of a chemical change which is accelerated by a fall of temperature. Compression of the glowing gas also leads to an increase in the intensity of the glow, and this indicates that the decomposition of the active nitrogen is a reaction in which two or more molecules are involved.

If the temperature of the active nitrogen is raised to  $100^{\circ}$ , the glow diminishes in intensity, but this is not accompanied by any diminution in the rate of decomposition of the gas. It thus appears that the conversion of active into ordinary nitrogen may take place in two distinct ways. One of these is a volume change, accompanied by the glow effect, the other a glowless transformation in which the surface of the walls of the containing vessel plays a part. H. M. D.

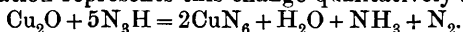
**The Absorption of Ammonia, Alone or with Hydrogen Sulphide, by Sulphurous Acid, with Formation of Ammonium Sulphate and Free Sulphur.** WALTHER FELD (*Zeitsch. angew. Chem.*, 1912, 25, 705—711).—If gas from a coal-retort or coke-oven, containing ammonia and hydrogen sulphide, is passed into a solution of ferrous thiosulphate, ferrous sulphide is precipitated:  $\text{FeS}_2\text{O}_3 + 2\text{NH}_3 + \text{H}_2\text{S} = \text{FeS} + (\text{NH}_4)_2\text{S}_2\text{O}_3$ . The ferrous sulphide is again converted into thiosulphate by dissolving in sulphurous acid:  $2\text{FeS} + 3\text{SO}_2 = 2\text{FeS}_2\text{O}_3 + \text{S}$ . The further reactions which take place are:  $\text{FeS}_2\text{O}_3 + (\text{NH}_4)_2\text{S}_2\text{O}_3 + 3\text{SO}_2 = \text{FeS}_3\text{O}_6 + (\text{NH}_4)_2\text{S}_4\text{O}_6$  (when heated)  $\text{FeSO}_4 + (\text{NH}_4)_2\text{SO}_4 + 2\text{SO}_2 + 3\text{S}$ ;  $\text{FeSO}_4 + 2\text{NH}_3 + \text{H}_2\text{S} = \text{FeS} + (\text{NH}_4)_2\text{SO}_4$ . The sulphur dioxide required is obtained by burning the sulphur and hydrogen sulphide produced.

If, as is usual in coal gas, the ammonia is considerably in excess of the hydrogen sulphide, a solution of ammonium polythionates may be used as absorbing reagent. Hydrogen sulphide is absorbed according to the equation:  $(\text{NH}_4)_2\text{S}_4\text{O}_6 + 3\text{H}_2\text{S} = (\text{NH}_4)_2\text{S}_2\text{O}_3 + 5\text{S} + 3\text{H}_2\text{O}$ . The tetrathionate is also converted into sulphate on heating:  $(\text{NH}_4)_2\text{S}_4\text{O}_6 = (\text{NH}_4)_2\text{SO}_4 + \text{SO}_2 + 2\text{S}$ , and ammonia is then absorbed:  $\text{SO}_2 + \text{S} + 2\text{NH}_3 + \text{H}_2\text{O} = (\text{NH}_4)_2\text{S}_2\text{O}_3$ . Sulphur dioxide, obtained by burning the separated sulphur, again converts the thiosulphate into tri- and tetra-thionate,  $2(\text{NH}_4)_2\text{S}_2\text{O}_3 + 3\text{SO}_2 = (\text{NH}_4)_2\text{S}_3\text{O}_6 + (\text{NH}_4)_2\text{S}_4\text{O}_6$ , and so ultimately into sulphate. The sum of the reactions involved is  $4\text{NH}_3 + 2\text{H}_2\text{O} + 3\text{SO}_2 = 2(\text{NH}_4)_2\text{SO}_4 + \text{S}$ . C. H. D.

**Reduction of Hydronitric Acid [Azoimide]. I. Structure of Hydronitric Acid.** JOHN W. TURRENTINE (*J. Amer. Chem. Soc.*, 1912, 34, 385—387).—The reactions of azoimide are shown to be analogous to those of nitric acid, and the structure of azoimide is therefore represented by the formula  $\text{H}\cdot\text{N}:\text{N}:\text{N}$ , that of nitric acid being  $\text{H}\cdot\text{O}\cdot\text{N}\leq\text{O}$ ; in one case, a quinquevalent nitrogen atom, the nucleus of the molecule, is united to nitrogen, and in the other case to oxygen. This formula for azoimide has already been arrived at by Thiele (*Abstr.*, 1911, i, 845) from organic considerations. E. G.

**Electrochemistry of Hydronitric Acid [Azoimide] and its Salts. II. Reduction of Hydronitric Acid by Cuprous Oxide.** JOHN W. TURRENTINE and RAYMOND L. MOORE (*J. Amer. Chem. Soc.*, 1912, 34, 375—382).—In an earlier paper (Abstr., 1911, ii, 693) it was shown that the corrosion efficiencies of magnesium, aluminium, and zinc exceeded 100% when the metals were used as anodes in a 2% solution of sodium azoimide, and in some cases approached 200%. These results were explained on the assumption that the metals dissolve electrochemically at a valency lower than that usually assigned to them. In all these experiments, nitrogen was evolved at the anode, thus apparently increasing the electrochemical efficiency and indicating that the azoimide ion was being reduced by the magnesian, aluminous, or zincous azoimide.

Experiments have now been made in order to determine whether cuprous oxide would react with azoimide in a similar manner. When 2% azoimide solution is added to yellow cuprous oxide, the latter is rapidly changed to a flocculent substance of darker colour. This substance is an unstable nitrogenous compound (probably cuprous azoimide), which in contact with excess of azoimide undergoes gradual transformation into cupric azoimide. In this reaction the azoimide suffers reduction with formation of ammonia and nitrogen. The following equation represents this change qualitatively:



The transformation takes place more readily in presence of sulphuric acid, and this is probably due to the protective coating of cupric azoimide being constantly removed by solution in the acid. The oxidation of cuprous azoimide by azoimide is greatly accelerated by light.

E. G.

**Action of Hydronitric Acid [Azoimide] on Cuprous Chloride and Metallic Copper.** JOHN W. TURRENTINE and RAYMOND L. MOORE (*J. Amer. Chem. Soc.*, 1912, 34, 382—384).—When cuprous chloride is treated with a dilute solution of azoimide, it loses its white, crystalline form and becomes bulky, yellow, and flocculent. On addition of hydrochloric acid, the substance resumes its original crystalline form. If cuprous chloride is treated repeatedly with fresh portions of the azoimide solution, a substance is produced which resembles that obtained by the interaction of cuprous oxide and azoimide (preceding abstract). This compound is free from chlorine, and appears to be cuprous azoimide.

When 2% solution of azoimide is added to finely-divided copper, nitrogen is slowly evolved, ammonia is produced, and the metal is gradually changed into cupric azoimide. The reaction is represented by the equation:  $\text{Cu} + 4\text{N}_3\text{H} = \text{CuN}_6 + \text{NH}_4\text{N}_2 + \text{N}_2$ .

E. G.

**Reactions in Silicic Acid Gel.** EMIL HATSCHKE (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 77).—The reactions were carried out as follows. To a 15% solution of sodium silicate acid was added in slight excess, and after the silicic acid had completely solidified, an aqueous solution of a salt hypertonic to that of the sodium salt in

the gel was poured over the latter and the reaction allowed to proceed. The acid and the positive ion of the salt were so chosen that a salt formed by double decomposition separated in the solid form in the gel. In this way lead chloride, copper, calcium, and strontium phosphates and calcium sulphate were obtained in crystalline form, the tendency to the formation of large crystals and crystal aggregates being greater in the inorganic gel than in the organic gels previously examined.

G. S.

**Occurrence of Argon in Commercial Oxygen Made from Liquid Air.** GEORGE W. MOREY (*J. Amer. Chem. Soc.*, 1912, 34, 491).—The composition of a sample of liquid oxygen prepared from liquid air has been found to be: O, 96.9%; A, 2.8%; N, 0.3%. This confirms Claude's observation (Abstr., 1910, ii, 1061) that the compressed oxygen of commerce obtained from liquid air contains about 3% of argon.

E. G.

**Solubility of Silver Chloride and Bromide in Sodium Sulphite Solutions.** ROBERT LUTHER and A. LEUBNER (*Zeitsch. anorg. Chem.*, 1912, 74, 389—394).—The silver halide, precipitated from boiling solution and well washed, is digested for an hour with the sulphite solution at 25°. The clear solution is titrated with iodine solution, and the silver is estimated by reducing with hot alkaline quinol, washing the precipitated silver, dissolving it in acid ferric ammonium sulphate, and titrating the ferrous salt formed with permanganate.

Complex ions are thus formed:  $\text{Ag}^+ + 2\text{SO}_3^{''} = \text{Ag}(\text{SO}_3)_2^{'''}$ . The constant  $[\text{Ag}(\text{SO}_3)_2^{''}]/[\text{Ag}^+][\text{SO}_3^{''}]^2$  has the value  $2.5 \times 10^8$  at 25°. The solubility of the silver halides is thus proportional to the concentration of the sulphite, as found by Valenta (Abstr., 1894, ii, 418).

C. H. D.

**The Constitution of Photohalides. III.** WILLEM REINDERS (*Chem. Weekblad*, 1912, 9, 247). ADRIAN P. H. TRIVELLI (*ibid.*, 248—257).—A continuation of this controversy (compare Reinders, Abstr., 1910, ii, 1062; 1911, ii, 39, 490; Trivelli, Abstr., 1911, ii, 281; this vol., ii, 158).

A. J. W.

**The Constitution of Portland Cement Clinker. II.** ERNST JÄNECKE [with K. H. SCHUMANN (*Zeitsch. anorg. Chem.*, 1912, 74, 428)].—The crystals of the compound  $8\text{CaO} \cdot 2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$  (this vol., ii, 159) have been examined in thin sections, and are found to be either rhombic or monoclinic, with refractive index  $>1.54$ . It is easily detected in ordinary Portland cement clinker, of which it forms the principal constituent

C. H. D.

**The Purity of Commercial Metals.** FRANZ MYLIUS (*Zeitsch. anorg. Chem.*, 1912, 74, 407—427).—An examination has been made of the principal metals supplied by Kahlbaum, in order to determine the total proportion of impurities in each. In the estimation of such small quantities of impurities, the removal of the principal metal is of chief importance, and it is necessary to avoid the formation of amorphous

precipitates. This involves the use of crystallisation processes, wherever possible. The following methods are recommended.

Zinc is dissolved in a mixture of nitric and sulphuric acids and saturated with ammonia, and a solution of hydrogen sulphide is then added until a further addition produces a white precipitate. The filtrate is evaporated just to dryness and dissolved in sulphuric acid, and the zinc is then separated by fractional crystallisation of the ammonium zinc sulphate. Antimony and arsenic are estimated in the mother liquor, whilst lead, cadmium, and copper are contained in the first sulphide precipitate. The zinc examined contains only 0.008% of impurities.

Cadmium is best separated as nitrate,  $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , as this salt is not isomorphous with other nitrates, and 97% of the metal may be removed by crystallisation from a solution containing free nitric acid. The mother liquor is then converted into sulphate, the lead extracted with ammonium acetate, and ammonia added to precipitate iron, the copper being estimated colorimetrically in the filtrate, cadmium and zinc precipitated with hydrogen sulphide, and other sulphides thrown down after acidifying. The cadmium examined does not contain more than 0.006% of impurities.

Tin is best separated by crystallising the double salt,  $(\text{NH}_4)_2\text{SnCl}_6$ , from a solution containing an excess of ammonium chloride. The final mother liquor, containing only 1–2% of the tin, is precipitated with hydrogen sulphide. The electrolytically purified tin contains about 0.006% of impurities, and lead only 0.002%, in addition to a minute quantity of oxide.

The following metals are commercially obtainable with less than 0.01% of impurities: gold, silver, platinum, mercury, copper, tin, lead, cadmium, and zinc. It is pointed out, however, that even this quantity is not negligible in many physical determinations, although it is practically without influence on the melting point. C. H. D.

**Ammonia System of Acids, Bases, and Salts.** EDWARD C. FRANKLIN (*Amer. Chem. J.*, 1912, 47, 285–317. Compare Franklin and Kraus, *Abstr.*, 1899, ii, 284; 1900, ii, 382; Franklin and Stafford, 1902, i, 748; Franklin, 1905, ii, 581).—Franklin and Kraus pointed out the analogies between liquid ammonia and water as electrolytic solvents, and showed that metathetic reactions take place in the former solvent as in the latter. Franklin subsequently formulated a system of acids, bases, and salts on the basis of ammonia as the typical substance, and in a manner analogous to the formulation of the ordinary system of oxygen acids, bases, and salts as derivatives of water. In the present paper, the system is further developed, and the relationships previously indicated are shown to be fully justified.

*Potassium ammonio-cadmiate*,  $\text{Cd}(\text{NHK})_2 \cdot 2\text{NH}_3$ , obtained by adding potassamide to cadmium iodide or nitrate in liquid ammonia, corresponds with the potassium ammonio-zincate described by Fitzgerald (*Abstr.* 1907, ii, 546).

When cuprous nitride is treated with a solution of potassamide in liquid ammonia, *potassium ammonio-cuprite*,  $\text{CuNK} \cdot 2\frac{1}{2}\text{NH}_3$ , is

produced in the form of colourless crystals, which readily lose  $1\frac{1}{2}$  mols. of ammonia, the remaining mol. being retained up to  $200^{\circ}$ .

By the action of potassamide on black thallium nitride in liquid ammonia, *potassium ammonio-thallate*,  $\text{TlNK}_2 \cdot 4\text{NH}_3$ , is obtained, which loses 2 mols. of ammonia when warmed to the ordinary temperature, and if heated at  $100^{\circ}$  is converted into  $\text{TlNK}_2 \cdot 1\frac{1}{3}\text{NH}_3$ .

It is suggested that the various mercury ammonia compounds described in the literature should not be regarded as ammonium salts in which the hydrogen is replaced by mercury, but either as normal mercuric salts with ammonia of crystallisation or as basic products resulting from the ammonolysis, or combined ammonolysis and hydrolysis, of the normal mercuric salts.

E. G.

**Influence of Non-electrolytes on the Solubility of Lead Chloride.** GIUSEPPE KERNOT and UMBERTO POMILIO (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1911, [iii], 17, 353—358).—The authors have investigated the influence of the presence of mannitol and of ethyl alcohol on the solubility of lead chloride. Mannitol increases the solubility of the salt, whilst ethyl alcohol diminishes it. In both cases irregularities are observed, probably owing to secondary actions, and the formula of Rothmund (Abstr., 1909, ii, 980) does not agree with the results obtained.

R. V. S.

**Lead Silicates. II. Optical and Thermal Analysis of the System  $\text{PbO-SiO}_2$ .** HERMON C. COOPER, EDWARD H. KRAUS, and A. A. KLEIN (*Amer. Chem. J.*, 1912, 47, 273—285).—Cooper, Shaw, and Loomis (Abstr., 1909, ii, 1009) prepared various lead silicate mixtures by fusing lead oxide and finely powdered quartz, and from a study of the heating curves and m. p. curve proved the existence of two definite compounds,  $2\text{PbO} \cdot \text{SiO}_2$  and  $\text{PbO} \cdot \text{SiO}_2$ . This result has been confirmed by the work of Hilpert and Weiller (Abstr., 1909, ii, 890) and Hilpert and Nacken (Abstr., 1910, ii, 955), which also indicates the probable existence of the compounds  $3\text{PbO} \cdot 2\text{SiO}_2$  and  $3\text{PbO} \cdot \text{SiO}_2$ .

A further thermal study of the system  $\text{PbO-SiO}_2$  and an optical investigation of the products of fusion and also of the minerals belonging to the system, have established the existence of the compounds  $\text{PbO} \cdot \text{SiO}_2$ ,  $2\text{PbO} \cdot \text{SiO}_2$ , and  $3\text{PbO} \cdot 2\text{SiO}_2$ . The properties of the first two compounds correspond with those of alamosite and barysillite respectively. The existence of the compound  $3\text{PbO} \cdot \text{SiO}_2$  is rendered probable by its sharp m. p. and peculiar optical character under the microscope. A specimen of lead silicate found under the hearth of a dismantled lead furnace appeared to be a complex and variable solid solution of somewhat variable and ill-defined crystallographic properties.

E. G.

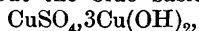
**Dissolution of Copper in Water.** J. PIONCHON (*Compt. rend.* 1912, 154, 865—867. Compare *ibid.* 1911, 153, 47).—If two copper plates in circuit with a sensitive galvanometer are immersed in water so as to form a pile, the electromotive force, if perceptible, is very small and rapidly becomes constant. On tapping one of the plates, the

galvanometer shows a marked deflexion every time the process is repeated, but the pile becomes less sensitive, and finally no deflexion is produced on tapping. The sensitiveness to shock is restored, however, by changing the water. This experiment suggests that the tapped plate loses copper ions more rapidly than the other, and that copper must pass into solution. Chemical tests give no indication of this, but the presence of copper is shown by the fact that after shaking with iron filings, the water regains its activity.

This method may be employed to ascertain whether water has been in contact with copper. W. O. W.

**Some Basic Copper Compounds.** WALTER F. A. ERMEN (*J. Soc. Chem. Ind.*, 1912, 31, 312—314. Compare Pickering, *Trans.*, 1907, 91, 1981).—Using *N*/10-solutions of the reagents, it is found that no matter whether sodium hydroxide is added to copper sulphate until all the copper is precipitated, or copper sulphate is added to sodium hydroxide until copper just begins to appear in the solution, the reacting quantities are always the same, namely, two molecules of copper sulphate and three of sodium hydroxide, the precipitate formed being the blue basic sulphate,  $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$ . The same result is obtained when the copper sulphate solution is kept boiling during the addition of the sodium hydroxide; if, however, copper sulphate solution is run into a boiling solution of sodium hydroxide, the black hydrated oxide is first formed, and this is not completely transformed into the blue basic sulphate, even on prolonged boiling. Indications of the existence of a green basic salt containing 3.5 atoms of copper to one  $\text{SO}_4$ -group have also been obtained.

When cold dilute solutions of copper sulphate and sodium carbonate are mixed until all the copper has been precipitated, or just ceases to be precipitated, one molecule of each reagent has reacted, but the carbonate initially formed breaks down at once and gives the blue basic carbonate,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$ . This loses water and turns green on standing, forming malachite,  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ ; treatment with sodium hydroxide removes all the carbonate. The addition of copper sulphate to boiling sodium carbonate solution gives black copper oxide, which is not further acted on by copper sulphate. When, however, sodium carbonate is run into boiling copper sulphate solution, not carbonate, but the blue basic sulphate,



is precipitated. The reactions are similar when sodium carbonate is replaced by sodium hydrogen carbonate.

When copper sulphate solution is added to a solution of ammonium hydroxide until a permanent precipitate is produced, one molecule of copper sulphate has reacted with four molecules of ammonia. The further addition of copper sulphate until the solution becomes colourless gives rise to the basic sulphate,  $\text{CuSO}_4 \cdot 2\text{Cu}(\text{OH})_2$ . The reaction is the same whether the copper sulphate is run into the ammonium hydroxide solution, or vice versa, and whether the copper sulphate is hot or cold in the latter case.

The compound  $\text{CuSO}_4 \cdot 4\text{NH}_3 \cdot \text{H}_2\text{O}$  is precipitated by the saturation of a copper sulphate solution with ammonia. It may also be obtained

by triturating crystallised copper sulphate with, or by adding anhydrous copper sulphate to, strong ammonia solution. It is also formed when  $\text{CuSO}_4 \cdot 5\text{NH}_3$  is exposed to moist air. T. S. P.

**The Action of the "Luminator" Apparatus for Treating Hard Water.** S. SUGDEN (*Chem. News*, 1912, 105, 161).—Hard water is allowed to flow over a polished aluminium plate, and although chemical action cannot be detected, the water deposits a soft mud in place of a hard scale when subsequently boiled. It is found that if polished aluminium foil is placed in a saturated solution of calcium sulphate, the crystals obtained on boiling down the solution contain less water than usual, and have the composition  $3\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

C. H. D.

**Influence of Painting on the Rusting of Iron.** KURT ARNDT (*Zeitsch. Elektrochem.*, 1912, 18, 233—234).—In connexion with the recent paper of Liebreich and Spitzer on this subject (compare this vol., ii, 259), the author shows from the literature that it has been by no means neglected, as these observers state. It is suggested that the coating may have got slightly loosened from the polished iron plates used by Liebreich and Spitzer, thus allowing the entry of air and moisture, and the employment of rough surfaces in the experiments is recommended.

G. S.

**Solubility of Wrought Tungsten and Molybdenum.** W. E. RUDER (*J. Amer. Chem. Soc.*, 1912, 34, 387—389).—An account is given of the action of various acids and other reagents on wrought tungsten and molybdenum. Both metals are found to be somewhat resistant to acids, owing to the formation of a coating of oxide. Tungsten is most rapidly attacked by fuming sulphuric acid, but, even in this case, only 1.2% was dissolved in eight hours. Molybdenum is more easily dissolved than tungsten, but it is fairly resistant to concentrated hydrochloric acid at temperatures below  $125^\circ$  and is not affected by hydrofluoric acid. The metals are not attacked by solutions of potassium hydroxide, but are gradually dissolved by the fused alkalis.

E. G.

**The Constitution of the Metatungstates.** HIPPOLYTE COPAUX (*Zeitsch. anorg. Chem.*, 1912, 74, 351—364).—A further reply to Rosenheim's views (Abstr., 1911, ii, 612) of the constitution of the metatungstates (compare Abstr., 1911, ii, 402). A new estimation of the water in barium metatungstate gives figures varying between 55 and  $56\text{H}_2\text{O}$ , which is higher than that assumed by Rosenheim. Determinations of the heat of neutralisation and titration experiments confirm the octabasic character of silicotungstic acid and the hexabasic character of metatungstic acid, but give abnormal results with phosphotungstic acid.

Attempts to prepare mercurous metatungstate and mercurous phosphotungstate were unsuccessful, mixtures of variable composition being obtained. Determinations of the electrical conductivity and

cryoscopic behaviour of the complex tungstates are also considered to favour the author's views. C. H. D.

**Explosibility of Uranium Nitrate.** W. N. IWANOFF (*Chem. Zeit.*, 1912, 36, 297. Compare Jost, this vol., ii, 224).—Some crystals of pure uranium nitrate, which were not quite dry, had been preserved by the author in a tightly stoppered bottle for three years in a dark cupboard. Neither the appearance of the crystals nor the analysis pointed to any change in composition, but on being weighed out slight detonations occurred; these detonations were very marked on shaking the crystals in a flask containing water. In the dark, the explosion of each crystal was seen to be accompanied by a bright light. There was no spinthariscopes effect, using barium platino-cyanide on the screen; light was produced, however, when a crystal of the salt fell on the screen. Freshly prepared crystals of uranium nitrate were not so active, and water produced no explosion. Both the old and fresh crystals showed the same triboluminescence. T. S. P.

**Some New Double Uranium Nitrates.** ANDRÉ LANCIEN (*Chem. Zentr.*, 1912, i, 208—209; from *Bull. Sci. Pharmacol.*, 1912, 18, 213—216).—*Cadmium uranyl nitrate*,  $\text{UO}_2(\text{NO}_3)_2 \cdot \text{Cd}(\text{NO}_3)_2 \cdot 30\text{H}_2\text{O}$ , forms yellow needles, and loses  $10\text{H}_2\text{O}$  in a vacuum over sulphuric acid. *Nickel uranyl nitrate*,  $3\text{UO}_2(\text{NO}_3)_2 \cdot 10\text{Ni}(\text{NO}_3)_2$ , forms greenish-yellow needles. *Rhodium uranyl nitrate*,  $2\text{UO}_2(\text{NO}_3)_2 \cdot \text{Rh}_2(\text{NO}_3)_6 \cdot 10\text{H}_2\text{O}$ , forms orange leaflets, and loses  $5\text{H}_2\text{O}$  in a vacuum. C. H. D.

**Reducing Power of Stannous Chloride in the Fused State.** CARLO SANDONNINI and P. C. AUREGGI (*Gazzetta*, 1912, 42, i, 227—233).—Fused stannous chloride reacts energetically with various metallic salts. The experiments here recorded were carried out with anhydrous materials in an atmosphere of dry nitrogen. In the case of barium sulphate, stannic chloride is evolved, and in the residue stannous chloride, stannic oxide, and stannous sulphide were recognised in addition to barium salts soluble in water. The reactions which probably occur are represented by the equations:  $2\text{BaSO}_4 + 2\text{SnCl}_2 = \text{SnCl}_4 + \text{SnO}_2 + 2\text{BaSO}_3$ ;  $4\text{BaSO}_3 = 3\text{BaSO}_4 + \text{BaS}$ ;  $\text{BaS} + \text{SnCl}_2 = \text{BaCl}_2 + \text{SnS}$ . It is possible that the reaction indicated by the equation:  $2\text{BaSO}_3 + 6\text{SnCl}_2 = 3\text{SnCl}_4 + 3\text{SnO}_2 + 2\text{BaS}$  also takes place.

With silver sulphate, stannic chloride is evolved, together with sulphur dioxide. The aqueous solution of the residue contains only a little stannous chloride, whilst the insoluble portion contains stannic oxide, silver and silver sulphide. The probable reactions are represented by the equations:  $2\text{Ag}_2\text{SO}_4 + 2\text{SnCl}_2 = \text{SnCl}_4 + \text{SnO}_2 + 2\text{Ag}_2\text{SO}_3$ ;  $2\text{Ag}_2\text{SO}_3 = \text{Ag}_2\text{SO}_4 + 2\text{Ag} + \text{SO}_2$ ;  $2\text{Ag}_2\text{SO}_3 + 6\text{SnCl}_2 = 3\text{SnCl}_4 + 3\text{SnO}_2 + 2\text{Ag}_2\text{S}$ .

In the case of copper sulphate, sulphur dioxide is also evolved, and in the solid residue stannic oxide and cuprous sulphide can be detected. It is probable that the first phase of the reaction proceeds according to the equation:  $2\text{CuSO}_4 + 2\text{SnCl}_2 = \text{SnCl}_4 + \text{SnO}_2 + 2\text{CuSO}_3$ ; the sulphite (which is not known in the pure state) then decomposes into copper oxide, sulphur dioxide, and sulphur, and in part regenerates the sulphate.

The reduction of cadmium sulphate is similar to that of copper sulphate.

The reaction of stannous chloride with barium sulphate may be employed for the purposes of qualitative analysis. It is only necessary to heat a mixture of barium sulphate and stannous chloride (5 mols.) in a porcelain dish until no more stannic chloride is evolved. From the solution of the residue, the excess of stannous chloride is precipitated, and the liquid then contains all the barium in solution.

R. V. S.

**Hydrates of Zirconium Oxychloride.** ÉDOUARD CHAUVENET (*Compt. rend.*, 1912, 154, 821—823).—The curve obtained by plotting heats of dissolution for different mixtures of zirconium oxychloride and water shows angular points corresponding with the existence of hydrates with 2, 3·5, 6 and 8H<sub>2</sub>O. An aqueous solution of zirconium tetrachloride deposits the octahydrate in needles, the composition of which is not altered by boiling the solution.

This hydrate is also precipitated when hydrochloric acid is added to its concentrated aqueous solution. In dry air it effloresces, forming the hexahydrate, whilst in a vacuum it yields the hydrate with 3·5H<sub>2</sub>O. The dihydrate is obtained by heating the preceding hydrates at 100—150° in a current of hydrogen chloride.

No evidence could be obtained for the existence of hydrates with 3, 4·5, 6·5 or 9H<sub>2</sub>O, described by other observers. These substances were probably mixtures.

W. O. W.

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## Mineralogical Chemistry.

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**Trans-Baikal Minerals.** S. D. KUSNETZOFF (*Bull. Acad. Sci. St. Pétersbourg*, 1912, [vi], 361—366. Compare Abstr., 1911, ii, 1004).—The following minerals are described :

Thorianite, with the composition :

ThO.	UO <sub>2</sub> .	Ceria earths.	Fe <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub> .	Total.
74·2	14·1	6·3	3·1	0·80	98·5

Monazite, with the composition :

P <sub>2</sub> O <sub>5</sub> .	Ce <sub>2</sub> O <sub>3</sub> .	La <sub>2</sub> O <sub>3</sub> .	Di <sub>2</sub> O <sub>3</sub> .	ThO <sub>2</sub> .	Y <sub>2</sub> O <sub>3</sub> and Er <sub>2</sub> O <sub>3</sub> .	SiO <sub>2</sub>	H <sub>2</sub> O.	Total.
27·50	27·10	30·80	2·00	8·20	2·50	1·65	0·75	100·50

T. H. P.

**New Manganese Phosphates from California.** WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1912, 2, 143—145).—The minerals described are from the gem-tourmaline mines at Pala, San Diego Co.

*Palaite*.—A flesh-coloured mineral,  $5\text{MnO}, 2\text{P}_2\text{O}_5, 4\text{H}_2\text{O}$  (anal. I), resulting from the alteration of lithiophilite, and itself altering to hureaulite. It forms crystalline masses, with distinct crystals (probably monoclinic) in the cavities.  $D\ 3.14\text{--}3.20$ ,  $n\ 1.655$  about, birefringence low.

*Stewartite*.—A hydrous manganese phosphate occurring abundantly in the Stewart mine as an alteration product of lithiophilite. It forms fine fibres arranged normally to the cleavage cracks of the lithiophilite, and small crystals (probably triclinic) were also observed.  $D\ 2.94$ ,  $n\ 1.65$  about, birefringence very high, pleochroic (colourless to yellow). Being intermixed with the other minerals, a pure sample could not be obtained for analysis.

*Salmonsitz*.—This occurs as buff-coloured cleavable masses, and results from the partial oxidation and hydration of hureaulite.  $D\ 2.88$ ,  $n\ 1.66$  about. Formula,  $\text{Fe}_2\text{O}_3, 9\text{MnO}, 4\text{P}_2\text{O}_5, 14\text{H}_2\text{O}$  (anal. II.).

*Sicklerite*.—Dark brown, cleavable masses with pale yellowish-brown streak, resulting from the alteration of lithiophilite.  $D\ 3.45$ ,  $n\ 1.74$  about, birefringence moderate, pleochroic (yellow to brown). Formula,  $\text{Fe}_2\text{O}_3, 6\text{MnO}, 4\text{P}_2\text{O}_5, 3(\text{Li}, \text{H})_2\text{O}$  (anal. III.).

	$\text{P}_2\text{O}_5$	$\text{Fe}_2\text{O}_3$	$\text{Mn}_2\text{O}_3$	$\text{FeO}$	$\text{MnO}$	$\text{CaO}$	$\text{Li}_2\text{O}$	$\text{H}_2\text{O}$ ( $110^\circ$ )	$\text{H}_2\text{O}$ ( $>110^\circ$ )	Insol.	Total.
I.	39.02	0.16	—	7.48	40.87	1.77	trace	—	10.43	0.89	100.62
II.	34.86	9.53	—	0.13	37.74	1.06	—	0.43	15.30	1.40	100.45
III.	43.10	11.26	2.10	—	33.60	0.20	3.80	—	1.71	4.18	99.95

L. J. S.

### Physiological Chemistry.

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The Influence of Muscular Activity on the Alveolar Tensions of Oxygen and Carbon Dioxide. THEODORE HOUGH (*Amer. J. Physiol.*, 1912, 30, 18—36).—An improvement in Haldane's method of collecting alveolar air is described, which is stated to give more accurate results. Moderate muscular work increases the alveolar tension of both gases, and the increase of carbon dioxide tension stimulates the respiratory centre. After the work there is no secondary fall of carbon dioxide tension; this confirms the results of Haldane and Douglas. With greater intensity of work, the alveolar tension of carbon dioxide falls immediately afterwards, and that of oxygen rises. This persists for twenty to thirty minutes.

W. D. H.

The Physiological Effects of Low Atmospheric Pressures as Observed on Pike's Peak, Colorado. C. GORDON DOUGLAS, JOHN S. HALDANE, YANDELL HENDERSON, and EDWARD C. SCHNEIDER (*Proc. Roy. Soc.*, 1912, 85, B, 65—67).—The stay at Pike's Peak

(14,000 feet above sea level, barometric pressure 457 mm.) lasted five weeks. The usual symptoms produced by low pressure were observed until acclimatisation occurred, signs of which began to appear in two or three days. The symptoms are all referable to lessened pressure of oxygen, and they disappeared after acclimatisation, except that hyperpnœa on exertion or on holding the breath for a few seconds lasted longer than usual. Periodic breathing was still seen occasionally, and blueness of the face and lips was present after powerful exertion. The respiratory exchange during rest was about the normal, and that during work was not markedly increased. Pulse and blood pressure were but little affected.

After acclimatisation, the alveolar carbon dioxide pressure fell from 40 to 27 mm. during rest or moderate exertion, which corresponded with an increase of about 50% in pulmonary ventilation. During severe exertion, this pressure was about half of what it normally is during similar exertion, which corresponded with an increase of 100% in the hyperpnœa. This change occurred gradually after going up, and disappeared gradually on coming down, the change taking a few days to reach completion. There was a considerable increase, which varied in the different members of the expedition, in the red corpuscles, and in the hæmoglobin of the blood; this occurred during the first three weeks. There was in addition (except in the first week) a slight increase in the volume of the blood. On coming down these changes gradually disappeared, and the normal was reached in about four weeks.

The oxygen pressure in the arterial blood rose during rest to about 35 mm. above the alveolar oxygen pressure (66% higher), and remained at a level of 12 mm. below the normal oxygen pressure at sea level. Immediately after the ascent, this pressure was 45 mm. below normal, and only slightly above the alveolar oxygen pressure. This is interpreted as due to a progressive increase in the activity of the alveolar epithelium in secreting oxygen inwards. On raising the alveolar oxygen pressure to normal, the difference between alveolar and arterial oxygen pressure diminished rapidly.

Acclimatisation thus depends on (1) increased lung ventilation, (2) increase of hæmoglobin, and (3) increased secretory activity of the pulmonary epithelium. This all takes time to develop, and in rapid ascents in balloons or aeroplanes would not occur.

W. D. H.

**The "Back Action" and "After Action" of Carbon Dioxide and the Biological Importance of the Carbonic Acid Normally Present in the Body.** P. ALBITZKY (*Pflüger's Archiv*, 1912, 145, 1—20).—A dissertation on the effects of carbonic acid, toxic and useful. Under the latter head the part it plays in respiration is especially dwelt on.

W. D. H.

**The Respiratory Exchange in Animals from which the Pituitary Body has been Removed.** R. ASCHNER and OTTO PORGES (*Biochem. Zeitsch.*, 1912, 39, 200—204).—The pituitary body was removed from a dog, which after the operation showed the known

characteristic of hypopituitarism. The measurements of the respiratory exchanges in such an animal indicated, as in the case of hypothyroidism, a general depression of metabolic processes. S. B. S.

**Composition of the Blood Gases during the Respiration of Oxygen.** GEORGE A. BUCKMASTER and JOHN A. GARDNER (*Proc. Roy. Soc.*, 1912, 85, B, 56—64).—From the analyses recorded from the examination of the blood of cat and man, the following conclusion is drawn: the inhalation of oxygen does not materially augment the quantity of this gas in the blood, or its average content of carbon dioxide. W. D. H.

**Manganese Normally in the Blood.** GABRIEL BERTRAND and FLORENTIN MEDIGRECEANU (*Compt. rend.*, 1912, 154, 941—943).—Employing the colorimetric method for the estimation of manganese (Abstr., 1911, ii, 542), human blood has been found to contain manganese to an extent not exceeding 0.02 mg. per litre. The amount in the blood of horses, oxen, pigs, rabbits, ducks, and hens is about the same, whilst that in sheep does not exceed 0.06 mg. per litre. Most of the manganese occurs in the plasma; the element is not present in hæmoglobin. W. O. W.

**The Adrenaline Content of the Blood.** JAMES M. O'CONNOR (*Arch. exp. Path. Pharm.*, 1912, 67, 195—232).—In the act of coagulation, substances originate which act like adrenaline; correct values for the adrenaline content of the blood in various districts of the circulation cannot therefore be obtained by examining the serum; the plasma itself must be investigated. In the plasma of the suprarenal vein, adrenaline can be readily identified, and its amount is stated to vary between one in a million and one in five millions. In other parts of the circulation, its detection is not possible; the tissues appears to destroy it very rapidly. W. D. H.

**The Calcium Content of the Cell-nucleus.** CLEMENS HÖRHAMMER (*Biochem. Zeitsch.*, 1912, 39, 270—279).—Blood corpuscles which contain a nucleus (fowl's blood), also contain calcium. Those corpuscles which are nucleus-free (ox-blood) are free from calcium. Nevertheless, both kinds behave similarly when placed in oxalate solutions, the action of which is similar to normal Ringer's fluid. On the other hand, certain other cells, which contain both a nucleus and calcium, are injured by oxalate. The author draws the conclusion that in those nucleus-containing cells which are not injured by oxalates, the nucleus plays only a subsidiary part in the vital processes. S. B. S.

**The Presence of Prothrombin and Thromboplastin in the Blood Platelets.** STANHOPE BAYNE-JONES (*Amer. J. Physiol.*, 1912, 30, 74—79).—By experiments with solutions of pure fibrinogen and isolated blood-platelets, it is shown, in confirmation of Morawitz, that the latter contain a substance (prothrombin) which after activation with calcium clots fibrinogen. Extracts of the platelets also contain a substance (thromboplastin) which causes the clotting of 'peptone'

plasma, presumably by neutralising the antithrombin present in such plasma. Disintegration and solution of the platelets when the blood is shed helps blood-clotting by liberating prothrombin and thromboplastin.  
W. D. H.

**The Enzymes of Rennet.** W. VAN DAM (*Bied. Zentr.*, 1911, 40, 856—859; from *Verslagen Landbouwkundige Onderzoek. Rijkslandbouwproefstat.*, 1910, 8).—The author ascribes the rennetic and proteolytic power of an extract of calf's stomach, not to the action of pepsin, chymosin, parachymosin, and the enzyme found by Petry, but to one and the same enzyme, the character of the change induced being determined by the conditions obtaining during the course of any given experiment. When a solution of pepsin from a calf's stomach is subjected to heat, the rennetic power is suspended, but can be recovered by dialysis in slightly acidified rain water, precipitation with solid ammonium sulphate, and further dialysis of the precipitate in 0.2% hydrochloric acid. This suspension of the rennetic power may be due to the presence of impurities.

Pepsin from pig's stomach is extremely sensitive towards alkaline or even neutral reaction. Since milk contains free hydroxyl ions, it is possible for the enzyme to be destroyed at the usual temperature (37.5°) observed in quantitative tests. Enzyme digested at the above temperature with 0.2% hydrochloric acid is also greatly affected, and this action is increased with further rises in temperature. The time for coagulation at body temperature is therefore not a trustworthy measure of the quantity of coagulation enzyme in pepsin solutions obtained from pig's stomach.  
H. B. H.

**Human Pancreatic Juice.** VI. JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1912, 39, 302—323).—The trypsin of human pancreatic juice, obtained from a fistula, becomes inactive when kept. In the course of three years the number of units, determined by the Fuld-Gross method, diminished only from between 125 and 250 units to 62.5. The juice undergoes proteoclastic change, as ascertained by the diminution of the coagulable proteins and the tryptophan reaction. It contains in addition to trypsin, also erepsin and a peptolytic ferment. The former, the action of which on Kühne's amphopeptone was investigated, differs from trypsin in that it is active even in juices, in which the trypsin is still inactive. The latter ferment becomes, however, spontaneously active when kept. Furthermore, whereas the action of trypsin is inhibited by dog's serum, the action of erepsin is accelerated. The other proteoclastic (peptolytic) ferment was investigated by ascertaining its action on glycyltyrosine. It also differs from erepsin, in that its action is inhibited by serum. Nuclease is absent in human pancreatic juice. The quantities of diastase and lipase were also investigated. Human pancreatic juice, like that of the dog, exerts a mydriatic action. Analyses of the chemical composition of the juice are given.  
S. B. S.

**The Influence of Serum and the Expressed Juices of Organs on the Fat-splitting Ferments.** D. MINAMI (*Biochem. Zeitsch.*, 1912, 39, 392—499).—In experiments carried out on the

action of pancreatic lipase and steapsin on monobutyrim, it was found that blood, liver, and muscles contain substances which activate the ferment. The action is not due to the salts in the preparations, and the actual nature of the activator is unknown. S. B. S.

**The Relationship between the Pancreas and Suprarenals.** D. MINAMI (*Biochem. Zeitsch.*, 1912, 39, 381—391).—In view of recent theories as to the connexion between the pancreas and suprarenals, experiments were carried out on dogs with pancreatic fistulæ to determine whether any relationship existed between the amounts of mydriatic substance secreted by the pancreas and changes in the suprarenals. The mydriatic effect was tested on the enucleated frog's eye. The author was unable to confirm the statement of Pick and Glaessner that the chromaffinic substance of the suprarenals disappears when a pancreatic fistula has been made. Neither could he trace any relationship between the amount of mydriatic substance secreted and the quality of the diet taken by the animals, or the amounts of ferments in the pancreatic juice. He doubts, furthermore, whether any relation exists between the mydriatic substance of the pancreatic juice and adrenaline. S. B. S.

**Action of Intestinal and Pancreatic Extracts on Various Organic Derivatives.** ERNEST GÉRARD and J. LEROY (*J. Pharm. Chim.*, 1912, [vii], 5, 329—336).—A résumé of previous work on the action of animal extracts on chemical compounds is first given, and it is then shown that aqueous extracts of (1) the small intestine and (2) mixed aqueous extracts of the small intestine and the pancreas hydrolyse (*a*) alkyl esters, such as salol and methyl salicylate, (*b*) amides, such as oxamide and succinamide, (*c*) anilides, such as acetanilide and propylacetanilide, but not isopropylacetanilide, (*d*) ureides, such as oxaluric acid, (*e*) nitriles, such as acetonitrile and lactonitrile, (*f*) oximes, such as acetaldoxime and benzaldoxime, (*g*) imides, such as succinimide. Under the conditions of these experiments the products of hydrolysis could be detected after three hours, but could not be found when extracts in which the enzymes had been destroyed by boiling were used. T. A. H.

**Fasting Studies. VII. The Putrefaction Processes in the Intestine of a Man during Fasting and during Subsequent Periods of Low and High Protein Ingestion.** C. P. SHERWIN and PHILIP B. HAWK (*J. Biol. Chem.*, 1912, 11, 169—178).—The subject of the experiment was a man weighing 76 kilos. Intestinal putrefaction as measured by the output of urinary indican was markedly decreased by fasting; after the fast, return to a low protein diet raised the output far above the normal; it was but slightly higher on a high protein diet. The drinking of copious or moderate amounts of water with meals decreases the output of indican. No uniform relationship between indican excretion and the output of bacteria in the fæces was found. W. D. H.

**The Biological Importance and Metabolism of Proteins. X. Total Nitrogen and Amino-acid Nitrogen in the Urine of Animals Fed on Flesh, or on the Digestive Products of the Same Introduced Intravenously.** GUISEPPE BUGLIA (*Zeitsch. Biol.*, 1912, 58, 162—184).—In spite of contradictory results which are difficult to interpret, the outstanding conclusion reached in the present research on dogs is that amino-acids introduced into the blood-stream are utilised in the tissues for the building up of protoplasm. If the food is given by the mouth, amino-acids are found to be absorbed as such and not re-converted into protein in the intestinal wall. When administered intravenously, very little amino-acid is excreted in the urine; it is rapidly utilised and oxidised in the tissues, and a considerable quantity can be injected if the injection is done slowly. Peristalsis of the intestine leading to diarrhœa, and also a certain amount of diuresis with slight albuminuria are observed. The action on the kidney is a direct one, and only in part due to hypertonicity of the solution. W. D. H.

**Artificial Nutrition.** FRANZ ROHMANN (*Biochem. Zeitsch.*, 1912, 39, 507).—In view of recent publications by Osborne and Mendel (Carnegie Institute of Washington, 1911), the author calls attention to the fact that he has carried out experiments in a similar way, and has also recently succeeded in maintaining animals with only one protein in their diet. S. B. S.

**A New Calorimeter for Small Warm-blooded Animals.** ARCHIBALD V. HILL (*Proc. physiol. Soc.*, 1912, i—ii; *J. Physiol.*, 44).—The calorimeter for mice and rats is constructed on the principle (Dewar flask) used in the author's previous instrument. W. D. H.

**Calorimetric Observations on Man.** J. S. MACDONALD (*Proc. physiol. Soc.*, 1912, iv—v; *J. Physiol.*, 44).—The calorimeter used was made on Benedict's model with some modifications. The performance of work entails an increased output of heat, which rises to a maximum at the end of one and a-half hours; this is then maintained until the work ceases. Sufficient variations in body temperature have not so far been found to explain the whole effect. Efficiency diminishes as the temperature of the body rises. W. D. H.

**The Distinction between Colloidal and Osmotic Imbibition in Muscular Tissue.** REINHARD BEUTNER (*Biochem. Zeitsch.*, 1912, 39, 280—289).—The experiments were carried out by determining the gains or losses in the weight of the tissues after varying intervals when placed in mixtures of varying concentrations of acids and salts (hydrochloric acid and sodium chloride, sulphuric acid and sodium sulphate, nitric acid and sodium nitrate). The period at which the tissue loses its irritability in various solutions was also noted. The author interprets the results obtained (some of which are plotted in curves) by assuming that the imbibition process in the living muscle is an osmotic process, whereas imbibition in the dead muscle is a process characteristic of colloids. Sulphuric acid accelerates the post-mortem imbibition less than hydrochloric acid, and in this respect its action is analogous to its other actions on proteins. S. B. S.

**The Purines of Muscle.** C. B. BENNETT (*J. Biol. Chem.*, 1912, 11, 221—234).—Muscle contains small amounts of adenine and guanine probably in the form of thymus-nucleic acid; there is more guanine than adenine. Inosic acid is present in varying quantity in striated, but absent from smooth, muscle. It represents only a fraction of the total hypoxanthine present; whether the remainder of the hypoxanthine is free is uncertain. Inosic acid is easily obtained by extraction with cold water, and so it is improbable that it is confined to the nuclei.

W. D. H.

**Chemical Pathology of Muscle.** GEORG GRUND (*Arch. exp. Path. Pharm.*, 1912, 67, 393—407).—In the degeneration of muscle which follows division of its nerves, the normal relationship of water and solids and the proportionate amount of various solids are upset; fat for instance is increased, but the characteristic change is an increase in protein-phosphorus; that is to say, the typical phosphorus-free proteins of muscle are replaced by others such as are found in less highly specialised tissues. In inanition all the proteins waste equally. The chemical change in degenerated muscle has its histological analogue in an increase of nuclei.

W. D. H.

**Osmotic Activity in the Egg of the Common Fowl.** A. D. GREENLEE (*J. Amer. Chem. Soc.*, 1912, 34, 539—545).—It is shown that when eggs are kept for a long time at 0° or a higher temperature, the amount of water in the white decreases. This decrease is not entirely due to loss by evaporation into the air, but partly to transference of water from the white to the yolk, this being effected by the process of osmosis. The yolk contains a very high percentage of solids and is enclosed in the vitellin membrane; this is surrounded by the white of the egg, which is much more dilute than the yoke. Water passes through the membrane from the more dilute to the more concentrated solution. This process continues until the membrane breaks and the white and yolk begin to lose their identity. The action proceeds with such regularity that, if the original weight of the egg is known, the loss of moisture to the atmosphere can be calculated with close approximation to the actual loss as shown by the balance. The rate of change in the water content increases with the temperature and decreases with the time. A formula has been developed by means of which, if one analysis of a sample of eggs has been made, it is possible to predict the condition of the eggs at any temperature for any given date within a reasonable period. The rate multiplied by the time gives the loss in weight, and the percentage of moisture remaining can be easily calculated.

E. G.

**Potassium and Sodium Content of the Different Organs of a Dog.** PIERRE GÉRARD (*Compt. rend.*, 1912, 154, 839—841).—The dog was an adult weighing 6.06 kilograms. The following figures give the ratio K/Na. Muscular tissue (tongue, heart, diaphragm, etc.) 1.53—2.73. The ratio was high as a rule in glandular tissue, being 3.58 in the spleen, 3.31 in the liver, 1.06 in the thyroid, but only 0.86 in the prostate. The nervous tissues showed a ratio higher than

unity, with a tendency to diminish with the proportion of grey matter; cerebrum, 1.96; mesenteric ganglia, 1.45; sciatic and pneumogastric nerves, 1.00. Veins, arteries, urethra, and trachea, 0.23—0.74. Hair, 0.27; skin, 0.61. Bones, 0.76; cartilage, 0.69; blood, 0.08. W. O. W.

**Chemistry and Toxicology of the Ascarides.** FERDINAND FLURY (*Arch. exp. Path. Pharm.*, 1912, 67, 275—392).—Among the inorganic constituents of these parasitic worms, chlorides and sulphates predominate. Iron is present, and partly originates from hæmoglobin. Half of the dry material consists of proteins, which yield the ordinary amino-acids. Uric acid and creatinine are absent. The cuticle consists of a keratin. The principal carbohydrate is glycogen, and glucoproteins are also present. Fatty acids and phosphatides occur; cholesterol is absent; glycerol is present only in traces, its place being taken by *ascaryl alcohol*,  $C_{32}H_{64}O_4$ , m. p.  $83^\circ$ ; when heated above its melting point it yields acraldehyde. Numerous enzymes are found in extracts of the worms. The extracts are also toxic, producing inflammatory and irritative effects. These appear to be mainly due to products of fatty acids. It is surmised that some of the symptoms observed in people who act as hosts to the worms may be due to a similar cause, and the anæmia produced by hæmolytic substances such as acrylic and oleic acids. If the worms die in the alimentary tracts, putrefactive products will also be absorbed. W. D. H.

**The Suprarenal Medullary Tissue in *Petromyzon fluviatilis*.** J. F. GASKELL (*J. Physiol.*, 1912, 44, 59—67).—In the *Petromyzon* (lamprey) chrome-staining tissue is widely distributed throughout the body in intimate relation to the large veins, to some extent to the large arteries, and still more intimately to the posterior nerve roots. It yields adrenaline, and is, in fact, identical with suprarenal medullary tissue. Extracts of all other tissues produced depressor effects. W. D. H.

**Oxidation Processes in the Regeneration and Heteromorphosis of Tubularia.** E. (GRAF) VON SCHÖNBORN (*Zeitsch. Biol.*, 1912, 58, 97—109).—The hydroid polype *Tubularia* will grow new hydroids when these are cut off, and when the root end is cut it will grow hydroids there too, not a new root. When the hydroids are cut off, the oxidation processes are reduced to one-half, and sink to their lowest during the time of regeneration. The oxidation when hydroids are grown at both ends is twice as great as in those animals which only have them at one end. W. D. H.

**The Influence of Organic and Inorganic Compounds on the Secretion of Milk.** GUSTAV FINGERLING (*Biochem. Zeitsch.*, 1912, 39, 239—269).—Experiments were carried out on goats, which were fed on a given diet poor in phosphorus consisting of straw, blood-albumin, molasses, starch, oil, sodium chloride, and calcium carbonate. During various periods, phosphorus contained in the following forms was added to this diet: lecithin, caseinogen, nuclein, nucleic acid, and disodium

phosphate. The quantities and composition of the milk secreted during these periods were ascertained. None of the above substances was found to exert a specific action on the milk secretion, influencing neither the quantity nor the composition of the milk. Neither the phosphorus nor calcium content of the milk ash was altered. The previous conclusion of the author, that the body is capable of building up organic phosphorus compounds from inorganic phosphates, is thus confirmed. When the phosphorus content of fodder is insufficient for the needs of the animal, the deficiency can be made up by the addition of inorganic phosphates. S. B. S.

**Creatine in the Urine of Children.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1912, 11, 253—256).—Analyses are given which support the finding of Rose, that children's urine is relatively rich in creatine. It is, however, probably not due to peculiar carbohydrate metabolism, but to a high level of protein consumption; it rises after a meat meal. W. D. H.

**Studies in Water Drinking. XII. The Allantoin Output of Man as Influenced by Water Ingestion.** L. T. FAIRHALL and PHILIP B. HAWK (*J. Amer. Chem. Soc.*, 1912, 34, 546—550).—Experiments are described which show that if the diet of a normal man is supplemented by large quantities of water, a marked increase takes place in the amount of allantoin excreted. It is suggested that this is due to stimulation of the oxidative mechanism of the organism, and that the excess of allantoin is produced by the oxidation of purine material which under ordinary conditions would have been excreted in some less highly organised form. This view is supported by the fact that the amount of uric acid excreted is reduced when large quantities of water are ingested. E. G.

**Influence of Sodium Chloride in Excess on Nutrition and Renal Elimination.** ALEXANDRE DESGREZ and (Mlle.) BL. GUENDE (*Compt. rend.*, 1912, 154, 939—941).—The addition of sodium chloride to the diet of a dog with an unlimited allowance of water increases the amount of urinary nitrogen, but diminishes the mean molecular weight of the nitrogen compounds excreted. If the quantity of drinking water is strictly limited, both the amount and mean molecular weight are diminished. W. O. W.

**The Elimination of Arsenic after Treatment with Organic Arsenic Compounds.** J. CHARLES BONGRAND (*Chem. Zentr.*, 1912, 274—275; from *Bull. Sci. pharmacol.*, 8, 152—157).—After treatment with hectin or salvarsan (606) by either subcutaneous or intramuscular injection, a rapid elimination of arsenic appears to be the rule. After preliminary mercurial treatment, or previous treatment with an organic arsenic compound, the elimination is somewhat irregular. In the case of soluble organic compounds, the elimination starts shortly after administration, but is slow, whereas in case of insoluble compounds the elimination is sudden, and takes place after intervals of varying durations. S. B. S.

**Absorption of Alcohol from the Urinary Bladder.** WILHELM VÖLTZ, AUGUST BAUDREXEL and WALTER DIETRICH (*Pflüger's Archiv*, 1912, 145, 186—209).—If solutions of alcohol are introduced into the urinary bladder, from 25 to 35% of the alcohol is absorbed within an hour, and 95% within six hours. If the animal (dog) is killed, the absorbed alcohol can be found in the tissues. If alcohol is given in the usual way, that excreted in the urine is also re-absorbed from the bladder. The alcohol absorbed from the bladder is probably absorbed as absolute alcohol.  
W. D. H.

**The Quantity of Alcohol Excreted by the Animal Organism under Various Conditions. III. Influence on the Secretion of Alcohol by the Breath and Urine of the State of Fullness of the Alimentary Canal.** WILHELM VÖLTZ, AUGUST BAUDREXEL, and WALTER DIETRICH (*Pflüger's Archiv*, 1912, 145, 210—228).—In dogs, the smallest value for the alcohol in the urine was found if the drug was given with a full meal, and the maximum if given on an empty stomach; the latter may be eight times greater than the former. This was confirmed by experiments on men. The amount of alcohol exhaled is also greater when it is given on an empty stomach.  
W. D. H.

**Creatine-destroying Bacilli in the Intestine.** F. W. TWORT and EDWARD MELLANBY (*J. Physiol.*, 1912, 44, 43—49).—From human faeces a bacillus was isolated which effectively destroys creatine. It is a large Gram-positive bacillus and a strict anærobe. A few varieties of the colon group of bacilli destroy creatine less effectively; so also does the tetanus bacillus. Bacilli with similar action were found in the large and small intestines of the cat. In the interpretation of creatine-feeding experiments, this factor will have to be considered.  
W. D. H.

**Estimation of Faecal Bacteria.** H. A. MATTILL and PHILIP B. HAWK (*J. exp. Med.*, 1911, 14, 433—444).—The method involves three serial centrifugalizations of a 2 gram sample of fresh faeces suspended in 0.2% hydrochloric acid. The bacterial suspension is concentrated, extracted with alcohol, and nitrogen determined in the residue. On a simple, easily digested diet, 53.9% of the total faecal nitrogen is of bacterial origin; this is higher than stated by others, but is probably more nearly true, because no extraction with ether was employed. The average daily amount of dry bacteria is 8.27 grams. The amount of bacterial nitrogen in the faeces is a valuable index of intestinal conditions.  
W. D. H.

**Post-Anæsthetic Glycosuria.** PHILIP B. HAWK (*Archives Intern. Med.*, 1911, 8, 39—57).—The glycosuria after ether anæsthesia in dogs lasts from nine to twenty-seven hours. If the dogs are fasting, the glycosuria is slight or absent. It is considered to be due to the ether stimulating the transformation of glycogen into dextrose; dyspnœa may be a contributing factor.  
W. D. H.

**A Case of Pentosuria Presenting Unusual Features.** J. H. ELLIOTT and H. S. RAPER (*J. Biol. Chem.*, 1912, 11, 211—216).—In a

case of pentosuria an attempt was made to estimate the pentose by Neuberg's method. Neuberg obtained twenty grams of pentose as diphenylhydrazone from twenty litres of urine, and the sugar from this was inactive arabinose. In the present case no insoluble hydrazone was obtained, although analysis of the osazone showed a pentose to be present, which is possibly *i*-ribose.

W. D. H.

**The Effect of a Diet of Polished Rice on the Nitrogen and Phosphorus of the Brain.** CASIMIR FUNK (*J. Physiol.*, 1912, 44, 50—53).—In the polyneuritis of birds (a condition analogous to Beri-beri) produced by a diet of polished rice, the brain shows a sensible loss of nitrogen and phosphorus, suggesting a breakdown of lipids.

W. D. H.

**Pigment Anomalies in Metabolism.** OSKER ADLER (*Chem. Zentr.*, 1912, i, 839—840; from *Zeitsch. Krebsforschung*, 11, 1—43).—As it is known that in cases of alcaptonuria, a colouring of the cartilage takes place (ochronosis), the author, with a view to investigating the pigment, has submitted homogentisic acid to oxidation by air in an alkaline alcoholic solution. In this way a black pigment ("alcaptone-black") was obtained. Similarly, from gentisic acid a black pigment was prepared. In view of the fact that black pigments are formed in carbolic acid bandages, phenol was submitted to oxidation by lead peroxide in sulphuric acid solution, and a dark brown pigment was obtained. The author followed cases of melanosis and melanuria, and found the following reaction characteristic of melanotic urine: 160 c.c. of urine, after acidification with lead acetate, are fully precipitated with normal lead acetate. After separating the lead from the precipitate in the usual way, a liquid is obtained of which 2 c.c. with 1 drop of dilute ferric chloride, 3 c.c. of acetic acid, and 1—2 c.c. concentrated sulphuric acid give a metallic violet colour, showing a sharp band in the spectrum near the *D*-line. Tryptophan and indole give similar reactions, but the positions of the band are somewhat different.

In view of the formation of pigments in malignant tumours, pigments were prepared by the oxidation of tyrosine, tryptophan, and  $\alpha$ - and  $\beta$ -phenylalanines by lead oxide in sulphuric acid. The tyrosine-black thus obtained is toxic, and is excreted in the urine (experiments on rats and mice). Attention is drawn to the pathological significance of this fact.

S. B. S.

**The Relative Toxicity of Dog's Normal and Hypertrophied Thyroids to Animals Susceptible to Thyroid Feeding.** O. O. STOLAND (*Amer. J. Physiol.*, 1912, 30, 37—41).—Normal dog's thyroid is more toxic to susceptible animals than the hypertrophied thyroid from goitrous dogs. The latter contains less iodine, and less toxic substance. In the case of rats, the loss of weight during the first few days of thyroid feeding is partly due to handling in feeding and weighing.

W. D. H.

**Effect of Intravenous Injections of Thyroid Pressure Liquid in Dogs and Cats.** G. H. CALDWELL (*Amer. J. Physiol.*, 1912, 30, 42—45).—Dogs and cats show high resistance to the specific

thyroid substance. The fact that cats show as great resistance as dogs to the pressure juice of dog's thyroid seems to show that the resistance of the latter is not due solely to the source of the material. The fatal results in rabbits may be due to their high susceptibility to increase of thyroid substance in the blood, or to the specific effect of the foreign proteins. In general, the three animals exhibit the same relative resistance to the thyroid juice introduced intravenously and to thyroid given by the mouth.

W. D. H.

**The Effects of Blood-transfusion in Parathyroid Tetany.** CLARA JACOBSON (*Amer. J. Physiol.*, 1912, 30, 47—55).—Intravenous injection once or twice daily of defibrinated blood of normal dogs into parathroidectomised dogs prolongs the life of those animals on the whole, but has no immediate or marked action on the tetany and depression symptoms. These transfusions have no obvious injurious effects on normal animals. Accepting the internal secretion hypothesis, the results indicate a rapid destruction and elimination, or a very slight concentration of the parathyroid secretion in the body fluids.

W. D. H.

**The Comparative Toxicity of Different Animal Tissues to Animals Susceptible to Thyroid Feeding.** H. E. FRENCH (*Amer. J. Physiol.*, 1912, 30, 56—62).—Thyroid (fresh, stale, desiccated, commercial, or prepared in laboratory) contains a substance which is decidedly toxic to some animals. Brain, liver, spleen, kidney, skeletal muscle give no such effects when prepared in the same way, and given in equal or even larger quantities. The nature of the substance is unknown, but it is evidently not due to autolysis or decomposition, or are the effects simply due to excess of protein.

W. D. H.

**Attempts to Produce Experimental Hyperthyroidism in Mammals and Birds.** ANTON J. CARLSON, J. R. ROOKS, and J. F. MCKIE (*Amer. J. Physiol.*, 1912, 30, 129—159).—Animals differ greatly in the effect which thyroid feeding produces. The cause of their resistance is unknown; probably the specific toxic effects are complicated with those due to excess of protein administered; the carnivora are more resistant than herbivora. The poisonous symptoms are loss of weight, gastro-enteritis, and diarrhoea, and a fatal result may ensue especially in ducks. Nervousness, tachycardia, and exophthalmos do not occur; in other words, the symptoms are not those of exophthalmic goitre. Of all animals man seems to be the most susceptible to thyroid feeding; monkeys exhibit great aversion to thyroid, and so cannot be used for experiment.

W. D. H.

**Antagonism between Salts and Anæsthetics. II. Decrease by Anæsthetics in the Rate of Toxic Action of Pure Isotonic Salt Solutions on Unfertilised Star-fish and Sea-urchin Eggs.** RALPH S. LILLIE (*Amer. J. Physiol.*, 1912, 30, 1—17).—The permeability-increasing and cytolytic action of isotonic solutions of sodium and potassium salts on the eggs is retarded by various

anæsthetics. The period during which the eggs remain alive in such solutions is thus prolonged. This protective action is less marked than that exercised by calcium or magnesium salts. The view that lipoids enter into the composition of the plasma-membrane is thus confirmed. Calcium chloride is less antitoxic against potassium than against sodium salts. Potassium cyanide in  $m/1000$ -concentration decreases the immediate toxic effect of sodium salts, but increases that of potassium salts.

W. D. H.

**The Neutralisation by means of Salts of Toxicity Produced by Acids.** JACQUES LOEB and HARDOLPH WASTENEYS (*Biochem. Zeitsch.*, 1912, 39, 167—173).—The maximal amounts of acid which do not act toxically on fish (*Fundulus*) in varying concentrations of the chlorides of calcium, potassium, and sodium were determined. The maximal amount of hydrochloric acid could be tolerated in  $m/4$ -solutions, which is about the blood-concentration of marine teleosts. The antagonistic action of the chlorides of calcium and sodium to the toxicity of acids is about the same, as might be expected from Pauli's researches on the antagonistic action of acids and salts on proteins. Some idea as to the action of salts and acids on the whole fish may be obtained by the study of their action on the skin and gills. Carbon dioxide acts toxically like other acids, and the toxic action can also be neutralised by salts.

S. B. S.

**The Antagonism to Sodium Bromide Poisoning.** JACQUES LOEB and HARDOLPH WASTENEYS (*Biochem. Zeitsch.*, 1912, 39, 185—199).—These experiments were carried out on fish. Concentrations of the bromide of even  $m/200$  cause the typical symptoms of bromine poisoning. The solution is rendered non-toxic by the presence of as many chlorine ions as there are bromine ions present. It makes no difference whether the chlorides of sodium, calcium, or magnesium are used for the purpose.

S. B. S.

**The Influence of the Anion on the Toxicity of Sodium and Calcium Salts.** JACQUES LOEB (*Biochem. Zeitsch.*, 1912, 39, 194—199).—The toxicity of salts (on *Fundulus*) is not an additive function of the ions. Sodium chloride is not so toxic as the chlorides of calcium or magnesium. On the other hand, calcium and magnesium are less toxic than sodium in the case of the bromides, hydroxides, nitrates, acetates, and sulphates. An explanation of these facts is given, in which the assumption is made that the relative toxicity of the ions varies with the concentrations.

S. B. S.

**The Comparative Toxicity of Concentrated and Diluted Arsenobenzene Solutions in Intravenous Injections.** CHARLES FLEIG (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 14, 893—902).—The immediate toxic effects of intravenous injections of salvarsan 606 (diaminodihydroxyarsenobenzene hydrochloride) in acid solution decrease inversely with the dilution. These poisonous effects are ascribed, not to the hydrochloric acid in the compound, but to a reaction of the phenol (OH) group with the albuminous matter of the blood, giving

rise to the formation of a precipitate which causes a mechanical blocking of the vessels. With dilute solutions this precipitate is produced in a finer state of division than with the more concentrated solutions, and the former do not, therefore, give rise to such severe symptoms.

Dilute acid solutions (0.6 gram in 400 c.c.) in artificial serum are, therefore, recommended for therapeutic use. W. J. Y.

**Pregnancy Toxæmia.** KARL GRUBE and KARL REIFFERSCHIED (*Med. Klinik*, 1912, No. 14. Reprint 7 pp.).—The alcoholic extract of the blood of pregnant rabbits has no action on other rabbits. The ethereal extract, however, is usually toxic, producing paralysis, convulsions, depression of blood-pressure, and death. The boiled extract has the same effect. The ethereal extract of non-pregnant rabbits is innocuous. The toxic extract is not poisonous to pregnant rabbits immediately before full term. W. D. H.

**The Behaviour of Yeast-Gum in the Animal Organism.** FRIEDRICH SIMON (*Zeitsch. physiol. Chem.*, 1912, 77, 218—228).—Yeast-gum administered to dogs and rabbits is in great measure absorbed in the intestinal tract, and in the rabbit it leads to an increase in the hepatic glycogen. W. D. H.

**Substances which Constrict and Dilate the Blood Vessels of the Surviving Frog.** Remarks on S. Samuelson's Paper. LEO POPIELSKI (*Arch. exp. Path. Pharm.*, 1912, 67, 408).—The author points out that workers in his laboratory were the first to state that pure choline produces a rise of blood-pressure, and that many organs (pancreas, thymus, brain, etc.) yield a pressor substance which is not adrenaline, to which the name *vasohypertensin* is given. W. D. H.

**The Fate of Xanthine and Caffeine in the Human Body.** WALTER LEVINTHAL (*Zeitsch. physiol. Chem.*, 1912, 77, 259—279).—The experiments recorded were mostly made on the author's own person. With xanthine it is shown that in the metabolic processes of the body, it is probably excreted quantitatively without breaking the purine ring; the main amount is oxidised to uric acid, and the remainder is excreted unchanged. Most was recovered if the xanthine was administered intravenously.

The experiments with caffeine were not so numerous or so conclusive; the small increase in purine nitrogen excreted may have been chiefly due to the diuretic action of the drug.

Experiments confirming the foregoing were also made on a gouty patient; in both health and gout, the increase in purine excretion after the administration of thymus was small. W. D. H.

**The Influence of Radium on the Body Temperature of Man.** HANS DARMS (*Chem. Zentr.*, 1912, i, 739; from *Zeitsch. exp. Path. Therapie*, 1911, 10, 168—177).—After inhalation of the emanation, there is a rise of temperature within the first half hour, followed by a constant fall. After drinking the emanation, there is within the first five minutes a fall, and afterwards a rise of temperature. S. B. S.

**The Behaviour of the Glucosides, Especially Arbutin, in the Organism.** ROBERT BASS (*Chem. Zentr.*, 1912, i, 741—742; from *Zeitsch. exp. Path. Therapie*, 1911, 10, 120—131).—The investigations were undertaken with the object of throwing light on the genetic relationship between the conjugated glycuronates, which are formed in the body, and the glucosides; and the capacity for causing scission of the glucosides by the body and by the individual organs was investigated. The behaviour of arbutin (glucoside of quinol) after ingestion by the human subject and by rabbits, and the behaviour of salicin (glucoside of salicyl alcohol) and arbutin, after one to three days' digestion with extracts of different organs (liver, pancreas, kidneys, serum, mucous membrane of small intestine, salivary glands, spleen) of man and various animals, were investigated. It was found that after oral ingestion, even of large doses (1.5 to 2.5 grams per kilo.) of arbutin by rabbits, the unchanged glucoside was never found in the urine, but only quinol. On subcutaneous injections, however, even after doses of 0.4 gram per kilo., the unchanged glucoside was found in the urine. Dogs can tolerate only about half the dose when subcutaneously administered. When the doses of arbutin given orally are smaller than the above mentioned, all the quinol is found in the urine in the form of the conjugated sulphuric or glycuronic acids. Quinol given in such doses, therefore, can hardly exert an antiseptic action in the organism. It appears that, as a general rule, the quinol enters into the conjugated form more rapidly than the hydrolysis of the arbutin takes place, and for this reason, arbutin does not easily act toxically. After administration of arbutin there is no more quinol glycuronate in the urine than after administration of quinol. These results are opposed to the conception that glucosides are precursors of the glycuronates.

It was found that the liver and kidneys of rabbit, cat, and pig, but not that of the dog, can hydrolyse arbutin and salicin. Certain glycuronates can also be hydrolysed by various organs. This capacity is specific for certain organs, and it seems possible that in addition to the formation of glycuronates in the organism, a destruction also takes place simultaneously in certain animals.

The arbutin was estimated in the urine by precipitation as lead salt, hydrolysis of the precipitated fraction (after separating lead, etc.) by sulphuric acid, and estimation of the dextrose thus formed by a fermentation method. The principal of the method used for the estimation of quinol is that of the reduction of ammoniacal silver nitrate, the details of which are given by the author in full. The hydrolysis of salicin was followed colorimetrically by means of ferric chloride, whilst the scission of glycuronates was estimated polarimetrically.

S. B. S.

**Creatine.** TORSTEN THUNBERG (*Zentr. Physiol.*, 1911, 25, 915—916).—Creatine increases the gaseous exchanges of surviving frog's muscle. The experiments were carried out with the use of the micro-spirometer, and the increase was progressive as the concentration of the creatine was increased from 10 to 100 millimols. per litre.

S. B. S.

**Pharmacological Action of Certain 2:5-Pyridines.** KARL ROBERT (*Chem. Zentr.*, 1912, i, 508—509; from *Zeitsch. exp. Path. Therapie*, 1911, 9, 614—638).—Thiopyrine has a stronger action on the nervous system, and increases the reflex excitability in smaller doses than antipyrine. In large doses it kills by paralysing the central nervous system. The minimal toxic dose for the hedgehog is 0.340 gram. Six grams given with the food over ten days were without harmful effect on a cock, and rabbits could tolerate large doses without injury either to the mucous membrane or kidneys. With the quantities employed, no effect was observed on an isolated frog's heart; 0.04 gram caused convulsions in a frog. Von Noorden's clinical investigations showed that it had antirheumatic, antineuralgic, and antipyretic properties, but it was not so well tolerated by the stomach as antipyrine. Selenopyrine acts similarly to the thio-compound, but not so strongly. The hydrochloride of iminopyrine was non-toxic in doses of 50 mg. to the cat's heart, and 1 to 2 grams *per os* were tolerated by dogs. 0.5 Gram subcutaneously administered was also without action. Two grams killed a dog of 4 kilos. in four days. It is without action on the blood. Anilopyrine hydrochloride killed frogs in doses of 5 mg. and rabbits in doses of 50 mg. with excitation of nervous system, followed by paralysis.

The hydrochloride of 5-phenylhydrazino-2-methylpyrine acts in concentrations of 1:200 to 1:3000 on cats and fowls' blood with the formation of met- and cat-hæmoglobin; the latter substance is not formed from the blood of rabbits or guinea-pigs. It paralyses the central nervous system, and lethal doses are insufficient to cause blood-changes. The methiodide of phenylhydrazinomethylpyrine has no action on the blood or central nervous system; it has, however, a curare-like action on the peripheral motor-nerve endings.

S. B. S.

**The Influence of Cocaine on Metabolism, with Especial Reference to the Elimination of Lactic Acid.** FRANK P. UNDERHILL and CLARENCE L. BLACK (*J. Biol. Chem.*, 1912, 11, 235—252).—Cocaine introduced subcutaneously in dogs causes a temporary rise of body temperature. Daily doses of 10 mg. per kilo. of body-weight cause no effect on the metabolism of nitrogen or fat. Doses of 15 mg. slightly impair fat utilisation and cause loss of body-weight. Doses of 20 mg. distinctly lower both fat and nitrogen utilisation. Lactic acid excretion is markedly increased in well-fed dogs and rabbits, but in inanition it is diminished. The increase may be associated with increased muscular activity. The ammonia output bears no relation to lactic acid elimination. Lactic acid and carbohydrate metabolism are presumably intimately associated, but there are indications that lactic acid may at times arise from more than one antecedent.

W. D. H.

## Chemistry of Vegetable Physiology and Agriculture.

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**Accumulation of Nitrogen by *Azotobacter chroococcum*.** GEORG RÖSING (*Centr. Bakt. Par.*, 1912, ii, 33, 618—623).—A summary of the results obtained at Bonn-Poppelsdorf (Remy, *Abstr.*, 1909, ii, 340; Remy and Rösing, *Centr. Bakt. Par.*, 1911, ii, 29, 36; *Abstr.*, 1911, ii, 758), and a reply to Kaserer (*Centr. Bakt. Par.*, 1911, ii, 31, 577).  
N. H. J. M.

**Potassium Requirements of *Azotobacter*.** J. VOGEL (*Centr. Bakt. Par.*, 1912, ii, 32, 411—421. Compare *Abstr.*, 1910, ii, 987).—The author's earlier experiments were repeated, and also those of Krzemieniewska, and the results lead to the conclusion that *Azotobacter* is able to grow and to fix nitrogen, if only to a slight extent, in the presence of only minute traces of potassium salts. Larger quantities of potassium induce a more economical consumption of the carbohydrate supplied (dextrose) and a more energetic assimilation of nitrogen.  
H. B. H.

**The Fixation and Release of Nitrogen.** LEONHARD FELSINGER (*Zeitsch. landw. Versuchs-wissen. Österr.*, 1910—1911, 14, 1039—1103).—A comprehensive research into the conditions governing nitrification and denitrification; experiments were carried out under aerobic and anaerobic conditions in different culture solutions impregnated with various types of soils, and the result of the addition of nitrates, nitrites, ammonium salts, dextrose, and organic fertilisers such as bone meal, dried blood, ground hoofs, and farmyard manure studied.

The relation between the carbon dioxide formed and the nitrifying changes was also observed; the nitrogen evolved during denitrification was collected, and the ratio of nitrate to nitrite present followed by estimations of these constituents during the process. F. M. G. M.

**The Retention of Ammoniacal Nitrogen on Limed and Unlimed Soils.** OTTO LEMMERMANN, E. BLANCK, B. HEINITZ, and I. VON WLODEK (*Landw. Jahrb.*, 1911, 41, 163—216).—The results of work extending over several years on the influence of different salts of lime on the nitrification of numerous ammonium salts under varying conditions of temperature, moisture, and in the presence or absence of other fertilisers. The analytical results are tabulated, and the general conclusion drawn that nitrification is more rapid in soils containing lime than in those in which this constituent is deficient.  
F. M. G. M.

**Toxic Effects of "Alkali Salts" in Soils on Soil Bacteria.**  
**II. Nitrification.** CHARLES B. LIPMAN (*Centr. Bakt. Par.*, 1912, ii, 33, 305—313).—An account of experiments conducted on similar lines to those previously reviewed (this vol., ii, 76). A number of

cultures were made with 100 grams of fine sand and 2 grams of fine blood meal, and to these were added various weights of sodium sulphate, chloride, and carbonate. Water was added in order to bring up the moisture to 18%, and after incubation at 28° for three weeks, the amount of nitrates formed in each culture was estimated.

The results indicate that the nitrification of organic matter in soils is inhibited by the presence of certain amounts of each of the alkali salts tested. Of these, sodium carbonate appears to be the most toxic, sodium sulphate least toxic, whilst sodium chloride occupies an intermediate position. The amounts of these salts sufficient to inhibit the formation of nitrates are: sulphate 0.35%, chloride 0.1%, and carbonate 0.025% of the weight of dry soil. Hence nitrifying bacteria, on the whole, are most sensitive to carbonate, which, as was shown in the earlier paper, exerts the greatest stimulative action on ammonia-producing bacteria. This behaviour of nitrifying bacteria agrees closely with that of higher plants, and disproves the assumption previously made, that the stimulative action of sodium carbonate on ammonifying bacteria would account for the large quantities of nitrates often found in "black alkali" soils.

H. B. H.

**The Bacterial Production of Acetylmethylcarbinol and  $\beta$ -Butylene Glycol from Various Substances.** II. ARTHUR HARDEN and (Mrs.) DOROTHY NORRIS (*Proc. Roy. Soc.*, 1912, B, 85, 73—78).—The lævorotatory, volatile, reducing substance obtained by Péré (*Ann. Inst. Past.*, 1896, 10, 417), from the products of the aerobic action of *B. subtilis* and *B. mesentericus vulgatus* on mannitol, and of *Tyrophthrix tenuis* on dextrose and glycerol has been identified as acetylmethylcarbinol. It is readily volatile in steam, gives the Voges and Proskauer reaction, and forms the phenyllosazone of diacetyl. The anaërobic fermentation of glycerol by *B. lactis aërogenes* does not give rise to any reducing substance. A quantitative study of the last action was made, and the products found to be ethyl alcohol, formic, acetic, lactic and succinic acids, carbon dioxide, hydrogen, and  $\beta$ -butylene glycol.

W. J. Y.

**Mobilisation of Phosphoric Acid of Soils under the Influence of Bacteria.** II. S. A. SEWERIN (*Centr. Bakt. Par.*, 1912, 32, 498—520. Compare Abstr., 1911, ii, 61).—When soils sterilised at high temperatures are inoculated with bacteria contained in an extract of normal soil, there ensues a reduction in the amount of soluble phosphorus compounds in the soil. Pure cultures of different bacteria were used for re-infection of the treated soils, and showed specific differences. Whilst *Bacillus pyocyaneus* and *B. radicicola* increased, *Bacterium-a* reduced the amount of easily soluble phosphorus compounds.

There does not appear to be any definite relation between carbon dioxide production, capacity of growth of the organism, and the production of soluble phosphorus compounds. The final amount is determined by the interaction of these factors and others which are bound up with the specific physiological properties of the bacteria.

H. B. H.

**The Formation of Hydrogen Sulphide from Cystine and Other Sulphur Compounds by means of Bacteria.** TAKAOKI SASAKI and ICHIRO OTSUKA (*Biochem. Zeitsch.*, 1912, 39, 208—215).—Most of the bacteria investigated were capable of forming hydrogen sulphide from cystine. Exceptions were the fluorescing bacteria, *B. pyocyaneus*, and various staphylococci. Mercaptan was not detected. The staphylococci behave differently towards sulphur and cystine. From the former they can form hydrogen sulphide. The proteins of the bacteria have no part in the hydrogen sulphide formation. Neither from taurine nor sulphates can bacteria form hydrogen sulphide. S. B. S.

**Biochemistry of Micro-organisms. V. Fermentation and Production of Formic Acid by Yeasts.** HARTWIG FRANZEN and O. STEPPUHN (*Zeitsch. physiol. Chem.*, 1912, 77, 129—182. Compare Abstr., 1911, ii, 60).—Experiments made with a number of pure yeasts, grown in wort or yeast water solutions to which sodium formate was added, prove conclusively that formic acid is both produced and fermented by the living yeast. Zymase behaved similarly to the living yeast, and it is considered that the production and fermentation of formic acid is due to enzyme action and that it is closely related to the actual decomposition of sugar into alcohol and carbon dioxide. Other possible methods of the formation of formic acid are considered, such as its production by the decomposition of amino-acids or by oxidation of dextrose, but it is shown that these are not applicable. Accordingly, formic acid is proved to be an intermediate product of alcoholic fermentation. E. F. A.

**The Formation of Volatile Acids by Yeasts after Fermentation under Aerobic Conditions.** A. OSTERWALDER (*Centr. Bakt. Par.*, 1912, ii, 32, 481—498).—When fermentation under aerobic conditions has taken place, there occurs sedimentation of the yeast cells, and at a later date, a new growth of organisms in the form of flocculent or even layers of yeast above the sediment. Under similar conditions the amount of volatile acids rises, within a period of four to five months, to about 1·8% (calculated as acetic acid).

These volatile acids do not appear to be due to simple oxidation of the alcohol present, or to the degradation of non-volatile acids. It is suggested that they are formed as products of metabolism during the secondary fermentation, possibly by means of oxydases. The amount of acid formed is more or less dependent on the variety of yeast.

H. B. H.

**Fermentation Experiments with Different Varieties of Yeast on Different Sugars.** PAUL LINDNER (*Chem. Zentr.*, 1912, 1, 510—511; from *Woch. Brauerei*, 1911, 28, 612—613).—The following carbohydrates were investigated: dextrose, mannose, galactose, lævulose, trehalose, sucrose, maltose, lactose, melibiose, raffinose, α-methylglucoside, xylose, and rhamnose. The same varieties of yeasts were employed as in the investigations of the author with Mohr. The simple sugars and trehalose, sucrose, and maltose under-

went fermentation, but not lactose. A doubtful fermentation was observed in certain cases with xylose and rhamnose. Melibiose is not fermented by top-yeast. The greatest differences were shown in the action of the yeast towards  $\alpha$ -methylglucoside, which appears, therefore, to be the substance best adapted for the differentiation of different varieties.

S. B. S.

**The Assimilability of Different Carbohydrates by Varieties of Yeast, etc.** PAUL LINDNER (*Chem. Zentr.*, 1912, i, 510; from *Woch. Brauerei*, 1911, 28, 561—563).—The author gives a tabular summary of the results of a previous work (carried out with Saito) in addition to investigations with melibiose and galactose, which are assimilated without undergoing fermentation.

S. B. S.

**Antiseptic Properties of Creosote.** K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 345—348).—Varying views are held concerning the particular constituents of creosote which produce its antiseptic action. The author has made a number of experiments with creosote, before or after subjection to treatment in various ways to remove the phenols, nitrogenous compounds, etc. The creosote was mixed in definite proportions with a gelatin medium, which was kept shaken until it solidified, so that the emulsified drops of creosote were distributed through the solid medium. The organisms examined were *Merulius lacrimans*, *Penicillium glaucum*, and a mould isolated in pure culture from putrefied strawberries.

The results show that, although the phenols and nitrogenous compounds by themselves exhibit considerable antiseptic properties, their presence in creosote only slightly increases the antiseptic power of the latter. Creosote freed from phenols and certain other constituents by treatment with sulphuric acid still exerts a decided antiseptic action.

T. H. P.

**Chemical Means of Protecting Plants from Frost.** N. A. MAXIMOFF (*Ber. deut. bot. Ges.*, 1912, 30, 52—65).—The introduction of neutral organic compounds, such as carbohydrates, alcohols, and acetone, into the plant cells can considerably increase the power of plants to resist the action of cold. The protective action is not directly connected with osmotic pressure and the lowering of the freezing point. The action varies with different substances, the sugars being the most effective, then glycerol, the monohydric alcohols, and acetone. Mannitol has a very slight protective action.

With the removal of the substance artificially introduced, the power of the plant in resisting cold returns to its original condition. Plants which are naturally able to resist the action of cold may be weakened in this respect by prolonged contact with water.

N. H. J. M.

**Action of Manganese on the Growth of Plants.** THEODOR PFEIFFER and E. BLANCK (*Landw. Versuchs-Stat.*, 1912, 77, 33—66).—Experiments in pots and on small plots (9 square metres) are described. The conclusion is drawn that under some conditions manganese salts may have a favourable effect on plant development;

it is, however, doubted whether the action of manganese is of practical importance, and more evidence is required before its employment can be recommended.

N. H. J. M.

The Action of some Carbon Derivatives on the Development of *Penicillium glaucum* and their Retarding Action in connexion with Solubility in Water and in Oil. JACOB BÖESEKEN and H. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 14, 928—935).—The influence on *Penicillium glaucum* was investigated of a number of carbon compounds of various types, these compounds serving as sole source of organic nutriment. Growth took place readily on compounds soluble in water but only sparingly soluble in oil, whilst compounds more readily soluble in oil than in water (*n*-butyric acid) only permitted growth in low concentrations, higher concentrations producing either a partial or complete inhibition. With compounds sparingly soluble in water, no interference was observed, although their solubility in oil was considerable (decoic acid).

Only a feeble growth or none at all took place on compounds, such as the higher fatty acids, which are nearly insoluble in water, or on compounds, such as formaldehyde, fairly soluble both in water and oil, and also on simple highly oxidised compounds like carbon dioxide, urea, and formic acid.

These phenomena are explained by supposing that the organism is protected by a layer of water, which the substances must traverse before entering the protoplasm. Substances insoluble in water will, therefore, have neither a nutrient nor a toxic action. Substances only sparingly soluble in water can only enter slowly and in insufficient quantity to produce retardation. On the other hand, compounds soluble both in oil and water can only act as a nutrient in low concentrations, and in higher concentrations will dissolve in the lipoids of the cell in sufficient quantity to produce inhibition.

An antiseptic, therefore, should be very soluble in oil, and also sufficiently so in water to penetrate readily into the cell.

W. J. Y.

The Interdependence of Protein Degradation in Plants, and their Respiratory Processes. I. The Action of the Oxygen of the Air on the Work of the Proteoclastic Ferment in Killed Plants. WLADIMIR PALLADIN and G. KRAALE (*Biochem. Zeitsch.*, 1912, 39, 290—301).—The autolysis of the proteins of killed plants which are rich in respiratory chromogens is strongly inhibited by the atmospheric oxygen. The looser the tissue the more strongly marked is this inhibition; thus, in the compact tissue of mushroom tops, the protein degradation was increased 15% in the absence of oxygen, whereas in the looser tissue of the stems it was increased 34%, and in the very loose tissue of the etiolated bean leaves it was increased 122%. The authors remark that in the study of the organs of killed plants or animals it is not sufficient to merely ascertain the optimal conditions (temperature reaction of the medium, etc.) for any given ferment; the action of other ferments present must also be taken into account, as these may produce products which are injurious to the ferment under consideration.

S. B. S.

**Limits of Germination of Seeds Submitted to the Action of Different Solutions.** PIERRE LESAGE (*Compt. rend.*, 1912, 154, 826—829).—Seeds of cress were steeped in solutions of alcohol of different concentrations for different periods, and then placed in water. After treatment with absolute or very dilute alcohol, the seeds retained their ability to germinate, whilst moderately dilute alcohol inhibited subsequent germination. The results were plotted in the form of curves, from which it was found that the time limit beyond which steeping in alcohol of any dilution will prevent germination is fifty days. The limit below which germination will invariably take place, whatever the concentration, is three hours. Similar curves were given by radish seeds steeped in solutions of sodium chloride.

W. O. W.

**Presence of Arsenic in Some Vegetable Foods.** F. JADIN and A. ASTRUC (*Compt. rend.*, 1912, 154, 893—896).—The organic matter in thirty-six different foods was destroyed by Bertrand's method (*Abstr.*, 1903, ii, 91, 310), and the arsenic estimated by Gautier's modification of Marsh's method. The following numbers give the weight of arsenic in mg. in 100 grams of material. Mushrooms 0.006, dry peas and beans 0.007—0.025, fresh vegetables 0.003—0.023, nuts 0.011—0.025, fruit 0.005—0.012. The highest proportion of arsenic was found in red haricots, 0.025, almonds 0.025, lettuce 0.023, celery 0.020.

W. O. W.

**Studies on Malic Acid. I. Transformation of Malic Acid into Sugar by the Tissues of the Maple (*Acer saccharinum*).** W. R. BLOOR (*J. Amer. Chem. Soc.*, 1912, 34, 534—539).—It is well known that during the ripening of fruits which contain malic acid, the acid disappears and the amount of sugar increases. The present investigation was undertaken in order to ascertain whether a similar change takes place in the sugar maple.

It has been found that when the tissue of maple shoots or buds is mixed with solutions of malic acid or malates and exposed to sunlight, a transformation of malic acid into sugar takes place, as is indicated by an increase of the reducing power and a decrease of the acidity of the solutions. A similar change takes place to a smaller extent in the dark at 38°. The agent to which the change is due is somewhat soluble in water, is destroyed by boiling, and is therefore probably an enzyme.

E. G.

**The Occurrence of Betaines in the Vegetable Kingdom.** KIYOHISA YOSHIMURA and GEORG TRIER (*Zeitsch. physiol. Chem.*, 1912, 77, 290—302).—The occurrence of betaines (stachydrine, betonicine, trigonelline) is sporadic and does not follow the natural orders. A number of examples are given of plants in various orders, some of which do, others of which do not, yield betaine. Choline was present in most.

W. D. H.

**The Lævorotatory Carbohydrate from the Rhizome of *Asclepias vincetoxicum*.** GEORGES MASSON (*Chem. Zentr.*, 1912, i, 356—357; from *Bull. Sci. pharmacol.*, 18, 282—283).—The rotatory

power of vincetoxin (asclepic acid) is due to the presence of a carbohydrate, which after purification with animal charcoal forms a white, hygroscopic substance with  $[\alpha]_D - 15.64^\circ$ . It reduces Fehling's solution after hydrolysis. S. B. S.

**Pectins of Aucuba and Sweet Orange.** VICTOR HARLAY (*J. Pharm. Chim.*, 1912, [vii], 5, 344—347).—The pectins isolated from aucuba fruits and sweet orange fruit rinds are described.

The dry ground pulp of aucuba fruits was extracted with boiling water and the extract precipitated with alcohol. The precipitate was purified by (1) boiling with alcohol ( $90^\circ$ ) and (2) solution in water, filtration, and re-precipitation with alcohol containing hydrochloric acid. It was then a brownish-white powder, containing 6.86% water and 1.80% ash, was soluble in water, did not reduce Fehling's solution, and was precipitated from its aqueous solution by lime water, baryta water, or copper sulphate solution. It had  $[\alpha]_D + 217.3^\circ$  (corr.) in water, and by Tollens' method yielded mucic acid, derived from galactan.

The white portion of sweet orange peel was freed from hesperidin by extraction with alcohol, and the pectin was then isolated by the method described above. It formed a white powder, giving an opalescent solution in water, which was precipitated by the agents mentioned above. It had  $[\alpha]_D + 176.6^\circ$  (corr.) in chloral hydrate solution, and on hydrolysis by dilute sulphuric acid gave arabinose and with nitric acid gave mucic acid, the latter derived from galactan.

T. A. H.

**The Pharmacognosy of Adenium Hongkel and Xanthoxylum ochroxylum.** MAURICE LEPRINCE (*Chem. Zentr.*, 1912, i, 586—587; from *Bull. Sci. pharmacol.*, 18, 337—345).—*Adenium Hongkel* (called Kidi Sarané on the West Coast of Africa, where it is native) contains a light yellow, amorphous substance,  $C_{19}H_{28}O_8$ , m. p.  $84-85^\circ$ ,  $[\alpha]_D + 134^\circ$ , which is quite insoluble in water. It is not a glucoside, and is a powerful heart poison of the digitalin group.

*Xanthoxylum ochroxylum*, from Central and South America, contains two alkaloids,  $\alpha$ - and  $\beta$ -xantherines, belonging to the group of berberine, two crystalline neutral substances,  $\alpha$ - and  $\beta$ -xanthoxylins, and a mixture of ethereal and fatty oils.

$\alpha$ -Xantherine,  $C_{24}H_{23}O_6N$ , obtained mostly from the bark, crystallises from benzene in colourless needles, m. p.  $186-187^\circ$ . It is coloured yellow when left exposed in air. The salts are similar to the berberine salts.  $\beta$ -Xantherine differs from the  $\alpha$ -alkaloid in the great solubility of the hydrochloride in water.

The fatty substances (6%) distil in a vacuum with slight decomposition, and are for the most part unsaponified on treatment with alcoholic potassium hydroxide. They have a sharp, burning, anæsthetic taste. When kept they change into a wax-like substance insoluble in petroleum. They act as an analgesic.  $\alpha$ -Xantherine has a paralytic action on the intracardial nervous system. S. B. S.

**Pharmacodynamic Investigations of *Catha edulis*.** JACQUES CHEVALIER (*Chem. Zentr.*, 1912, i, 371; from *Bull. Sci. pharmacol.*, 18, 264—275).—The author gives a general account of the uses, occurrence, and pharmacognosy of the plant. To obtain *katine* from it, the powdered leaves are ground with dilute ammonia to a thick paste, which is extracted twenty-four hours' later with 80% alcohol. After evaporation of the solvent a syrupy residue is obtained, which yields a precipitate on treatment with ammonia. This, after drying, and the mother liquor are extracted with chloroform. The alkaloid is dissolved out with acidified water, precipitated with dilute ammonia, again taken up with chloroform, from which it is extracted with acid, and again precipitated. It has a composition represented by the formula  $C_{10}H_{15}ON_2$ . Yield, 0.11—0.125%. The leaves of the older plants give the best yield. It is hard to obtain it crystalline, but it gives a crystalline *sulphate* and *hydrochloride*. It has a sedative action on the nerves like cocaine and small doses of morphine; it is not, however, either an analgesic or local anæsthetic; it has a stimulant action on the heart and muscles similar to that of cocaine.

S. B. S.

**Chemical Examination of Jambul Seeds.** FREDERICK B. POWER and THOMAS CALLAN (*Pharm J.*, 1912, [iv], 34, 414—417).—These seeds, derived from *Eugenia Jambolana*, Lam., have been examined already by Elborne (*ibid.*, 1888, 921), Pottiez (*Ann. Pharm.*, Louvain, 1899, 5, 373, 490), and Boersch (*Apoth. Zeit.*, 1899, 510; 1900, 92; 1901, 350).

An alcoholic extract of the seeds yielded on steam distillation: (A) a dark-coloured aqueous liquid, (B) a soft resin, and (C) essential oil,  $D_{20}^{20}$  0.9258,  $n_D^{20}$  1.501 in a 50 mm. tube, which was pale yellow, had an agreeable odour, and on distillation, under 25 mm. pressure began to boil at 118°, gave a large fraction, b. p. 145—155°, and a final small fraction, b. p. 155—170°.

The aqueous liquid (A) on extraction with ether afforded gallic acid already found by Elborne (*loc. cit.*). It also contained some jambulol (see below), tannin, a sugar, which yielded *d*-phenylglucosazone, and indefinite products.

The soft resin (B) was extracted in turn by light petroleum, ether, chloroform, ethyl acetate, and alcohol. The light petroleum extract consisted of resin and fatty matter. The latter after hydrolysis with alcoholic potash yielded (1) unsaponifiable matter, a mixture of an alcohol and a hydrocarbon, as well as traces of a phytosterol and (2) a mixture of oleic, linoleic, stearic, and palmitic acids. The ether, chloroform, and ethyl acetate extracts consisted of indefinite amorphous products, but the ethyl acetate extract contained some jambulol (see below). The portion finally dissolved by alcohol was separated into readily soluble, amorphous resin and a sparingly soluble substance, *jambulol*,  $C_{16}H_{31}O_4(OH)_5$ , which crystallises (with solvent) from pyridine in brown needles, is sparingly soluble in sodium carbonate, but readily in potassium hydroxide solution, forming an intensely yellow liquid, from which it is re-precipitated by acids. It is insoluble in organic solvents, except pyridine, and does not melt at 340°. Jambulol yields a *pentacetyl* derivative, m. p. 335° (decomp.), pale

brown leaflets from boiling nitrobenzene, and a *pentabenzoyl* derivative, m. p. 333°, small, colourless plates. The seeds are free from alkaloid, glucoside, and enzyme. The statement of Pottiez (*loc. cit.*) that they contain quercitol and cinnamic acid could not be confirmed, nor that of Boersch that they contain a glucoside, "antimellin." T. A. H.

**Pectins of *Kalmia latifolia* Leaves and *Verbascum thapsus* Roots.** EMILE VERDON (*J. Pharm. Chim.*, 1912, [vii], 5, 347—353. Compare Bourquelot and Bridel, *Abstr.*, 1910, i, 817; Bourquelot and Fichtenholz, this vol., ii, 196).—The pectins of these two plants have been isolated by the method employed by Bourquelot and Hérissé (Abstr., 1898, i, 607), using material which had first been extracted with alcohol, and are described.

*Verbascum thapsus* roots yield 0.66% of pectin as a grey powder, containing 6.89% of ash, soluble in water to an opalescent liquid, and having  $[\alpha]_D + 157.55^\circ$  (corr.). The aqueous solution is coagulated by lucerne pectase, on hydrolysis by dilute sulphuric acid yields arabinose, and on treatment with dilute nitric acid furnishes mucic acid.

*Kalmia latifolia* leaves furnished 0.65% of pectin, and the mother liquors on keeping deposited about 0.16% of a second product, *B*. The pectin is a whitish powder containing 19.24% of water, and yielding 3.50% of ash. It is soluble in water, forming a viscous, opaque liquid, which becomes limpid when shaken with powdered talc and filtered. It has  $[\alpha]_D + 158.62^\circ$ , is precipitated by the usual reagents, such as lime water, and coagulated by pectase. With nitric acid it gives mucic acid, and with dilute sulphuric acid is hydrolysed to arabinose.

Product *B* is a whitish powder containing 1.649% of ash, and having  $[\alpha]_D + 97.18^\circ$ . It swells in water and finally dissolves, yielding an opalescent, viscous liquid. It is not coagulated by pectase, and is not precipitated by the reagents which precipitate pectins, or does it yield mannose on hydrolysis. It reduces Fehling's solution only after hydrolysis by dilute sulphuric acid under pressure at 105°. With nitric acid, it yields mucic acid. T. A. H.

**The Resin of *Khaya Madagascariensis*.** A. GÉRARD (*Chem. Zentr.*, 1912, i, 357; from *Bull. Sci. pharmacol.*, 18, 148—151).—The plant belongs to the family of the *Meliaceae*. The resin from the bark is partly soluble in water (54.8% of the dried substance). The solution is dextrorotatory. The resin contains an oxydase, peroxydase, and emulsin, but no myrosin. The organic constituents contained galactans and pentosans. Starch is absent. S. B. S.

**The "Encrusting" Pigment of the Sugar-cane.** L. G. LANGGUTH-STEUERWALD (*Chem. Zentr.*, 1912, i, 831—832; from *Med. Prefestation Java-Suiker industrie*, 1911, 365—379).—For the preparation, the material was extracted for two days with 3% sodium hydroxide solution, and Fehling's solution was added to this extract, which precipitates the resinous matters as copper salts; from the filtrate, the pigment was obtained as a flocculent precipitate by acidification with sulphuric acid. This has the character of an acid, is

soluble in alcohol, but only slightly soluble in water and insoluble in ether and benzene. It has the composition represented by the formula  $(C_5H_7O_2)_x$ . For it the name *saccharetin* is proposed; it is in many of its properties analogous to the phlobaphens, and is to be regarded as a constituent of the encrusting woody matter, especially lignin. With phloroglucinol and hydrochloric acid it gives an intense red coloration, and with aniline sulphate and sulphuric acid, an orange colour. On dry distillation it yields pyrogallol; on warming with dilute acids, vanillic acid and vanillin. On fusion with potassium hydroxide it yields protocatechuic acid and catechol. S. B. S.

**Action of Acids, Alkalis, and Some Inorganic Salts on Plants.** K. K. GEDROIZ (*Bied. Zentr.*, 1912, 41, 179—181; from *J. exper. Landw.*, 1910, 10, 669).—Water culture experiments in which mustard, flax, vetches, lucerne, and barley were grown in  $N/0.01$ - to  $N/0.001$ -solutions of nitric, hydrochloric, sulphuric, phosphoric, acetic, citric, and oxalic acids, in  $N/0.06$ - to  $N/0.002$ -solutions of alkali hydroxides, and in solutions of different strengths of magnesium and potassium chlorides, potassium and calcium nitrates, and potassium, magnesium, and calcium sulphates.

Flax was found to be the most sensitive to acids, mustard the next, vetches third, and barley fourth. In solutions of salts, mustard is more sensitive than flax.

Magnesium sulphate is more toxic to barley and vetches than alkali hydroxide and citric acid, and the strong acids are more toxic than alkalis and salts in concentrations which kill the plants. Comparing the highest concentrations which are without injury to plants, it is found that alkalis are more toxic than weak acids. Strong acids are more toxic to mustard and flax than alkalis, whilst with barley and vetches strong acids and alkali are about equal.

Sulphuric acid and magnesium sulphate dissociate almost equally in  $N/0.01$ -solutions, and since the former is much more toxic than the latter, it follows that H ions are more toxic than Mg ions. It is also shown that OH ions are more toxic than  $SO_4$  and  $NO_3$ , and that the H ion is probably more toxic than the OH ion. N. H. J. M.

**The Action of Certain Basic Compounds on Seedlings. Comparison with their Action on Micro-organisms.** THOMAS BOKORNY (*Centr. Bakt. Par.*, 1912, ii, 32, 587—605).—Small quantities of ammonia and other basic substances lead to a granulation of the plasma-protein in cells of certain *algae* and *infusoria*, and eventually bring about death of the organism. Similarly, such substances retard or inhibit the germination of seeds, although wheat, barley, mustard, hemp, vetches, peas, and beans appear to exhibit specific differences in their sensitiveness to different compounds.

Of the compounds tested, ammonia and aniline are extremely toxic, caffeine, antipyrine, and ethylamine less so, and nicotine hydrochloride and potassium hydroxide appear to stimulate growth. H. B. H.

**Chemical and Physical Nature of Red Soils.** E. BLANCK (*J. Landw.*, 1912, 60, 59—73).—Analysis of laterite soils ("Roterden") and red soils ("rote Erden") formed in cooler climates showed no essential

differences. It was found, however, that the surface of "Roterden" in relation to the amount of ferric oxide and soluble alumina is much greater than that of "rote Erden." The conclusion is drawn that the difference in the two classes of soil is due to the condition of the free sesquioxides, and it is considered that the partly colloidal condition of the iron oxide in "Roterden" is the cause of their greater surface.

N. H. J. M.

**Oxidation in Soil.** MICHAEL X. SULLIVAN and F. R. REID (*J. Ind. Eng. Chem.*, 1911, 3, 25—30).—A continuation of the work of Russell and others on: (1) The methods of testing oxidation in soils. (2) Effect of various treatments on soil oxidation, such as poisons and antiseptics, dry heat, steam heat, incineration, acids on incinerated and on normal soils. (3) The influence of various salts with and without certain organic acids and their salts. (4) Influence of various factors in soil oxidation, such as water content, cropping, and fertilisers. (5) Relation of organic matter to soil oxidation. (6) The effect of excessive oxidation.

The following conclusions are drawn: (a) soils have the power to oxidise aloin. (b) This oxidising power is increased by adding water until the optimum moisture is reached, by the commonly used fertilisers in conjunction with plant growth, and by salts of manganese, iron, aluminium, calcium, and magnesium in the presence of simple organic hydroxy-acids.

(c) Oxidation in soil is comparable to oxidation in plants and animals.

(d) The oxidative powers of the soil appear to be mainly non-enzymotic, and to be brought about by interaction between inorganic constituents and certain types of organic matter. It may be produced by organic matter in a state of autoxidation and by inorganic oxygen carriers, such as manganese and iron.

(e) Oxidation is greater in the soil than in the subsoil, and greater in fertile than in barren soils.

F. M. G. M.

**Decomposition of Different Organic Hydrocarbons in Soils, Especially under the Influence of Lime.** OTTO LEMMERMANN, KEIJIRO ASO, H. FISCHER, and L. FRESENIUS (*Landw. Jahrb.*, 1911, 41, 217—256).—An enquiry as to the influence of various salts (especially lime salts) on the rate of decomposition of organic matter in soils; it was found that in the presence of calcium carbonate or potassium hydroxide an increased amount of organic matter was decomposed. The respective influence of kainite, superphosphate, and farmyard and other manures was also investigated.

F. M. G. M.

**Composition of the Clay obtained by the Schloesing-Grandeau Method.** E. BLANCK (*J. Landw.*, 1912, 60, 75—81).—The amounts of silica and of aluminium and ferric oxides were estimated in the clay separated from various soils. The results show that the relation of  $\text{SiO}_2 : \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$  = about 2.1. The products were not uniform in composition, but showed a general similarity. The

composition has nothing to do with the chemical nature of kaolin, the clay is only in part kaolin, consisting chiefly of free quartz.

N. H. J. M.

**The Co-operation of Organisms in Clay-formation.** PAUL ROHLAND (*Biochem. Zeitsch.*, 1912, 39, 205—207).—The odour of certain clays, which can be removed by ferric saccharate solutions, suggests to the author the possibility that clay may owe its formation to the action of micro-organisms.

S. B. S.

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## Analytical Chemistry.

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**A Flat Filter.** FRANZ HUNDESHAGEN (*Zeitsch. öffentl. Chem.*, 1912, 18, 92—94).—In a cylindrical funnel provided with a perforated disk are placed two filter papers, the diameter of which should be about 3 cm. greater than that of the disk. The edges of the papers are torn radially for a distance of about 1.5 cm. from the circumference while they are held together, and the papers then turned slightly so that the slits do not coincide; the papers are now placed on the disk, the edges pressed against the sides of the funnel, and moistened with water so as to form a tight joint. W. P. S.

**Filtering Cap for Pipettes.** H. STOLTZENBERG (*Chem. Zeit.*, 1912, 36, 378).—Small caps of filter paper felt, fitting over the tip of a pipette, are useful when it is desired to withdraw small quantities of clear liquid from a turbid solution. C. H. D.

**Simple Stand for Electrolysis with Gauze Electrodes without Disturbance of the Liquid.** A. FISCHER and REMIGIUS FRESENIUS (*Zeitsch. anal. Chem.*, 1912, 51, 294—296).—A stand designed specially for electrolytic preparations and estimations in which gauze electrodes are employed. L. DE K.

**Apparatus for Solubility Determinations in the Absence of Atmospheric Carbon Dioxide.** THOR EKECRANTZ and H. PALME (*Zeitsch. anal. Chem.*, 1912, 51, 292—294).—The solution to be titrated (lime or baryta water, etc.) is placed in a Erlenmeyer flask fitted with a doubly perforated cork, through which pass a soda-lime tube and a tube bent at a right angle; the latter is connected at the lower end by means of a small rubber tube to a tube somewhat enlarged, and plugged with cotton wool (*a*). The upper end of the tube is connected to a similar tube, which is fitted to a filtering tube (*b*), in which is placed a fairly large filter; the end of the tube should be raised slightly above the filter. The stem of the filtering tube, which is fitted with a tap (below *b*), passes through the cork of a 50 c.c.

pipette, the upper part of which is enlarged and has a lateral tube connected to a vertical soda-lime tube (*d*), which can be closed with a piece of rubber and a pinchcock; the lower end of the pipette is closed in the same manner (*c*) like a burette. After closing (*d*) a current of air is drawn or forced through the apparatus, (*a*) is lowered into the liquid, (*c*) is closed and a slight suction applied at (*d*), and, owing to the double filtration, the liquid runs quite clear into the pipette. When this is filled, the tap is turned off and the liquid is drawn off by opening (*c*). This quantity, however, is rejected, and a fresh lot is collected for the titration. The apparatus can also serve for filtering volatile liquids without loss; in such case, the two soda-lime tubes may be joined by means of a rubber tube, and a closed space is thus obtained.

L. DE K.

**Estimation of Halogens in Some Organic Compounds.** MONTHULÉ (*Ann. Chim. anal.*, 1912, 17, 133).—A known weight of the substance (such as iodised tannin, brominised peptones, etc.) is dissolved, and a definite amount of standard silver nitrate is added. Nitric acid and pure zinc are added, and when the latter has completely dissolved, the solution is made up to a definite bulk. The excess of silver is then titrated in the usual manner in an aliquot part of the filtrate.

L. DE K.

**A Hygienic Limit for Potable Waters.** ARISTIDE DANÉ (*Bull. Soc. chim.*, 1912, [iv], 11, 261—262).—It is pointed out that before deciding that a water is abnormally high in chlorides, a number of waters known to be above suspicion should be collected in the same district and examined, and the suspected water should not be condemned unless it contains twice the mean quantity of chlorides present in good waters from the same area. The presence of saline ammonia is regarded as unimportant unless a positive result is obtained with Nessler's reagent, without concentration or distillation, and the same applies to nitrites. For the latter a solution of indole in alcohol is recommended, the water having previously been acidified with acetic acid. For the biological test the following solution is recommended: pancreatic peptone 2 grams, sodium chloride 1 gram, water 100 grams. This should be neutralised exactly with sodium hydroxide, using litmus as indicator, and should be kept in stoppered bottles holding from 15 to 30 grams, one-third full, after being sterilised in an autoclave at 110° during twenty minutes.

T. A. H.

**Perchloric Acid in Electro-chemical Analysis.** WALTER S. HENDRIXSON (*J. Amer. Chem. Soc.*, 1912, 34, 389—392).—Goldblum and Terlikowski (this vol., ii, 261) have shown that the perchloric acid in nickel and cobalt perchlorates can be estimated electrolytically, the metals being deposited and the acid left in solution. In view of this work, the author has given an account of some experiments which he has made on the electrolytic estimation of copper, silver, and cadmium from perchloric acid solutions, which have given good results. In the case of cadmium, traces of the metal remain in solution, but, neverthe-

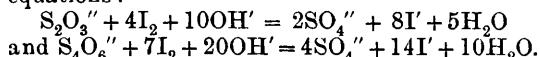
less, it is considered that cadmium can be separated electrolytically from dilute perchloric acid as completely as from any other solvent. E. G.

**The Estimation of Sulphuric Acid.** K. K. JÄRVINEN (*Chem. Zentr.*, 1912, i, 526—527; from *Ann. acad. sci. Fennicae*, A 2, (4), 1—22, (16) 1—31).—It is not possible to precipitate barium sulphate in a pure state from solutions containing metals. The best result is obtained by precipitating with benzidine hydrochloride, dissolving the precipitated sulphate in hydrochloric acid, and adding barium chloride. The precipitate then retains a little barium chloride, and some barium sulphate remains in solution. Precipitation with acid *N*/5-benzidine hydrochloride in boiling solution, followed by titration of the washed precipitate with sodium hydroxide and phenolphthalein in boiling solution, gives results which are only 0.1—0.2% too high.

Ammonio-copper sulphate or chloride yields with benzidine a compound, which probably has the composition  $C_{12}H_8(NH_2CuCl)_2$ .

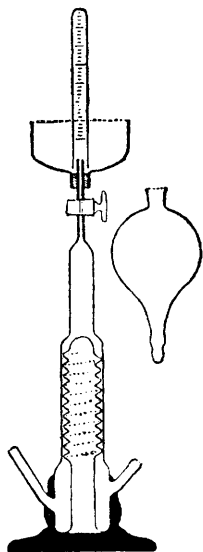
C. H. D.

**The Behaviour of Iodine Towards Thiosulphate and Tetrathionate in Alkaline Solution.** EMIL ABEL (*Zeitsch. anorg. Chem.*, 1912, 74, 395—406. Compare Batey, Abstr., 1911, ii, 436).—The observation of Topf (Abstr., 1887, 688) that thiosulphate is partly oxidised by iodine to sulphate in alkaline or sodium hydrogen carbonate solution has been generally overlooked. Both sodium thiosulphate and tetrathionate may be accurately titrated in alkaline solution by adding an excess of iodine and titrating back after acidifying, the oxidation to sulphate being quantitative according to the equations:



The experiments described show that this method of titration is accurate. The actual mechanism of the reaction is different from the equations given above, as tetrathionate is not an intermediate product in the oxidation of thiosulphate to sulphate.

C. H. D.



**Improved Apparatus for the Volumetric Estimation of Nitrogen.** FERRY (*Zeitsch. anal. Chem.*, 1912, 51, 367).—The apparatus will be readily understood from the figure. The gas is collected over mercury and aqueous potassium hydroxide. The use of a spiral ensures a complete absorption of carbon dioxide. By opening the stopcock the nitrogen enters the graduated tube, and hence is not measured over the ley. The mercury serves as a seal. The pressure can be regulated by raising or lowering the levelling

bulb. In order to prevent a regurgitation of the liquids at the end of the combustion, a three-way cock is inserted between the apparatus and the combustion tube.

L. DE K.

**An Unrecognised Source of Error in the Kjeldahl-Gunning Method for the Estimation of Nitrogen.** PERCY A. W. SELF (*Pharm. J.*, 1912, [iv], 34, 384—385).—The author has found that if during the boiling with sulphuric acid and potassium sulphate (Gunning's modification of Kjeldahl's process) too much free acid is used up, a loss in ammonia takes place; this becomes most serious when the liquid approaches the composition of potassium hydrogen sulphate. In order to avoid this source of error, at most 3·5 grams of a sample consisting mainly of carbohydrates should be taken for analysis, and 1·5—3 grams of a sample containing 80—90% and 5—10% of fat respectively. This is then treated with 25 c.c. of sulphuric acid, and 12 grams of potassium sulphate; at least 16 grams of free acid should be left after the operation is finished.

L. DE K.

**Volumetric Method for the Estimation of Hydrazine.** GEORGE S. JAMIESON (*Amer. J. Sci.*, 1912, [iv], 33, 352—353).—A quantity of hydrazine sulphate not exceeding 0·1 gram is placed in a 250 c.c. stoppered bottle, together with 20 c.c. of water, 30 c.c. of hydrochloric acid, and 6 c.c. of chloroform. A solution containing 3·567 gram of potassium iodate per litre is then run in gradually, with constant shaking, until the chloroform, after increasing and then diminishing in colour, is just bleached: 1 c.c. = 0·000534 gram of hydrazine. The process can also be applied to the sparingly soluble double sulphates of hydrazine with zinc, cobalt, nickel, and cadmium.

L. DE K.

**Estimation of Phosphoric Acid by means of Citro-Molybdic Acid Solution.** CH. MULLER (*Bull. Assoc. chim. Sucr. Dist.*, 1912, 29, 619—622).—It has been shown by Pellet that the addition of ammonium citrate to the molybdic acid reagent causes the ammonium phosphomolybdate precipitate to have a constant composition, and the author records the results of a number of experiments carried out with the object of ascertaining the quantity of citrate which it is necessary to add for this purpose. The most trustworthy results are obtained when 1 c.c. of ammonium citrate solution (prepared according to Petermann's formula) is added to every 50 c.c. of molybdic acid reagent employed for the precipitation of the phosphoric acid; if a larger proportion of citrate is added, the results obtained are too low. The yellow precipitate should be dried at 100—105° before being weighed, and 0·03 gram added to the weight in order to correct for the solubility of the precipitate in the precipitating solution and washing solution, when the total volume of these does not exceed 500 c.c. The factor 0·0374 is used to convert the weight of the precipitate into phosphoric anhydride.

W. P. S.

**Phosphomolybdate Estimation of Phosphoric Acid in Soils.** SAMUEL J. M. AULD (*Analyst*, 1912, 37, 130—136).—The direct weighing of the phosphomolybdate precipitate should be avoided owing to the difficulty of controlling the amount of ammonia. When direct weighing is adopted, Carnot's method should be employed, using the

factor 0.0378. If the precipitate is dissolved in ammonia the residue should be weighed in the uniformly blue condition, as it is difficult to remove the ammonium salts without decomposing the residue to an indefinite extent. According to whether the residue is heated until partly or until quite blue, the factors should be 0.0389 and 0.0393 respectively.

As the ordinary phosphomolybdate precipitate is decomposed by ammonia, it is best to re-precipitate with nitric acid, filter through a Gooch crucible, wash, and ignite the residue until dark blue and of constant weight. The factor is 0.0396.

A quicker method is to wash the re-precipitated phosphomolybdate by decantation, evaporating to dryness, and igniting the residue.

N. H. J. M.

**Accurate Volumetric Estimation of Phosphoric Acid in Phosphate Rock.** JOHN G. FAIRCHILD (*J. Washington Acad. Sci.*, 1912, 2, 114).—The method is a modification of Pemberton's alkali hydroxide titration, which in its original form gave results 1.5% too low. This error is reduced (average error 0.03%  $P_2O_5$ ) by precipitating the soluble phosphate with barium chloride in excess. The precipitated barium phosphate undergoes hydrolysis, necessitating moderate sized portions for titration.

L. J. S.

**Estimation of Phosphoric Acid in Presence of Colloidal Silicic Acid.** PETR. G. MÉLIKOFF and M. BECAIA (*Compt. rend.*, 1912, 154, 775—776. Compare this vol., ii, 202).—The ordinary method for estimating phosphoric acid by means of ammonium molybdate gives too high results when colloidal silicic acid is present, owing to the precipitation of silicomolybdates. The method previously described for the separation of phosphorus and silicon should be employed in these circumstances.

W. O. W.

**A Spectroscopic Method of Estimating Carbon Monoxide.** H. HARTRIDGE (*J. Physiol.*, 1912, 44, 1—21).—A spectroscopic method for the estimation of carbon monoxide in combination with hæmoglobin is described, and the apparatus figured. It is rapid, and possesses other advantages over older (for example, the carmine) methods.

W. D. H.

**Estimation of Carbon Dioxide.** HARFORD M. ATKINSON (*Chem. News*, 1912, 105, 136).—A carbonic acid apparatus differing from the usual type by having a side-bulb into which is placed by the aid of a paper cone the carbonate to be tested. After introducing the necessary volume of decomposing acid, 1—1.5 gram of marble is added, and as soon as this has dissolved the cork holding the usual sulphuric acid drying tube is inserted.

After weighing, the flask is inclined so as to make the acid come into contact with the substance, and when this is dissolved, the flask is re-weighed.

No suction or heating the liquid is required when using this apparatus.

L. DE K.

**Natural Analytical Classification of the Metals based on the Properties of their Salts with Naphthenic Acid: Reactions of these Salts in Non-aqueous Solutions.** K. W. CHARITSCHKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 348—354).—The author's experiments show that the properties of the salts formed with naphthenic acid may be used as a means of separating metals into groups, and that, in some cases, the reactions (with hydrogen peroxide, etc.) of these salts in non-aqueous solvents serve for the separation and estimation of the metals. These reactions have an advantage over those effected in aqueous solutions in that the properties of the salts are not modified by such processes as hydration or hydrolysis, or association of the solvent. This method bridges, to a considerable degree, the differences shown in other analytical methods between oxides, such as  $\text{Ag}_2\text{O}$  and  $\text{Fe}_2\text{O}_3$ , of similar type.

Of the oxides of the type  $\text{RO}$ , the following are brought into one group:  $\text{CuO}$ ,  $\text{FeO}$ ,  $\text{CoO}$ ,  $\text{NiO}$ ,  $\text{CdO}$ ,  $\text{SnO}$ ,  $\text{PbO}$ ,  $\text{HgO}$ , and  $\text{MnO}$ . The naphthenates corresponding with these oxides are characterised by considerable solubility in hydrocarbons.  $\text{ZnO}$ , in agreement with the position of zinc in the periodic system, does not find a place in this group, its naphthenate being only slightly soluble in hydrocarbons and hence resembling more those of the alkaline earths. Also  $\text{Fe}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$  seem to form a separate group, giving naphthenates sparingly soluble in hydrocarbons, and, when dissolved, not precipitable by hydrogen sulphide.

Examination of the acids synthesised by Zelinsky from the above point of view shows that the reactions of cobalt, copper, and ferrous salts with hydrogen peroxide are given exclusively by *cyclopentane-carboxylic* compounds, so that these reactions are characteristic of the pentamethylene ring. This result is applied to the investigation of various problems. For instance, the menthane obtained by reducing the chloride prepared from menthol with hydriodic acid yields cyclic acids when oxidised in the air in presence of alkali. Since these acids react in ethereal solution with copper sulphate in a similar manner to the acids from naphtha, it is concluded that change from a hexamethylene to a pentamethylene derivative occurs during either the reduction of menthol or the subsequent oxidation.

From dilute solution, metals such as copper, lead, mercury, etc., may be extracted in a concentrated form by shaking the solution with a small quantity of a strong solution of naphthenic acid in light petroleum.

The method serves well for the detection of cobalt in presence of nickel, the separation of iron from aluminium, the investigation of sulphides of the metals, and their preparation in the pure state, etc.

T. H. P.

**The Applicability of the Mercury Cathode, Especially in the Electro-analytical Separation of Metals.** PAUL BAUMANN (*Zeitsch. anorg. Chem.*, 1912, 74, 315—350).—The objections to the use of the mercury cathode in analysis have been shown by Böttger (*Abstr.*, 1909, ii, 619) and Adlers and Stähler (*Abstr.*, 1909, ii, 764)

to be groundless. The possibilities of separation are reviewed, and it is shown that the order of potential differences is considerably different from that found for platinum cathodes.

The mercury is conveniently purified by prolonged shaking with chromic acid solution, followed by distillation from a cast iron retort in a current of carbon dioxide. The ether required must be heated for some time with potassium hydroxide before being distilled, otherwise it reacts with the mercury.

A cylinder of Jena glass is used, 40 mm. in diameter and 70 mm. high, provided with a glass tap just above the level of the mercury. The tap is replaced by a stopper when weighing. The anode is a stout platinum wire, carrying two horizontal platinum gauze disks, and is rotated during the electrolysis. Electrical heating is used when hot solutions are required. The quantity of mercury used is about 60 grams, and this is washed with alcohol and ether and dried in a current of air before weighing.

Mercury in mercurous or mercuric solution may be separated from bismuth or copper, and silver from bismuth, in about an hour at the ordinary temperature. The separation of copper from antimony, and of copper or bismuth from cadmium, requires a temperature of 70°. It has not been found possible to separate zinc and cadmium quantitatively.

The estimation of halogens in neutral solution may be performed in a simpler manner than that described by Hildebrand by using the cell described above, with a silvered anode. In order to avoid alkalinity of the solution, it is advisable to add a sufficient quantity of cadmium or nickel sulphate, so that an equivalent quantity of these metals is deposited on the cathode in place of the alkali metal.

For ordinary purposes it is unnecessary to provide for the determination of the cathode potential, the total difference of potential giving sufficiently good results.  
C. H. D.

**The Standardisation of Sodium Hydroxide Solution for Nitrogen by means of Ammonium Chloride.** ARTHUR GESERICK (*Chem. Zentr.*, 1912, i, 527—528; from *Woch. Brauerei*, 1911, 28, 557—558).—One gram of ammonium chloride, dried over sulphuric acid, is distilled with sodium hydroxide into standard sulphuric acid, and the excess of acid titrated with the alkali.  
C. H. D.

**Estimation of Calcium in the Presence of Magnesium.** E. C. CARRON (*Ann. Chim. anal.*, 1912, 17, 127—129).—The solution containing the chlorides of calcium and magnesium and a certain quantity of ammonium chloride and ammonia is concentrated to 60 or 80 c.c. After almost neutralising with hydrochloric acid, 20 c.c. of ammonium (or sodium) hydrogen sulphite are added, and the liquid is heated to initial boiling. As soon as a precipitate begins to form, 20 c.c. of ammonia (22° Baume) are added with stirring, which causes the formation of insoluble normal calcium sulphite. This is then collected and washed with dilute ammonia, and converted into sulphate by moistening with a solution of ammonium sulphate in sulphuric acid and subsequent drying and ignition.

To the filtrate is added some solid ammonium carbonate, and then a slight excess of hydrochloric acid. When the sulphur dioxide has disappeared, the magnesium is precipitated in the usual manner by ammonia and sodium hydrogen phosphate. L. DE K.

**Estimation of Calcium Carbonate in Soils.** HERBERT S. SHREWSBURY (*Analyst*, 1912, 37, 128—129. Compare Marr, *Abstr.*, 1909, ii, 938).—The soil (10 grams) is shaken for ten minutes with 100 c.c. of approximately  $N/4$ -acetic acid, allowed to settle, and decanted through a filter cone. A control experiment is made at the same time in which distilled water is used instead of acetic acid. The filtrates of each (25 c.c.) are evaporated in platinum dishes, ignited for thirty minutes, and the residues treated with 10 c.c., or more, of  $N/10$ -acetic acid. The excess of acid is titrated with  $N/10$ -alkali, the number of c.c. of the control subtracted from that obtained from the acid soil extract, and the result multiplied by 0.2. The product gives the percentage of calcium carbonate in the soil.

With soils containing more than 5% of calcium carbonate, less than 10 grams should be used. N. H. J. M.

**Analysis of Calcined Magnesite.** L. DEDE (*Chem. Zeit.*, 1912, 36, 414).—The process does not differ materially from the one usually employed, but in order to get trustworthy results, some precautions should be taken. First of all only 0.1 gram of the material should be taken for analysis, and the filtrate from the silica must be evaporated so as to separate the traces remaining. The second filtrate is then diluted to 200 c.c., 0.5—1 gram of ammonium chloride is added, and any iron, etc., precipitated by adding ammonia and boiling until this is almost expelled. The separation of small amounts of calcium is the most troublesome point, but good results are obtained as follows: the filtrate is diluted to 400 c.c., acidified with hydrochloric acid, and mixed with oxalic acid in slight excess. After heating to boiling, a slight excess of ammonia is added, and then at once 50 c.c. of boiling solution of ammonium oxalate (1:24). After four hours (not longer) the calcium oxalate is collected, washed, and finally burnt to oxide; it is free from magnesia.

The filtrate is acidified with hydrochloric acid, one gram of ammonium hydrogen phosphate is added, and the solution heated to boiling. After neutralising by ammonia with phenolphthalein as indicator, the precipitate should not be flocculent; if so, there is not sufficient phosphate present. Addition of one-fourth of the volume of ammonia now completes the precipitation. L. DE K.

**Volumetric Estimation of Glucinum.** BENNO BLEYER and A. MOORMAN (*Zeitsch. anal. Chem.*, 1912, 51, 360—367).—*Iodometric process.*—Twenty-five c.c. of an approximately  $N/10$ -solution of a normal glucinum salt are heated with 10—20 c.c. of a solution of potassium iodate (30 grams per litre) and one gram of potassium iodide in a current of hydrogen, and the iodine liberated is collected in a solution of potassium iodide and titrated with  $N/10$ -sodium thiosulphate; 1 c.c. of this = 0.000455 gram of glucinum.

*Acidimetric process.*—Normal glucinum salts behave like an acid to phenolphthalein, and may consequently be titrated with *N*/10-sodium hydroxide. Glucinum sulphate should be converted into the chloride by means of barium chloride. The solution should be slightly warm, and the pink colour should remain permanent. If, as is mostly the case, the liquid contains free acid, aqueous sodium hydroxide is added until the precipitate formed has just redissolved. After diluting to a definite volume, an aliquot part is titrated with *N*/10-acid with phenolphthalein, and another portion with methyl-orange, as indicator. The difference in the two titrations represents the acid in combination with the glucinum.

L. DE K.

**Estimation of Lead, Nickel, and Zinc by Precipitation as Oxalates and Titration with Potassium Permanganate.** H. L. WARD (*Amer. J. Sci.*, 1912, [iv], 33, 334—336).—To the boiling solution of a soluble lead, zinc, or nickel salt is added a sufficiency of oxalic acid, and then, to ensure complete precipitation and the formation of a pure oxalate, an equal volume of acetic acid is added; in the case of lead, ammonium oxalate may be used as precipitant.

The oxalate is collected, washed, treated with hot dilute sulphuric acid, and at once titrated with standard permanganate. When dealing with nickel, the green colour may be bleached by suitable dilution and cautious addition of cobalt sulphate.

L. DE K.

**Sources of Error and the Electrolytic Standardisation of the Conditions of the Iodide Method of Copper Analysis.** AMOS W. PETERS (*J. Amer. Chem. Soc.*, 1912, 34, 422—454).—In order to find a volumetric method for the accurate estimation of copper in the alkali tartrates from sugar analyses, a study has been made of the iodide method in which the iodine liberated in equivalent quantity from potassium iodide is estimated by titration with standard sodium thiosulphate solution.

It has been found that the ordinary methods of standardising thiosulphate solutions do not give the same value as copper does, and the standardisation therefore can only be correctly effected by means of a standard copper solution, the value of which has been determined by electrolytic deposition from a given volume, or which has been made from copper of known purity. It has been suggested by Bray and McKay (*Abstr.*, 1910, ii, 996) that the discrepancy between the iodine and copper methods is due to the adsorption of iodine by cuprous iodide, but this view is now shown to be untenable. A tartrate-cyanide electrolyte for the deposition of copper is described, which yields a good deposit with the use of high voltage, high current density, and the application of heat.

The preparation of solutions of copper or its compounds for estimation by the iodide method may be effected by dissolving the substance in as small a quantity as possible of slightly diluted nitric acid. After adding water and powdered talc, the mixture is boiled for five to ten minutes to expel the nitrous acid. After cooling and diluting, the solution is ready for estimation.

The accuracy of the results is affected by varying concentrations of

mineral acid and by the presence of salts. Concordant results are obtained in neutral and acetic acid solutions, free from salts. When much salt is present, sulphuric acid should be used rather than acetic acid in order to obtain prompt liberation of the iodine and a sharp end-point.

The results obtained by the iodide method are independent of the concentration of the copper solution or of the volume titrated, and those obtained on large and on small amounts of copper in the same or different volumes are strictly comparable.

As the result of the investigation, it has been found that the iodide method, if properly controlled, is both rapid and accurate. E. G.

**A Rapid and Accurate Method for the Analysis of White Metal.** JAY C. BENEKER (*J. Ind. Eng. Chem.*, 1911, 3, 637—638).—The drillings are dissolved in either a mixture of hydrochloric and nitric acids or in hydrochloric acid saturated with bromine, and the separation of the copper, lead, iron, and zinc sulphides carried out with sodium sulphide as described by Rössing (*Abstr.*, 1902, ii, 230), these metals being subsequently estimated by Low's iodometric method (*Technical methods of ore analysis*).

The filtrate containing tin, antimony, and possibly arsenic sulphides is digested with a slight excess of hydrochloric acid, the mixed sulphides collected, and transferred in the filter paper to an Erlenmeyer flask; a measured excess of *N*/10-iodine solution, 30—50 c.c. of concentrated hydrochloric acid, and about 2 grams of tartaric acid added, and the flask closed with a stopper carrying a thin glass tube to condense and retain any iodine vapour evolved on heating.

The flask is heated, whereby the sulphides are all converted into iodides, the tin being completely oxidised, whereas the antimony remains as tri-iodide; the flask is cooled, any iodine washed back from the tube, and the excess of iodine titrated with *N*/10-sodium thio-sulphate. The liquid is filtered, neutralised with sodium carbonate, and titrated in the presence of hydrogen sodium carbonate with *N*/10-iodine solution (Mohr's method), whereby the antimony tri-iodide is oxidised to antimony penta-iodide ( $\text{SbI}_5$ ); this indicates the amount of antimony present, whilst the tin is calculated by difference from the amount of iodine consumed in the first titration. F. M. G. M.

**New Volumetric Method for the Estimation of Mercury.** GEORGE S. JAMIESON (*Amer. J. Sci.*, 1912, [iv], 33, 349—351).—The mercury must be in the state of mercurous chloride; mercuric chloride may be reduced by means of phosphorous acid. About 0.5 gram is placed into a 250 c.c. stoppered bottle, and 20 c.c. of water, 30 c.c. of strong hydrochloric acid, also 6 c.c. of chloroform are added. Solution of potassium iodate (preferably standardised by means of pure iodine) is then run in gradually with continuous shaking until the chloroform which at first increases in iodine colour finally becomes colourless. One mol. of potassium iodate represents 4 atoms of mercury.

The process may be applied successfully to the estimation of calomel in preparations containing lactose, etc. L. DE K.

**The Estimation of Manganese in Vanadium and Chromo-vanadium Steels.** JOHN R. CAIN (*J. Ind. Eng. Chem.*, 1911, 3, 630. Compare this vol., ii, 390).—The author considers that a slight modification of Watter's method (*Meth. Chem. Eng.*, 1911, 9, 244) for estimating manganese may be preferable in the presence of a high vanadium content, and proceeds as follows. After the precipitation of chromium and vanadium by cadmium carbonate as previously described (this vol., ii, 391), the filtrate from these metals is treated with 25 c.c. of concentrated nitric acid and boiled until free from fumes, cooled, oxidised with "bismuthate," filtered through asbestos, reduced with a measured excess of ferrous solution, and titrated in the usual way. F. M. G. M.

**Standardisation of Potassium Permanganate Solution by Sodium Oxalate.** RUSSEL S. McBRIDE (*J. Amer. Chem. Soc.*, 1912, 34, 393—416).—A study of the use of sodium oxalate for the standardisation of solutions of potassium permanganate has shown that the only likely causes of variation from the normal course of the reaction are loss of oxygen from the solution and oxidation of part of the oxalic acid by atmospheric oxygen, and that the latter phenomenon is scarcely appreciable. The greatest error observed due to loss of oxygen did not exceed 0.2%, and this source of inaccuracy can be obviated by carrying out the experiment in the following manner.

Sodium oxalate (0.25—0.3 gram) is dissolved in 250 c.c. of water at 80—90°, and 10 c.c. of a mixture of equal parts of sulphuric acid and water are added. The solution is immediately titrated with *N*/10-potassium permanganate with continuous and vigorous stirring. The permanganate solution must not be added at a rate of more than 10—15 c.c. per minute, and the last  $\frac{1}{2}$ —1 c.c. must be introduced drop by drop, allowing each drop to be completely decolorised before adding the next. The excess of permanganate used to produce the end-point colour must be estimated by matching the colour in another beaker containing the same quantity of acid and hot water. The solution should not be allowed to cool below 60° by the time the end-point is reached. By following this method, the results will be accurate within 0.1%, and probably within 0.05%. E. G.

**Estimation of Iron and Aluminium.** HERMANN BORCK (*Zeitsch. angew. Chem.*, 1912, 25, 719—720).—The principal source of error in the separation of iron and aluminium by heating the oxides in hydrogen chloride is the loss of weight of both porcelain and platinum boats. The method is accurate if silica boats are used, and it is not necessary to submit the hydrogen chloride to special purification.

In the precipitation of iron and alumina as basic acetates, it is better, instead of adding alkali carbonate until just turbid, to add a few drops of methyl-orange, and then add ammonia until the colour is just changed. Ammonium acetate then precipitates both compounds in a flocculent form. C. H. D.

**Removal of Chlorine in the Titration of Iron.** FRANZ MICHEL (*Chem. Zeit.*, 1912, 36, 345).—The iron ore or slag (or the mixture of alumina and ferric oxide obtained in the ordinary course of analysis) is evaporated repeatedly on the boiling water-bath with 15–20 c.c. of a mixture composed of 10 c.c. of dilute sulphuric acid (1 : 1) and 90 c.c. of fuming hydrochloric acid until the oxides have dissolved. The residue is then dissolved in dilute sulphuric acid (1 : 5), and again evaporated to a small bulk. In order to expel the hydrochloric acid completely, 3–5 c.c. of 3% potassium permanganate are added, and the liquid evaporated until all odour of free chlorine is gone. A little sulphurous acid is added to dissolve suspended manganic compounds, and after neutralising the greater part of the free acid with sodium carbonate solution, the ferric oxide is reduced by boiling with excess of sulphurous acid, in a flask fitted with a rubber cork and a narrow tube. When the odour of sulphur dioxide has quite gone, 50 c.c. of dilute sulphuric acid are added, the liquid is again heated, and then titrated, as usual, with standard permanganate.

L. DE K.

**The Analysis of Ferrozirconium.** LUDWIG WEISS and WALDEMAR TRAUTMANN (*Zeitsch. anal. Chem.*, 1912, 51, 303–304).—The authors consider that Wunder and Jeanneret's process (this vol, ii, 96) is quite useless, as zirconium dioxide after fusion with sodium hydroxide is, after extraction with water, decidedly soluble in hydrochloric acid. Moreover, fusion with sodium hydroxide fails to completely remove silica and alumina; these facts are found in the older literature.

L. DE K.

**Rapid and Correct Estimation of Tungsten in Ferro-tungsten.** RUDOLF FIEBER (*Chem. Zeit.*, 1912, 36, 334).—0.5 Gram of the finely powdered sample is treated first in a 250 c.c. beaker with 10–15 c.c. of bromine, applying a gentle heat; 30 c.c. of strong hydrochloric acid are then added, and, if necessary, a further 5–10 c.c. of bromine. The excess of bromine is expelled by heating gradually on an asbestos plate, and in order to expel any silicon, 1–2 c.c. of strong nitric acid and 2–3 drops of hydrofluoric acid are added. The solution is now concentrated as much as possible, the residue is taken up with 40 c.c. of dilute hydrochloric acid (1 : 5), boiled, and allowed to settle. The precipitate is collected on a filter, washed alternately with hot water and dilute hydrochloric acid, moistened with ammonium nitrate, ignited, and weighed as tungstic acid. It should be tested for any silica by evaporation with sulphuric and hydrofluoric acids.

L. DE K.

**A Blue Colour-Reaction of Phosphotungstic Acid (?) with Uric Acid and Other Substances.** OTTO FOLIN and ARCHIBALD B. MACALLUM (*J. Biol. Chem.*, 1912, 11, 265–266).—The blue colour produced when phosphotungstic acid and an alkali are added to uric acid can be used to estimate uric acid in dilute solutions, but cannot be used for such estimations in urine, as other substances in that fluid give the same colour. It is characteristic of phenols, and of aromatic

compounds which contain a hydroxyl group in the para-position. Different samples of phosphotungstic (and phosphomolybdic) acid give different intensities of colour, and doubt is expressed whether the material which gives the reaction is really the acid, but may be some impurity.

W. D. H.

**Estimation of Tin and Antimony in Soft Solder.** JOSEPH H. GOODWIN (*J. Ind. Eng. Chem.*, 1911, 3, 42).—A rapid volumetric method for estimating tin and antimony in soft solders containing 0—2% antimony, 30—60% tin, 40—70% lead, and not more than traces of other metals as adapted from Low (Abstr., 1907, ii, 304).

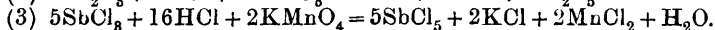
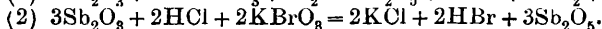
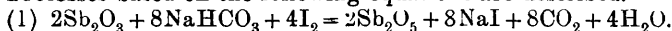
**Antimony.**—Two grams of filings in a 300 c.c. Erlenmeyer flask are treated with 5 grams of hydrogen potassium sulphate crystals and 10 c.c. of sulphuric acid (D 1·8). The flask is shaken over a bare flame until most of the free acid and all the sulphur is expelled; when cool, 25 c.c. of cold water and 5 c.c. of hydrochloric acid (D 1·2) are added, and the mixture reheated until solution is complete and any sulphur dioxide removed, 100 c.c. of cold water are added, and the antimony rapidly titrated with *N*/20-potassium permanganate solution which has been standardised with sodium oxalate prepared according to Sørensen's method.

**Tin.**—Two grams of filings in an Erlenmeyer flask are treated with 5 c.c. of 15% sodium carbonate solution followed by 20 c.c. of hot water and 25 c.c. hydrochloric acid (D 1·2); one drop of a strongly acid (hydrochloric) 5% solution of antimony chloride is added, and the flask closed with a one holed rubber stopper carrying a capillary U-tube of 1 mm. bore, the short arm of which just reaches through the stopper, whilst the long arm almost touches the surface upon which the flask is placed. The contents of the flask are slowly boiled until the solder, with the exception of a small black precipitate of antimony, has completely dissolved, when without interrupting the boiling, a solution of 15% sodium carbonate is placed under the extremity of the U-tube and by cooling the flask allowed to suck into it. When cold a further quantity (15 c.c.) of the sodium carbonate solution is added along with some starch liquor, and the tin rapidly titrated with *N*/20-iodine solution.

F. M. G. M.

**Estimation of Antimony in Red Caoutchouc Ware.** WALTER SCHMITZ (*Gummi Zeit.*, 1911, 25, 1928—1930, 2002—2003).—A discussion of various methods suggested for estimating antimony in technical laboratories, for which purpose the gravimetric methods as sulphide ( $\text{Sb}_2\text{S}_3$ ) and oxide ( $\text{Sb}_2\text{O}_3$ ) are considered unsuitable.

Processes based on the following equations are described.



the caoutchouc in each case having been previously decomposed by Kjeldahl's method either with or without the addition of mercury and potassium hydrogen sulphite.

The second paper is a reply to Frank's criticism of the above methods (compare following abstract).

F. M. G. M.

**Estimation of Antimony in Red Caoutchouc Ware.** FRITZ FRANK (*Gummi Zeit.*, 1911, 25, 2002).—Polemical. A criticism of Schmitz's methods of estimating antimony (compare preceding abstract).  
F. M. G. M.

**Estimation of Unsaturated Organic Compounds with Potassium Bromide-bromate Solution.** G. OTTO GAEBEL (*Arch. Pharm.*, 1912, 250, 72—91).—The process depends on the determination of the amount of bromine absorbed by the compounds, the source of the bromine being a solution containing potassium bromate and bromide in such quantity that, on addition of acid, enough bromine is liberated to give a *N*/10-bromine solution (compare Rupp and Lehmann, *Abstr.*, 1911, ii, 535, and Rupp and Kroll, *ibid.*, p. 1133). The process is similar to that of Hübl for the determination of the iodine numbers of oils, and the excess of bromine is determined by addition of potassium iodide and titration of the iodine liberated by means of sodium thiosulphate.

The method gives iodine numbers which are comparable with those given by Hübl's solutions in the case of oils and fats having a low iodine number; for example: olive oil, lard, suet, and cocoa-butter, but with oils having a high iodine number the results are in general lower than those given by Hübl's solution, so that for these materials the process offers no advantages.

A number of experiments were also made with pure acids, and it was found that cinnamic acid and crotonic acid could be estimated in this way, but that maleic and fumaric acids absorbed no bromine under these conditions, and that abnormal results were given by styracin, cinnamein, sorbic and phenylpropionic acids (compare Ingle, *Abstr.*, 1904, ii, 456; de Jong, *Abstr.*, 1910, ii, 81).  
T. A. H.

**Estimation of "Benzine" and Benzene Hydrocarbons in Oil of Turpentine.** JULIUS MARCUSSON (*Chem. Zeit.*, 1912, 36, 413—414, 421—422).—A modification of the well-known nitric acid method: 10 c.c. of the sample are added drop by drop (the time extending over half an hour) to 30 c.c. of nitric acid (D 1·52) cooled to  $-10^{\circ}$ . After waiting another fifteen minutes, 75—80 c.c. of nitric acid (D 1·4) are added, and "benzine" present will separate as an oily layer. The solution is now transferred to a half litre flask containing 150 c.c. of water, the neck of which holds 10 c.c. graduated to 0·1 c.c. Unless the amount of adulteration is known to be very large, the liquid is heated for fifteen minutes on the water-bath to dissolve completely the oxidation products of the turpentine. If after some hours oily drops are visible either at the bottom or on the surface, benzene hydrocarbons were present. Sulphuric acid (D 1·16) is now added so as to increase the density of the liquid and to force the nitro-products into the neck, where their volume is read off. This divided by 1·15 represents with sufficient accuracy the original benzene hydrocarbons.

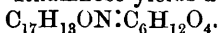
It should be remembered, however, that commercial "benzines" (petroleum products) often contain an appreciable amount of aromatic hydrocarbons.

The assay of turpentine based on its solubility in sulphuric acid is worthless.

L. DE K.

**Estimation of Lecithin.** R. C. COLLISON (*J. Biol. Chem.*, 1912, 11, 217—220).—The most satisfactory method found was that in which the combined alcohol and ether extracts of tissues are analysed for phosphorus without previous treatment with ether and filtration, provided the reagents are free from water. W. D. H.

**Distinction between Aldoses and Ketoses.** MARIO BETTI (*Gazzetta*, 1912, 42, i, 288—294).— $\alpha$ -Aminobenzyl- $\beta$ -naphthol forms well crystallised compounds of aldehydo-aminic type with aldoses, but does not react with ketoses, and consequently may serve for the identification and separation of these compounds. *d*- $\alpha$ -Aminobenzyl- $\beta$ -naphthol ( $[\alpha]_D^{20}$  58·90°) and *d*-mannose in aqueous-alcoholic solution yield the compound  $C_{17}H_{13}ON:C_6H_{12}O_5$ , which forms colourless needles, m. p. 207—208°.  $\alpha$ -Aminobenzyl- $\beta$ -naphthol and *d*-galactose form an analogous compound which crystallises in small prisms, m. p. 206° (decomp.). The dextrose derivative has already been described (Abstr., 1907, i, 314). It was not found possible to isolate any product of the action of  $\alpha$ -aminobenzyl- $\beta$ -naphthol on formose, lævulose, or *d*-sorbinose. Rhamnose yields a compound



The separation of dextrose and lævulose was readily effected by means of  $\alpha$ -aminobenzyl- $\beta$ -naphthol. R. V. S.

**Estimation of Dextrose in Leather.** J. GORDON PARKER and J. R. BLOCKEY (*J. Soc. Chem. Ind.*, 1912, 31, 268—269).—Whilst all tannins are precipitated completely from neutral solutions by either normal or basic lead acetate, such is not the case in acid solutions. This fact possibly explains the reason why larger quantities of dextrose are found in leather when normal lead acetate is employed to remove tannins than when basic lead acetate is used; organic acids present in vegetable tanned leathers prevent the complete precipitation, although the acidity would be diminished by the use of basic lead acetate. As any unprecipitated tannin may reduce Fehling's solution and cause the dextrose results to be too high, normal lead acetate should not be used in the estimation. W. P. S.

**Fische's Reaction.** GEORGES HALPHEN (*Ann. Falsif.*, 1912, 5, 105—115).—This test for the detection of invert sugar in honey yields the most trustworthy results when carried out in the following manner: Two c.c. of an ethereal extract of the honey are treated with 2·5 c.c. of absolute alcohol, 0·3 c.c. of hydrochloric acid, and 0·02 gram of resorcinol. The bright red coloration which is produced by the interaction of the resorcinol and the traces of 3-hydroxy-5-methylfurfuraldehyde contained in the invert sugar (compare Abstr., 1911, ii, 660) is also yielded by certain essential oils and other aldehydic substances. Should the honey under examination contain traces of these, a preliminary extraction with light petroleum will effect their removal, whilst the furfuraldehyde compound remains insoluble in this solvent and may be extracted subsequently by treatment with ether. W. P. S.

**Fiehe's Reaction in the Analysis of Honey.** L. STOECKLIN (*Ann. Falsif.*, 1912, 5, 116—121).—The ether employed in this test should be treated previously with a mixture of potassium chromate and dilute sulphuric acid, then washed with water, shaken with potassium hydroxide solution, allowed to separate, and filtered. Chlorine should not be present in the hydrochloric acid used. The resorcinol reagent is best prepared by dissolving 2·8 grams of resorcinol in 100 c.c. of water, adding a small quantity of blood-charcoal, and filtering the solution after agitation; 36 c.c. of the filtrate are then mixed with 64 c.c. of hydrochloric acid, D 1·19. The test is carried out by grinding 5 grams of the honey with 20 c.c. of ether in a mortar, filtering the ethereal extract, and then adding the latter to 10 c.c. of the reagent placed previously in a test-tube. A blank test with the ether and reagent should be carried out at the same time.

W. P. S.

**Tables for Sugar Estimations.** DOMKE (*Zeitsch. Ver. deut. Zuckerind.*, 1912, 302—311).—Tables are given: (1) to determine the sucrose concentration from the apparent specific gravity at 20°; (2) to determine the concentration at 20° from the ratio  $q = p_3 - p_1/p_2$ , where  $p_1$  is the weight of water to fill the pycnometer,  $p_2$  that of the sucrose solution taken, and  $p_3$  the weight of sugar solution + water to fill the pycnometer; (3) to calculate the concentration read at any temperature in degrees Brix to that at 20°; (4) to give the number of kilograms of sucrose in a cubic metre of solution for any given percentage concentration.

E. F. A.

**Calculation of the Concentration of Sucrose Solutions from the Specific Gravity by means of the Tables of the "Normal Eichungs Kommission."** O. SCHREFELD (*Zeitsch. Ver. deut. Zuckerind.*, 1912, 312—318. Compare Domke, preceding abstract).—It is shown how to calculate the true density of sucrose from the apparent density, and thus the tables of the commission are made generally applicable.

E. F. A.

**Estimation of Formic Acid, Alone or Mixed with its Homologues, by means of Alkaline Permanganate.** A. FOUCHET (*Bull. Soc. chim.*, 1912, [iv], 11, 325—328).—The method depends on the oxidation of formic acid by potassium permanganate, in presence of sodium carbonate, as first suggested by Péan de Saint-Gilles (*Ann. Chim. Pharm.*, 1859, 3, 55). The following solutions are used: potassium permanganate, 5 grams in 1 litre; sodium carbonate, 50 grams in 1 litre; ferrous ammonium sulphate, 20 grams, and sulphuric acid, 30 grams in 1 litre; sulphuric acid, 500 c.c. in 1 litre.

Forty c.c. of the sodium carbonate solution and 20 c.c. of the permanganate are placed in each of two flasks, and to one of these 0·05 gram of the material to be examined, dissolved in a little water, is added, the same quantity of water being added to the other. The flasks are now warmed in the water-bath during three minutes, cooled, and 20 c.c. of diluted sulphuric acid and 50 c.c. of the ferrous ammonium sulphate solution added to each. The excess of ferrous

ammonium sulphate is then estimated in each case by means of the potassium permanganate solution. The difference in the amounts used in the two cases represents the amount of formic acid in the material, each c.c. of permanganate solution being equivalent to 0.00351 gram of formic acid. For very small quantities of formic acid the permanganate solution may be diluted to 0.1%, and the ferrous ammonium sulphate solution in like proportion. T. A. H.

**Analysis of Lactic Acid.** A. A. BESSON (*Chem. Zeit.*, 1912, 36, 297. Compare also Abstr., 1911, ii, 1140).—A reply to Klapproth (this vol., ii, 211). T. S. P.

**Estimation of [Combined] Oxalic Acid in the Needles of Coniferæ.** JOHANNES OTTO (*Zeitsch. anal. Chem.*, 1912, 51, 296—300).—Three to four grams of the dried and powdered sample are heated with 150 c.c. of 1% hydrochloric acid for half-an-hour on the boiling water-bath. The filtrate and washings are evaporated to 200 c.c. to coagulate some organic colloids. After acidifying with 2*N*-acetic acid, the solution is precipitated at the boiling heat with an excess of a 10% solution of calcium acetate. The calcium oxalate is collected, washed, and burnt to ash. In order to free the precipitate from traces of iron and manganese, the ash is dissolved in hydrochloric acid, and after adding ammonia a little bromine vapour is passed. The filtrate is then heated to boiling and the calcium again precipitated with excess of ammonium oxalate. After washing, the precipitate is dissolved in dilute sulphuric acid, heated to 40°, and the oxalic acid is titrated with permanganate.

A table is given showing the amount of total oxalic acid in samples of various origin; the amount increases with the age.

L. DE K.

**The Use of the Ester Method for the Detection of Mono-amino-acids in the Presence of Polypeptides.** EMIL ABDERHALDEN and RUDOLF HANSLIAN (*Zeitsch. physiol. Chem.*, 1912, 77, 285—288).—Examples are given which show that mono-amino-acids can be detected and estimated by the ester method in the presence of polypeptides. W. D. H.

**The Detection of Benzoic and Salicylic Acids in Milk.** E. PHILIPPE (*Chem. Zentr.*, 1912, i, 288—289; from *Mitt. Lebensmittel-unters. Hyg.*, 2, 377—383).—One hundred c.c. of milk are treated with 40 c.c. of Fehling's copper sulphate solution, 10 c.c. of *N*/10-sodium hydroxide, and 150 c.c. of water, the mixture is thoroughly shaken, and after filtration acidified with 5 c.c. of concentrated hydrochloric acid and extracted with ether. The latter, after evaporation, leaves a residue, which, in the event of 2 mg. or more of the acids being present, crystallises. If the crystals are sublimed, the acid present can be ascertained by the form of the crystals. Salicylic acid can be estimated quantitatively by the iron chloride reaction. Von den Heide and Jakob's or Jonescu's methods can be employed for the detection of the benzoic acid. S. B. S.

**Estimation of Benzoic, Hippuric, and Phenaceturic Acids in Urine.** H. STEENBOCK (*J. Biol. Chem.*, 1912, 11, 201—209).—Dakin's method for isolating benzoic acid was found to yield quantitative results when followed by sublimation. Hippuric acid and phenaceturic acid occurring together can be estimated as benzoic and phenylacetic acids respectively by sublimation followed by titration. No salts of non-conjugated benzoic or phenaceturic acids were found in cow's urine. W. D. H.

**A New Method for the Estimation of Hippuric Acid in Urine.** OTTO FOLIN and FRED F. FLANDERS (*J. Biol. Chem.*, 1912, 11, 257—264).—A full description of the method, of which a preliminary notice has already appeared (this vol., ii, 396). W. D. H.

**The Detection of Salicylic Acid.** OTTO LANGKOPF. (*Chem. Zentr.*, 1912, i, 444; from *Apoth. Zeit.*, 1911, 26, 1057).—All hydroxy-acids hinder the reaction between ferric chloride and salicylic acid, as do also oxalic, formic, butyric and acetic acids, phosphates, dextrose, etc. H. W.

**The Permanence and Susceptibility of the Ferric Chloride-Salicylic Acid Reaction.** Approximate Estimation by this means of Free Salicylic Acid in Aspirin and Other Acetylated Salicylic Acids. H. LINKE (*Chem. Zentr.*, 1912, i, 444; from *Apoth. Zeit.*, 1911, 26, 1083—1085).—The author finds that the ferric chloride-salicylic acid coloration is not permanent as generally assumed. After one hour, the violet coloration becomes reddish-violet, and after twelve hours, brownish-yellow. If the solution is stronger than one in 50,000, change of colour does not occur until after several days. On the other hand, the coloration becomes more intense when the reaction is applied to such substances as aspirin tablets. This is attributed to the progressive hydrolysis of the *o*-acetoxybenzoic acid present. The limit of susceptibility is placed at one in 900,000.

Quantitative determinations of salicylic acid were made by comparing the coloration given by the substance under investigation with that given by standard solutions of salicylic acid (concentration one in 50,000—200,000) under similar conditions. H. W.

**The Detection of Salicylic Acid.** F. VON BRUCHHAUSEN (*Chem. Zentr.*, 1912, i, 445; from *Apoth. Zeit.*, 1912, 27, 9).—The ferric chloride reaction for salicylic acid depends on the presence of the ferric ion. It does not occur in the presence of sodium phosphate, because ferric phosphate is not dissociated in aqueous solution, or in the presence of hydroxy-acids, since the latter form complexes with ferric chloride which do not contain the ferric ion. H. W.

**Detection of Uric Acid in Blood.** CARL WEBER (*Pharm. Zeit.*, 1912, 57, 252).—The blood is treated with sodium chloride and potassium phosphate in order to precipitate proteins, and, after these have been removed by filtration, the solution is evaporated to a small

volume and saturated with ammonium chloride. The uric acid is thus precipitated as ammonium urate, which is collected and treated with a few drops of hydrochloric acid. The crystals of uric acid which separate out may be identified by their appearance under the microscope and by means of the murexide test, the latter being rendered more sensitive by the use of dilute nitric acid. The uric acid may be estimated by dissolving it in a definite volume of *N*/50-piperidine solution and titrating the excess of the latter with *N*/200-sulphuric acid, using phenolphthalein as indicator. Each c.c. of the piperidine solution is equivalent to 0.84 mg. of uric acid. W. P. S.

**Iodometric Estimation of Uric Acid [in Urine].** HUBERT CARON (*Ann. Chim. anal.*, 1912, 17, 123—127).—A criticism of Pizzorno's process (*Abstr.*, 1911, ii, 667), which the author finds to be untrustworthy, because the treatment with animal charcoal causes a loss of uric acid. On the other hand, on prolonged contact of impure uric acid and iodine more of the latter is absorbed; these two sources of error may occasionally compensate each other, and this may account for Pizzorno's satisfactory test experiments.

A preliminary precipitation as ammonium biurate is recommended.

L. DE K.

**Examination of Benzaldehyde for Chlorine Compounds.** GEORG HEYL (*Chem. Zentr.*, 1912, i, 677; from *Apoth. Zeit.*, 1912, 27, 49—50).—One to two grams of chlorine-free lime are ground with 10—15 drops of benzaldehyde, covered with a small additional quantity of lime, and heated, at first gently, and then to redness. After cooling, the mass is treated with 6 c.c. of water, acidified with nitric acid, filtered, and the filtrate tested with silver nitrate. In this manner the presence of one drop of monochlorobenzene in 50 grams of benzaldehyde can be detected. H. W.

**Microchemical Testing of Some Alkaloids.** [Miss] ALICE GRUTTERINK (*Zeitsch. anal. Chem.*, 1912, 51, 175—234; *Chem. Weekblad*, 1912, 9, 124—163).—A lengthy article, reference to which must be made for the numerous illustrations of crystals, etc.

The following reagents have proved very useful for obtaining characteristic microscopic slides: *m*-Nitrobenzoic acid for strychnine (hydrastimide); *p*-nitrobenzoic acid for strychnine and tropacocaine; 3:5-dinitrobenzoic acid for hydrastine, novocaine, brucine, and strychnine; trinitrobenzoic acid for novocaine, tropacocaine, strychnine, and brucine (coniine); dinitroanisic acid for hydrastimide; gentisic acid for cinchonine; trihydroxybenzoic acid for quinidine; opianic acid for brucine; meconic acid for quinidine; mellitic acid for quinidine and cinchonidine; naphthalenesulphonic acid for cocaine and strychnine; *p*-nitrophenylpropionic acid for hydrastine, hydrastine, strychnine, tropacocaine, and cinchonidine (nicotine, hydrastimide); *o*-cresotic acid for hydrastimide. Potassium permanganate was found to be a valuable reagent for the micro-detection of hydrastine, hydrastine, tropacocaine, and cotarnine.

The alkaloids in parenthesis have not yet been fully investigated. A large number of micro-reactions for other alkaloids are also given.

L. DE K.

**The Behaviour of Alkaloids towards Quinone and Chloral Hydrate.** EDUARD SCHÄR (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 318—320).—*p*-Benzoquinone, dissolved in sulphuric acid containing 10% of water, gives intense colorations with morphine, codeine, narceine, and brucine, but not with narcotine, berberine, strychnine, veratrine, atropine, cocaine, quinine, or caffeine.

An 80% solution of chloral hydrate may be used in place of sulphuric acid as a solvent for alkaloids in colour reactions. Salts of alkaloids do not react with quinone in this reagent, but free alkaloids produce a coloration, with varying velocity. The effect is produced by the alkaline reaction of the alkaloid, other alkaline substances behaving similarly.

C. H. D.

**Alkaloidal Assay of Calabar Beans.** ARTHUR H. SALWAY (*Amer. J. Pharm.*, 1912, 84, 49—51).—It has been pointed out already (*Trans.*, 1911, 99, 2148) that assay of these beans by the process prescribed in the United States Pharmacopeia gives a smaller yield of alkaloid than can be actually isolated. This appears to be due to the phenolic character of physostigmine (eserine), which renders it difficult to extract from alkaline liquids by ether. The author finds that it is more easily extracted from liquids rendered alkaline with sodium carbonate than when sodium hydrogen carbonate is used, and therefore suggests the following process: Twenty grams of the drug finely powdered are agitated with 200 c.c. of ether, 10 c.c. of 10% aqueous sodium carbonate solution added, and the mixture well shaken at intervals during four hours. One hundred c.c. of the clear ethereal solution are run into a separator, and *N*/10-sulphuric acid added until the liquid is acid. The separator is well shaken, the acid layer drawn off, and the treatment repeated twice, using 10 c.c. of *N*/10-acid each time. The acid liquids are combined, made alkaline with 10% sodium carbonate solution, and shaken with ten successive portions (20 c.c. each time) of ether. The combined ethereal extracts are washed with 5 c.c. of distilled water. The solvent is then distilled off, the residue dissolved in 5 c.c. *N*/10-sulphuric acid, and the excess of acid titrated with *N*/50-alkali, using iodeosin as indicator.

T. A. H.

**The Colorimetric Estimation of Colchicine.** RUDOLF FABINY (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 230—231).—Three c.c. of a solution of colchicine in water, containing 0.2 gram in 300 c.c., are acidified with 0.5 c.c. of concentrated hydrochloric acid, and boiled for three minutes. Addition of 0.5 c.c. of 1% ferric chloride solution produces a dark green coloration, which becomes fully developed after an hour in darkness. The solution is then diluted to 100 c.c. The solution to be examined is compared with the standard in a colorimeter.

C. H. D.

**Assay of Digitalis.** JAMES BURMANN (*Bull. Soc. chim.*, 1912, [iv], 11, 221—228).—In previous papers the author has pointed out the disadvantages of physiological methods for the assay of digitalis, and

has shown that Keller's chemical method estimates only  $\psi$ -digitoxin (Abstr., 1910, ii, 1010). He now describes the following process for the assay of digitalis preparations. One hundred grams of digitalis extract in 20% alcohol (dialysé de digitale) are mixed with 60 grams of dry alcohol, and diluted to 190 grams with 50% alcohol. To this 30 grams of lead sub-acetate solution (D 1.240) and 30 grams of dry alcohol are added, and the mixture shaken and filtered. One hundred and twenty-five grams of the filtrate are treated with hydrogen sulphide, and the lead sulphide filtered out on a Buchner funnel and washed with 50% alcohol. The filtrate is evaporated under reduced pressure to 50 c.c., 2 c.c. of 10% ammonia added, and this exhausted by hot chloroform in an extraction apparatus. The chloroform extract is filtered, the solvent distilled off, and the residue dried at 100°. The latter is then dissolved in 3 grams of chloroform, 7 grams of dry ether added, and then 50 grams of light petroleum. The precipitate is washed by decantation once with 60 grams of light petroleum, then dried at 100° in a current of warm air, and weighed. On recrystallising from alcohol, the characteristic crystals of both digitoxin and  $\psi$ -digitoxin are found, and these can be isolated by treatment with appropriate solvents. Comparative trials of the same preparations by this process and that of Keller show that the residue obtained by this method contains usually about 22% of digitoxin, and this was confirmed by physiological trials on frogs and rabbits, the lethal dose of this residue being 0.0076 gram as against 0.0099 gram for Keller's residue.

T. A. H.

**The Colorimetric Estimation of Morphine.** RUDOLF FABINY (*Verh. Ges. deut. Naturforsch. Aerzte*, 1912, ii, [1], 228—230).—The colour reaction of morphine discovered by Radelescu (Abstr., 1906, ii, 638) may be made quantitative. A standard solution is prepared by dissolving 0.3 gram of morphine in a litre of 10% sulphuric acid. Ten c.c. of this solution are taken, and more dilute solutions are prepared by taking smaller volumes and diluting to 10 c.c. with 10% sulphuric acid. Solid sodium nitrite is then added, crystals of the same size being added to each solution, and when the evolution of gas is over, 10 c.c. of concentrated potassium hydroxide are added, and diluted to 100 c.c. The red colorations are then compared in a colorimeter. The method is found to give accurate results.

C. H. D.

**Detection of Blood in Fæces.** W. DOCKHORN (*Pharm. Zeit.*, 1912, 57, 165).—The tests recommended for the detection of blood in fæces are the guaiacum test, the benzidine test (compare Abstr., 1911, ii, 348), and the phenolphthalein test, the latter test depending on the conversion of phenolphthalin into phenolphthalein by the action of blood in the presence of hydrogen peroxide. A test in which aloin is used, which is similar to the guaiacum test, may also be employed; it is stated that the addition of a few drops of chloroform increases the sensitiveness of this test.

W. P. S.

## General and Physical Chemistry.

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**The Absorption and Refraction Methods.** KARL AUWERS (*Ber.*, 1912, 45, 963—976. Compare Hantzsch, this vol., ii, 313).—Polemical; mainly on the relative value of the absorption spectrum and the refractivity in the investigation of the constitution of organic substances. D. F. T.

**Spectra of the Arc Light Aureol.** HEINRICH HERTENSTEIN (*Zeitsch. wiss. Photochem.*, 1912, 11, 69—87).—The arc flame spectra of various metals and their halogen salts have been examined and compared with the corresponding arc and flame spectra. In this part of the paper, the observations made with copper are recorded. The arc flame spectrum consists of a series of bands shaded off towards the red end of the visible region. As compared with the arc spectrum, that of the arc flame extends further at the less refrangible end, but not so far at the violet end. This difference is attributed to the lower temperature of the arc flame. The copper lines which are visible in the arc flame spectrum are those which are of greatest intensity in the arc spectrum.

The influence of the surrounding atmosphere was also investigated by observations in carbon dioxide and in a mixture of equal volumes of air and oxygen. In carbon dioxide the intensity of the bands is appreciably reduced, whilst the effect of an increased supply of oxygen is to alter the relative intensities of the lines. In particular, the lines of the first and second subsidiary series are considerably reduced in intensity by the excess of oxygen. H. M. D.

**Krypton and the Auroral Spectrum.** T. W. PAGE (*Proc. Physical Soc.*, 1912, 24, 138—140).—In view of the coincidence of the green auroral line  $\lambda=5570$  with the green krypton line, it has been suggested that the aurora is due to some electrical discharge phenomenon in which krypton is concerned. The yellow krypton line  $\lambda=5871$  is not found, however, in the auroral spectrum, and experiments have therefore been made to ascertain whether changes in the relative intensities of the two krypton lines are brought about by alterations in the nature of the electrical charge. This does not appear to be the case, the two lines being of approximately equal intensity both in the ring discharge and the canal ray spectrum.

H. M. D.

**Structure of Some Spectral Bands.** R. FORTRAT (*Compt. rend.*, 1912, 154, 1153—1156).—A discussion of apparent irregularities amongst the components of the green carbon band, certain hydrocarbon bands, and the water vapour bands,  $\lambda=3064$ , 2811, 2608, and 2449 Ångstrom units. W. O. W.

**Wave-lengths in the Iron Spectrum.** HENRI BUISSON and CHARLES FABRY (*Ann. Physik*, 1912, [iv], 38, 245—246).—The wave-

lengths of three lines, not previously measured by the authors, are in good agreement with the values given by Eversheim (this vol., ii, 110).  
H. M. D.

**The Zeeman Effect for Copper, Iron, Gold, Chromium, Nickel, Palladium, Manganese, and Argon in the Visible Spectrum.** O. LÜTTIG, W. HARTMANN, and C. PETERKE (*Ann. Physik*, 1912, [iv], 38, 43—70).—A detailed examination has been made of the influence of a magnetic field on various lines in the spectra of the above elements, the use of an echelon grating enabling the requisite dispersion to be obtained with magnetic fields of small intensity. By this means the errors resulting from the lack of homogeneity of the field are to a large extent avoided. The data are tabulated and compared with the results obtained by previous observers.

H. M. D.

**The Spectral Extension of Ultra-red and Ultra-violet Vibrations and its Relation to the Different Crystal Systems.** KURT EISENMANN (*Ber. Deut. physikal. Ges.*, 1912, 14, 315—321).—Expressions are deduced for the frequencies of vibration of the atom and electron, and these are applied in the calculation of the maximal energies for the atoms of different elements, assuming that the number of the neighbouring atoms which exert an influence on the vibrations of a particular atom is dependent on the crystalline system to which the element in question belongs.

H. M. D.

**Influence of Temperature on the Ultra-red Absorption of Gases.** EVA VON BAHR (*Ann. Physik*, 1912, [iv], 38, 206—222. Compare Abstr., 1909, ii, 630; 1910, ii, 914).—The influence of temperature on the absorption of ultra-red rays by gases has been investigated by experiments with carbon monoxide, carbon dioxide, nitrous oxide, methane, and ethyl ether at room temperature, and at about 170°.

The absorption curves, which have been constructed from the bolometer readings, show that a rise of temperature is accompanied by a broadening of the absorption band when the volume of the absorbing gas is kept constant. If by admission of air or other inert gas, the pressure in the absorption apparatus at the lower temperature is made equal to the pressure exerted by the gas at the higher temperature, the temperature effect becomes more obvious. In these circumstances, the absorption curve corresponding with the higher temperature is found to lie appreciably lower than the curve for the room temperature, and the broadening of the band is very pronounced. The observed change in the character of the absorption points to a damping down of the absorbing particles as a result of a rise in temperature. This damping effect cannot be due to the collisions between the molecules, but to intramolecular changes. It may also be inferred from the observations that the ultra-red absorption is continuous.

H. M. D.

**Absorption Spectra and the Solvate Theory of Solution.** HARRY C. JONES (*Phil. Mag.*, 1912, [vi], 23, 730—742).—A summary of work, details of which have been published previously (compare Abstr., 1909, ii, 359; 1910, ii, 370; 1911, ii, 166, 168).

H. M. D.

**The Absorption of Light by Inorganic Salts. V. Copper and the Alkali Metals.** ROBERT A. HOUSTON (*Proc. Roy. Soc. Edin.*, 1912, 32, 40—49).—An apparatus is described which is suitable for spectrographic measurements in the infra-red, visible, and ultra-violet spectrum. The light from the slit is rendered parallel by a concave nickel mirror, passes through the fixed prism, so placed that the middle of the spectrum suffers minimum deviation, and is brought to a focus by a second nickel mirror, which can be rotated about a vertical axis. The illumination with nickel mirrors is about one-half of that with quartz lenses, but a larger aperture can be used, owing to the better collimation. The apparatus has also the advantage of automatic focussing, and the quartz prism may be replaced by one of glass or rock salt without any alteration except of the mirror angles, and a slight tilting of the plate.

The photometer employed contains a quartz rhomb to divide the beam, and two diffuse reflecting surfaces of opaque silica. The two spectra are brought into contact on the plate. A cell containing the solution to be examined is placed in the path of one beam and one containing water in the other, and a series of exposures made for different positions of the source of light.

The absorption curves of cupric sulphate, chloride, bromide, and nitrate agree completely in the infra-red. In the ultra-violet, a trace of the nitrate band is seen in the case of the nitrate.

Lithium, sodium, potassium, rubidium, and caesium sulphates, sodium chloride, bromide and nitrate, and silver nitrate absorb less than water in the infra-red. The absorption in the ultra-violet is very small, except in the case of the nitrates.

C. H. D.

**The Absorption of Light by Inorganic Salts. VI. The Cobalt Chloride Colour Change.** ALEXANDER R. BROWN (*Proc. Roy. Soc. Edin.*, 1912, 32, 50—61. Compare preceding abstract).—The absorption of aqueous solutions of cobalt chloride has been measured at different temperatures, but on account of experimental difficulties the method has been preferred of diluting a concentrated solution of the anhydrous chloride in absolute alcohol with water, and measuring the extinction coefficient at different dilutions. This value appears to vary very little with the concentration in alcoholic solutions free from water. The quantity of the red modification increases with the amount of water. The red modification is not the hexahydrate, which has a different absorption spectrum. A mass action calculation indicates that the salt may contain  $15\text{H}_2\text{O}$ . The change of colour on heating the solution is to be ascribed to the change from the polyhydrate to the amorphous salt.

C. H. D.

**The Shape of Ultra-microscopic Gold Particles.** R. GANS (*Ann. Physik*, 1912, [iv], 37, 881—900).—The nature of the absorption curve for colloidal gold solutions has been calculated on the assumption that the particles have the form of ellipsoids of rotation, the refractive index and absorption coefficient of the particles being supposed to have the same value as metallic gold. In the case of spherical particles, the absorption maximum is situated in the green, but as the ratio of the lengths of the axes changes from unity in either direction, the maximum is displaced towards the red end of the spectrum. The experimental data obtained by Steubing (*Abstr.*, 1908, ii, 600), when examined in the light of these results, show that the colloidal gold particles in the ruby-red solutions are approximately spherical. The blue solutions of the same degree of dispersity contain, on the other hand, particles which deviate considerably from the spherical form.

The nature of the polarisation of the light, which is scattered by the gold particles, also points to deviations from the spherical configuration.  
H. M. D.

**Dynamic Isomerism.** HENRY E. ARMSTRONG, THOMAS M. LOWRY, SYDNEY YOUNG, CECIL H. DESCH, JAMES J. DOBBIE, MARTIN O. FORSTER, and ARTHUR LAPWORTH (*Brit. Assoc. Report*, 1911, 91—94).—The form of the absorption curves of organic substances indicates that general absorption may frequently be due to the presence of a band with its head beyond the limits of ordinary measurement. The position can in many cases be arrived at indirectly by measuring the magnetic rotatory dispersion. This indicates that in the majority of saturated organic compounds the absorption lies in the far ultra-violet at  $\lambda$  1300 to 1400. The shallow bands which appear in acetone and similar compounds at  $\lambda$  3000 to 4200 are almost without influence on the optical properties within the visible region. The absorption is brought nearer to the visible region by introducing an ethylene linking, as in allyl alcohol, or a benzenoid linking, as in phenylethylcarbinol.  
C. H. D.

**Absorption Spectra of Nitro-compounds in the Ultra-violet.** ARTHUR HANTZSCH and KURT VOIGT (*Zeitsch. physikal. Chem.*, 1912, 79, 592—598).—The authors (compare this vol., i, 151) and Zelinsky and Rosanoff (*Abstr.*, 1911, ii, 1044) have arrived at totally different conclusions from the results of an examination of the ultra-violet absorption spectra of nitro-compounds. It is now maintained that this result is not due to the unsatisfactory nature of the method, but to the fact that Zelinsky and Rosanoff have not applied it properly.

From their observations Zelinsky and Rosanoff have drawn the conclusion that there is no essential difference in the absorption of mono- and di-nitroparaffins. They have, however, overlooked the fact, already pointed out by Baly (*Trans.*, 1908, 93, 1747), that a solution of sodium nitromethane is not stable in solution, but immediately begins to pass over into a salt of nitroacetaldoxime, which, as a conjugated *aci*-nitro-

compound, shows strong selective absorption, even in 0.0001 molar solution.

The general conclusions of the authors are as follows. The true nitro-group shows weak selective absorption at high concentrations (0.1—0.01 normal). The simple *aci*-group shows weak general absorption. The introduction of further NO<sub>2</sub> groups or other unsaturated negative groups scarcely influences the absorption of true nitro-compounds, but enormously increases that of *aci*-nitro-compounds and makes it selective in character. This conjugated *aci*-nitro-group may be formulated by means of a subsidiary valency formula, thus :

$R \cdot C \begin{array}{c} \text{---} X \\ \diagup \quad \diagdown \\ \text{NO} \cdot O \end{array} M$  (where X = NO<sub>2</sub>, CO, CN, C<sub>6</sub>H<sub>5</sub>, etc.), and differs fundamentally in character and strength of absorption from the "simple" *aci*-nitro-group C:NO·OM. G. S.

**The Fluorescence of Iodine Vapour Excited by Polarised Light.** J. FRANCK and G. HERTZ (*Ber. Deut. physikal. Ges.*, 1912, 14, 423—425).—By measurements of the distribution of the intensity of the fluorescent light in different directions relatively to the plane of polarisation of the exciting beam of light, it has been found that the directions of vibration of the light-emitting particles are not uniformly distributed, and that the direction at right angles to the plane of polarisation is preferentially adopted by the vibrating particles.

H. M. D.

**Transformation of the Resonance Spectrum of Fluorescent Iodine into a Banded Spectrum by Admixed Gases.** J. FRANCK (*Ber. Deut. physikal. Ges.*, 1912, 14, 419—422).—In presence of small quantities of the inert gases, the line spectrum emitted by iodine vapour when subjected to the action of monochromatic light is transformed into a banded spectrum. It is now shown that this effect is not peculiar to the inert gases, but is brought about by admixture with other gases, such as hydrogen, nitrogen, and oxygen. Since the inert gases have no electro-affinity, the total light emission is not diminished as a result of the transformation, but in the case of other gases the change in the nature of the spectrum is accompanied by a decrease in the quantity of light emitted, the magnitude of which increases with the electro-affinity of the admixed gas. H. M. D.

**New Classes of Oxyluminescent Substances.** MARCEL DELÉPINE (*Compt. rend.*, 1912, 154, 1171—1173. Compare Abstr., 1910, i, 295, 545, 612).—The essential condition for the spontaneous phosphorescence of a sulphur compound appears to be that it should contain the element in a readily oxidisable state; the presence of a sulphur-carbon grouping or of the S:CO-group is not necessary. The following compounds phosphoresce at the ordinary temperature with formation of sulphurous and sulphuric acids: S:PCl<sub>2</sub>, S:P(OMe)Cl<sub>2</sub>, S:P(OEt)Cl<sub>2</sub>, S:P(OPr<sup>a</sup>)Cl<sub>2</sub>, S:P(OMe)<sub>3</sub>, S:P(OEt)<sub>3</sub>, S:PEtCl<sub>2</sub>. The following compounds are not phosphorescent: S:P(O·C<sub>5</sub>H<sub>11</sub>)Cl<sub>2</sub>, S:PPBr<sub>3</sub>, S:P(OMe)<sub>2</sub>Cl, S:P(OMe)<sub>2</sub>SMe. W. O. W.

**Circular Polarisation of Liquid Crystals.** PAUL GAUBERT (*Compt. rend.*, 1912, 154, 995—997).—When the cover glass of a microscopic preparation of a doubly refracting liquid, in which the molecules are more or less orientated perpendicularly to the glass, is pressed with a needle, a spherulite is seen barred with a black cross, the centre of which corresponds with the centre of pressure. Most of the molecules are now orientated parallel to the glass. In the case of some liquid crystals, epipolar colours are produced through circular polarisation. These are best observed with a fused mixture of cholesterol propionate and nonoate. The optical appearances presented by this type of liquid are fully described. W. O. W.

**The Magneto-optical Effects in Chlorine and Iodine.** A. HEURUNG (*Ann. Physik*, 1912, [iv], 37, 1046—1048. Compare Abstr., 1911, ii, 963).—Polemical against Wood (this vol., ii, 325). The variable rotation of the plane of polarisation of the light in the neighbourhood of the sodium *D*-lines cannot be accepted as a basis for the explanation of the magneto-optical effects in the case of iodine vapour.

H. M. D.

**Method for Examining the Purity of Optically Active Compounds.** ERNST DEUSSEN (*J. pr. Chem.*, 1912, 85, [ii], 484—488).—In support of the view that the high rotatory power of  $\beta$ -caryophyllene nitrosite and hydrochloronitrosite (this vol., i, 368) is to be referred to the influence of the chromophoric group, the author points out that the aryliminocamphors described by Forster and Thornley (*Trans.*, 1909, 95, 943) are all coloured and possess a very high rotation.

The rotatory power of specimens of  $\beta$ -caryophyllene nitrosite, caryophyllene glycol, caryophyllenenitroanilide, and cadinene dihydrochloride in varying states of purity have been determined for Na (589  $\mu\mu$ ) and Hg (491  $\mu\mu$ ) light at 22°. With a somewhat impure specimen of the nitrosite it was found that  $[\alpha]_{\text{Na}}$  diminished from 1615.4° to 1536.3° as the concentration of the solution increased from 0.1265 to 3.4308, whilst  $[\alpha]_{\text{Hg}}$  increased from 1286° to 1764.2°. With a pure specimen of the nitrosite,  $[\alpha]_{\text{Na}}$  falls from 1833.5° to 1604.7° and  $[\alpha]_{\text{Hg}}$  from 1398° to 1190.4° as the concentration increased from 0.09888 to 2.7468. The pure nitrosite thus shows anomalous rotatory dispersion. It is suggested that these and similar variations in the rotation may be utilised for examining the purity of optically active compounds, and in particular of such substances as terpenes, alkaloids, and proteins, the purity of which is difficult to control by the usual methods.

F. B.

**Direct and Indirect Light Reactions.** CHR. WINTHER (*Zeitsch. wiss. Photochem.*, 1912, 11, 92—103).—On the basis of Planck's theory of energy quanta, the author has calculated for a series of photochemical reactions the quantity of energy which is necessary for the chemical change, and compared this with the quantity of light energy which is absorbed. In the case of the change occurring in the silver bromide photographic plate, the decomposition of Eder's solution, the oxidation of hydrogen iodide and of oxalic acid, the absorbed light

energy is smaller than the chemical energy. The reverse holds for the decomposition of ferric oxalate, the conversion of anthracene into dianthracene, the decomposition of ammonia, and the bleaching of dyes. Changes belonging to the first group represent "indirect light reactions"; these are all accompanied by a diminution of free energy, are very sensitive towards impurities, and the action of the light consists in producing a catalyst. Reactions of the second group represent "direct light reactions," and these are not necessarily accompanied by a diminution of free energy, but may be reversible reactions.

H. M. D.

**Action of Ultra-violet Light on Chlorine.** ERNEST B. LUDLAM (*Phil. Mag.*, 1912, [vi], 23, 757—772).—The behaviour of chlorine towards ultra-violet light has been investigated in a series of experiments in which comparative observations were made on air, chlorine, and mixtures of these gases. Pure dry air is not ionised to any large extent by light of wave-lengths greater than  $180\mu$ , although the ionisation produced by shorter wave-lengths is very considerable. The addition of a trace of water vapour to dry air increases the ionisation to an enormous extent. If very small quantities of chlorine are added to ordinary air, the ionisation is also increased to some extent, but the addition of larger quantities has the opposite effect, the ions and nuclei which are otherwise formed in air being destroyed by the addition of considerable quantities of chlorine. Pure chlorine is not appreciably ionised by the action of ultra-violet rays, and condensation nuclei do not appear to be formed.

The observations show that the atom of chlorine does not readily give up an electron under conditions which readily lead to the expulsion of electrons in the case of the electro-positive elements. In reference to the union of hydrogen and chlorine under the influence of light, it is suggested that the hydrogen atom may lose an electron, which will then combine with the chlorine atom and result in the chemical combination of the atoms.

H. M. D.

**The Reduction of Mercuric Salt by Ferrous Salt and Light.** CHR. WINTHER (*Zeitsch. wiss. Photochem.*, 1912, 11, 60—68).—When aqueous solutions containing ferrous and mercuric chlorides are subjected to the action of light from a quartz mercury lamp, mercurous chloride is precipitated. The rate of reduction under different conditions has been examined in some detail.

When the concentration of the mercuric chloride is constant and relatively small, the rate is nearly independent of the concentration of the ferrous salt. For a given concentration of the latter, the rate increases at first with the amount of mercuric chloride and then diminishes. The maximum appears to be attained when the two salts are present in equimolar quantities.

In the case of solutions containing small quantities of mercuric relatively to ferrous chloride, the sensitiveness increases with the dilution, but this is not the case for solutions containing equimolar quantities. Such solutions do not vary to the same extent when the concentration is changed, and the maximum sensitiveness is shown by solutions containing the two salts in 3-molar concentration.

The presence or absence of oxygen is without appreciable influence on the equimolar solution, but oxygen reduces the quantity of mercurous chloride obtained when a large excess of ferrous chloride is present.

The most active light rays are those of wave-length less than  $265\mu$ , as is shown by comparative experiments in quartz, uviol glass, and ordinary glass vessels. H. M. D.

**The Hertz-Halwachs Effect and Photo-chemical Actions.** G. REBOUL (*Le Radium*, 1912, 9, 155—160).—When ultra-violet rays are allowed to fall on plates of copper or silver covered with thin layers of the corresponding halogen salts, electrons are emitted, and the photo-electric effect associated with this has been investigated. The plate under examination was connected with an electrometer, the intensity of the photo-electric effect being measured by the rate of leakage of the charge from a parallel plate connected up to a battery of small storage cells.

The intensity of the effect increases with the time of exposure to the ultra-violet rays, and if the exposed plate is kept in the dark for some time, a further increase is found on renewed exposure. A similar phenomenon is exhibited by a copper plate covered with a thin layer of oxide.

If the exposure to the ultra-violet rays is continued for a sufficiently long time, a maximum ionisation current is obtained, and the plates exhibit fatigue when the exposure is further prolonged. The decay in the intensity of the effect is accompanied by a darkening of the covering film.

Experiments made with films of different thicknesses show that the emission of electrons increases with increasing thickness of the halogen salt layer, whereas the fatigue effect and the colour change are more quickly and clearly developed in the case of the thin films.

A comparison of the potential current curves, which are obtained in the action of the active rays on polished copper and on copper coated with bromide, shows that the ions formed in the two cases are of the same kind.

The observations afford evidence that the emission of electrons is not conditioned by the chemical change which the halogen salts undergo on exposure to the ultra-violet light. The darkening of the covering film is brought about by visible rays without any accompanying photo-electric effect, and it seems more likely therefore that the observed increase in the emission of electrons on continued exposure is due to a change in the valency of the metal, such as would result if sub-halides were formed. H. M. D.

**A Critical Study of Spectral Series. II. The  $p$ - and  $s$ -Sequences and the Atomic Volume Term.** WILLIAM M. HICKS (*Proc. Roy. Soc.* 1912, A, 86, 413. Compare Abstr., 1910, ii, 86).—The sequences or types of formulæ which give the principal and sharp series in the case of the alkali metals are found to express respectively the sharp and principal series in the case of elements belonging to the second and third groups of the periodic table. Further evidence has

been obtained that these sequences depend on the atomic volumes of the elements.

The spectrum of europium indicates that this element fills the gap between cadmium and mercury. The probable densities of europium and radium deduced from the series formulæ are 12.58 and 5.10 or 6.12 respectively.

H. M. D.

**Protective Action of Colouring Matters.** ELIZABETH F. STEVENSON (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 249—252).—The fact discovered by Lüppo-Cramer (*Photographische Probleme*, p. 28) that erythrosin, a crystalloid substance, exerts a protective effect on colloidal silver bromide, has been further investigated. It is shown that erythrosin has very little solvent action on silver bromide, that it does not appreciably alter the number of colloidal particles in a given volume of solution, but that it is markedly adsorbed by the submicrons of the silver bromide. As a result of this adsorption the rate of migration of the colloidal particles in the electric field is considerably increased, which is explained on the assumption that it is mainly the anions of the dye which are adsorbed. Eosin, fluorescein, and Congo-red also increase the stability of colloidal solutions of silver bromide.

G. S.

**Bleaching of Methylene-blue in the Visible Spectrum.** P. LASAREFF (*Zeitsch. physikal. Chem.*, 1912, 79, 638. Compare this vol., ii, 219).—Reference is made to papers by Gebhard (see following abstract) and von Hübl (*Wien. Mitteilungen*, 1909, 268) on this subject.

G. S.

**Bleaching of Methylene-blue in the Visible Spectrum.** KURT GEBHARD (*Zeitsch. physikal. Chem.*, 1912, 79, 639—640. Compare *Phot. Korrespondenz*, 1911, 364; Lasareff, previous abstract).—A gelatin plate containing methylene-blue and glycerol is bleached in strong sunlight more rapidly in a vacuum than in the presence of air. On re-oxidation in the dark, the colour of the plate bleached in a vacuum is completely restored, but that bleached in sunlight has a different shade. This is due to the fact that in sunlight an oxidation of part of the dye occurs simultaneously with the reduction, and in certain circumstances the colour of the dye may not return in the dark, the substance being completely destroyed.

In agreement with von Hübl (*loc. cit.*) and contrary to the results of Lasareff, the reduction of methylene-blue was only observed in the presence of glycerol.

G. S.

**Ozonisation of Oxygen by  $\alpha$ -Rays.** S. C. LIND (*Monatsh.*, 1912, 33, 295—310; *Le Radium*, 1912, 9, 104—106; *Amer. Chem. J.*, 1912, 47, 397—415).—The conversion of oxygen into ozone by the  $\alpha$ -rays from a tiny bulb containing radium emanation and sufficiently thin in the wall to allow the  $\alpha$ -rays to escape has been studied quantitatively. The number of ozone molecules formed has been compared with the number of pairs of ions produced by the  $\alpha$ -rays in the gas during the experiment. In several series of experiments

the ratio of these quantities varied inexplicably to a considerable extent. But the order of the two quantities was always the same, and in no case did the number of ozone molecules exceed a greater limit than half the number of pairs of ions, although it fell as low as one-tenth in one experiment. The conclusion is drawn that the ozone is produced by the reaction between oxygen ions and molecules, and that unknown causes result in a loss of the ozone formed, in some circumstances. The ratio of the concentration of ozone to oxygen was in no case greater than 1:1000. Oxygen, from the electrolysis of potassium hydroxide, both moist and dry, streaming through and stationary within the apparatus, was employed. F. S.

**The Secondary Rays Excited by the  $\alpha$ -Rays from Polonium.**  
I. V. E. POUND (*Phil. Mag.*, 1912, [vi], 23, 813—837).—The  $\delta$ -rays emitted by surfaces of brass and carbon subjected to bombardment by the  $\alpha$ -rays of polonium in an almost perfect vacuum were found to decrease with lapse of time, which was traced to the removal of the gas occluded by the surface. This "fatigue effect" was greater for carbon than for brass. A carbon surface thoroughly fatigued by being left in the exhausted apparatus for a week did not recover on re-admitting air or hydrogen and allowing it to remain a week before re-exhausting. If kept in the vacuum only a short time, exposure of the surface to air very considerably reduces the fatigue. If the surface is freed from occluded gas before being exposed to the  $\alpha$ -radiation there is no trace of fatigue. It appears that the effect of the field in increasing the velocity of the  $\alpha$ -rays and therefore their degree of reflexion from the bombarded surface produces a slight contributory effect, which increases the apparent fatigue, in the case of brass surface, but not of carbon. F. S.

**The Distribution of  $\beta$ -Rays Among the Single Products of the Active Deposit of Thorium.** OTTO HAHN and LISE MEITNER (*Physikal. Zeitsch.*, 1912, 13, 390—393).—The penetrating  $\beta$ -rays, with velocity above 0.72 (that of light being unity), from the thorium active deposit, do not come, as previously assumed, from thorium-*D* only, but for the greater part from thorium-*C*. The absorption curves of the  $\beta$ -rays in aluminium were compared for thorium-*C* + *D* and for thorium-*D* alone, separated from the former by recoil methods.

The thorium-*C* + *D* was separated from the solution of the thorium active deposit by means of nickel. The  $\beta$ -rays of thorium-*C* + *D* are absorbed exponentially, the half value being 0.41 mm. of aluminium. Those from thorium-*D* alone are also absorbed exponentially, the half-value being 0.32 mm. The calculated half-value for thorium-*C* alone is 0.48 mm. The  $\beta$ - and  $\gamma$ -ray time-curves for pure thorium-*C*, separated by nickel from the solution of the active deposit, should if thorium-*D* were initially absent rise from zero to a maximum as thorium-*D* is regenerated, on the assumption that thorium-*D* alone of the members of the series gives penetrating rays. On the contrary the  $\beta$ -ray time-curve rose from an initial value, 0.72 of the maximum, which was attained in ten minutes, and corresponded with

the theoretical curve drawn on the assumption that under the conditions of measurement 65% of the total  $\beta$ -ray ionisation comes from thorium-*C* and 35% from thorium-*D* when these two products are in equilibrium. The  $\gamma$ -ray time-curve was completely different and rose from an initial value only about 5% of that at the maximum, which was attained in from fourteen to sixteen minutes. Hence thorium-*C*, which gives little, if any,  $\gamma$ -radiation, gives 65% of the total penetrating  $\beta$ -radiation, whereas thorium-*D* gives nearly all the  $\gamma$ -rays and only 35% of the  $\beta$ -rays.

F. S.

**Absorption of  $\gamma$ -Rays by Gases and Light Substances.** J. CHADWICK (*Proc. Physical Soc.*, 1912, 24, 152—156).—The absorption coefficients of the  $\gamma$ -rays from radium after passing through sheets of lead, 3 mm. and 10 mm. thick, have been measured in air, carbon dioxide, and hydrogen under high pressures. For the rays which had passed through 3 mm. of lead, the coefficients were found to be 0.000062, 0.000102, and 0.000042 respectively at normal temperature and pressure. For rays which had traversed 1 cm. of lead, the coefficients obtained were 0.000059 for air and 0.000092 for carbon dioxide.

Measurements were also made with liquid air, and the coefficients found in this way are in satisfactory agreement with the values calculated from the data for air under pressure, indicating that the absorption of  $\gamma$ -rays is not affected by temperature.

The absorption of the two groups of rays was also determined in aluminium, iron, lead, wood, water, and several aqueous solutions.

H. M. D.

[The Ionisation of Liquid Hydrocarbons.] A. GOLDMANN (*Le Radium*, 1912, 9, 153—155).—The experimental data obtained by Bialobjeski (*Abstr.*, 1911, ii, 837) in the investigation of the conducting properties of various fractions of American petroleum when subjected to  $\beta$ - and  $\gamma$ -rays of radium are criticised. According to the thickness of the layer of hydrocarbon, the values obtained for the sum of the ionic mobilities vary within wide limits, and these numbers have therefore no particular significance. Contrary to Bialobjeski's opinion, the relationship between the strength of the ionisation current and that of the electric field is shown to be consistent with the relationship deduced by Jaffé (*Abstr.*, 1909, ii, 208; 1910, ii, 481).

H. M. D.

**Ionisation by Collision in Helium.** ERNEST W. B. GILL and F. B. PIDDUCK (*Phil. Mag.*, 1912, [vi], 23, 837—849. Compare *Abstr.*, 1908, ii, 798).—The influence of small quantities of foreign gases on the ionising power of the ions in helium has been examined. From the observations it appears that the impurities have a much larger influence on the positive than on the negative ions. If  $\alpha$  and  $\beta$  denote the numbers of new ions which are generated per centimetre by a negative and a positive ion respectively, the effect of the addition of 0.75% of air to helium (at a pressure of 5 mm.) is to reduce  $\alpha$  by about 8%, whilst  $\beta$  is altered to the extent of nearly 40%. It is supposed that the difference in question is due to the greater ease

with which the impurities attach themselves to the relatively slowly moving positive ions. The positive ions, thus loaded, are less effective in producing fresh ions by collision, because of the longer time required to reach the velocity necessary for ionisation.

In consequence of the reduction of  $\beta$  by traces of air or other gases, the sparking potential is increased to a very considerable extent. In pure helium, the observed minimum sparking potential was 156 volts, which is much smaller than that for other gases, nitrogen 298 volts, argon 233 volts, and hydrogen 273 volts being the three lowest sparking potentials recorded previously.

H. M. D.

**Theory of Ionisation by Collision.** JOHN S. TOWNSEND (*Phil. Mag.*, 1912, [vi], 23, 856—859).—Polemical against Campbell (this vol., ii, 411). Numbers obtained recently for the rates of diffusion of negative ions in air at different pressures indicate that the great majority of the ions must be in the electronic state at any given moment.

H. M. D.

**The Passage of Homogeneous Röntgen Rays through Gases.** E. A. OWEN (*Proc. Roy. Soc.*, 1912, A, 86, 426—439).—The action of the homogeneous rays emitted by iron, nickel, copper, zinc, arsenic, selenium, strontium, and molybdenum radiators on air, carbon dioxide, and sulphur dioxide has been examined.

In all these gases, the coefficient of absorption of the homogeneous radiation is approximately inversely proportional to the fifth power of the atomic weight of the element emitting the characteristic rays. According to the data given by Barkla and Sadler, the same relationship appears to hold for the absorption of the rays by carbon, magnesium, and aluminium.

The absorption and the ionisation are proportional to the pressure of the gas. Relative to that in air, the ionisation in carbon dioxide and in sulphur dioxide is approximately constant for the various homogeneous rays emitted by the different radiators.

A new form of Röntgen ray bulb is described, in which the primary rays are allowed to strike the radiator immediately after they leave the anti-cathode. This enables the size of the radiator to be reduced, and yet, at the same time, it is possible to make use of a greater solid angle of rays than in an ordinary bulb with a much larger radiator.

H. M. D.

**Velocities of Ions in Dried Gases.** ROBERT T. LATTEY and HENRY T. TIZARD (*Proc. Roy. Soc.*, 1912, [A], 86, 349—357).—Measurements have been made of the velocities of the positive and negative ions which are formed by the action of Röntgen rays on dry hydrogen and carbon dioxide. The velocity of the positive ions in the case of both gases is proportional to  $X/p$ , where  $X$  is the potential gradient and  $p$  the pressure of the gas. The velocity of the negative ions increases, however, more rapidly than  $X/p$ . Both results agree with those obtained in previous observations in dry air.

Values representing the molecular masses of the ions have been calculated from the velocity data. From these it appears that the positive ion is of large mass and represents an aggregate of at least twenty-five molecules of the gas in which it is formed. These large

positive aggregates appear to be stable even under the influence of a fairly strong field. The negative ions are much smaller in size and are less stable, the mass of the ion being diminished when its velocity is increased either by an increase in the potential gradient or by a diminution in the pressure. From a comparison of the results with those obtained in experiments with imperfectly dried gases, it appears that gas molecules are more easily removed than water molecules when the velocity is increased.

H. M. D.

**Simple Molecules as Carriers of Electricity in Gases and a New Method of Measuring Molecular Diameters.** W. ALTBERG (*Ann. Physik*, 1912, [iv], 37, 849—880).—The velocity of the most rapidly moving positive and negative ions in a gas, subjected to the action of Röntgen rays, has been measured by a method in which the movements of the ions in an electric field between gauze condenser plates were compensated by forcing the gas through the field at a measured rate. From observations in air, carbon dioxide, oxygen, nitrogen, and hydrogen, it is found in all cases that the velocity of the positive and negative carriers of electricity is such as to show that the most rapidly moving ions are represented by particles of the dimensions of the simple molecules.

The mobilities of the gaseous ions have been employed for the calculation of the molecular diameters by means of Leonard's formula, and the values thus obtained are compared with those derived from (a) the density of the substance in the liquid state, (b) the viscosity, and (c) the absorption of slowly moving cathode rays in the gas.

Some experiments were also made in reference to the nature of the ions in mixtures of air and nitrogen, and the behaviour of gas mixtures is discussed from the theoretical point of view. H. M. D.

**Luminosity of Gases under the Influence of Cathode Rays.** ERNST GEHRCKE and R. SEELIGER (*Ber. Deut. physikal. Ges.*, 1912, 14, 335—343).—Experiments are described which show that the luminosity of gases subjected to the action of cathode rays exhibits changes in colour and intensity when the velocity of the cathode rays is altered. The change in velocity was brought about by the action of a longitudinal electrical field, and experiments in air, nitrogen, argon, helium, hydrogen, iodine, and mercury vapour showed that in all cases a reduction in the speed of the cathode rays was accompanied by a colour change from the blue to the red end of the visible spectrum. Below a certain velocity, the luminous emission from the gas is displaced in the direction of greater wave-lengths, and below a certain limiting lower velocity, the cathode rays are no longer able to excite luminescence. The two limiting velocity values are dependent on the nature of the gas. These experiments support the view that the difference in the luminous emission of the negative glow and the positive column observed in the discharge through gases is due to the difference in the velocities of the exciting electrons.

H. M. D.

**Emission of Negative Electrons by Heated Metals.** KARL FREDENHAGEN (*Ber. Deut. physikal. Ges.*, 1912, 14, 384—397. Compare *Abstr.*, 1911, ii, 571).—Further experiments relating to the emission

of electrons by heated alkali metals have been made, and these seem to show that the positive result, obtained previously, is due to secondary effects. Observations were made with sodium and potassium, which were subjected to double distillation in the highly exhausted electrode apparatus, and current measurements were made for potential differences varying from 2 to 100 volts. When the apparatus was exhausted as completely as possible, the currents indicated were very small in comparison with those recorded in presence of traces of air, hydrogen, or nitrogen at the same temperature. When, at a given temperature, a series of readings was repeated after the lapse of considerable time intervals, the conductivity was found to undergo continuous diminution. From these observations, the author draws the conclusion that the emissions of electrons has not yet been definitely proved to be a characteristic property of the metals when raised to high temperatures. The relatively enormous effects observed in many cases are due to the presence of gaseous impurities, the interaction of which with the metal or with traces of other substances in the surface of the metal gives rise to the emission of electrons. The fact that the observed emission increases exponentially with the temperature can be readily accounted for on the assumption that the emission of electrons is due to secondary processes, the speed of which is controlled by rates of diffusion or of chemical reaction.

H. M. D.

**Fluorescent Röntgen Radiation from Elements of High Atomic Weight.** J. CROSBY CHAPMAN (*Proc. Roy. Soc.*, 1912, A, 86, 439—451. Compare this vol., ii, 316).—An examination of the radiation emitted by the group of elements containing tungsten, gold, platinum, lead, bismuth, thorium, and uranium, by a method which permits of the elimination of the scattered radiation, has shown that this group (*L*) gives off homogeneous rays similar in type to those which are emitted by the elements of atomic weight between calcium and cerium (group *K*). The values of the absorption coefficient in aluminium have been determined in each case.

If  $W_L$  represents the atomic weight of an element in group *L*, which gives out a radiation of a certain penetrating power, and  $W_K$  is the atomic weight of an element in group *K*, which would emit the same radiation, then the relationship between the two atomic weights can in all cases be expressed by the empirical formula

$$W_K = \frac{1}{2}(W_L - 48).$$

From experiments with lead and bismuth, it appears that the elements of high atomic weight exhibit the same selective absorption phenomena in the neighbourhood of an absorption band as the elements of group *K*. This seems to show that the mode of production and the type of the radiation of both groups are the same.

H. M. D.

**Recombination of Ions in Carbon Dioxide and Hydrogen at Different Temperatures.** HENRY A. ERIKSON (*Phil. Mag.*, 1912, [vi], 23, 747—749).—The coefficient of recombination of ions has been measured in carbon dioxide and hydrogen at different temperatures.

In carbon dioxide, the coefficient was found to increase from 2.6 at 100° to 5.89 at -64°, and in hydrogen from 0.45 at 23° to 6.00 at -179°. The probable cause of the variation in the rate of recombination is to be found in the influence of temperature on the thermal velocity of the ions. At a given moment, the ions in a gas may be divided into two groups, in one only of which can recombination take place. When the temperature is altered, the number of ions in one group is increased and in the other diminished. At a high temperature nearly all the ions will have velocities greater than the limiting velocity, and the coefficient of recombination as well as its temperature coefficient will be small. At a low temperature, nearly all the ions will have velocities smaller than the limiting value, and the rate of recombination will be relatively large. The theoretical curve showing the influence of temperature on the coefficient of recombination is of the same character as the experimental curve. H. M. D.

**Radioactivity and Molecular Structures.** W. A. DOUGLAS RUDGE (*Proc. Camb. Phil. Soc.*, 1912, 16, 465—480).—A spiral of nickel wire in a magnetic field, alternately heated and cooled by the intermittent passage of a current above and below 300°, the critical temperature at which it passes from the magnetic to the non-magnetic state, produced no effect on an electroscope. Hydroferrocyanic acid decomposed by heat with evolution of hydrogen cyanide inside an electroscope in general did not affect the leak, but certain irregularities were observed. If the hydrogen cyanide was removed by a rapid current of air, no effect resulted. Otherwise the rate of leak was enormously increased. The increased leak decayed at different rates, to half-value in two or three hours in one instance, and in a few days reached a steady value higher than the natural leak. Hydrogen cyanide prepared in seven other ways showed no unusual effect, that evolved from hydroferrocyanic acid being peculiar. The leak was greater when the leaf was positively charged than when it was negatively charged. The residue from the hydroferrocyanic acid when introduced into the electroscope gave a small and uncertain effect. If the hydrogen cyanide was passed through dry cotton wool, it retained its effect, but not when the wool was moist. No effect was obtained when chromium was reduced from acidic to basic form by heating potassium dichromate with oxalic acid, or by heating potassium permanganate alone or with reducing agents. The conclusion is drawn that the effects observed are not of a radioactive character, but that hydrogen cyanide prepared by heating hydroferrocyanic acid is very strongly ionised, and that the residue has, and retains for a long period, the power of ionising the air. F. S.

**The Question Whether an Active Element Exists between Uranium and Uranium-X.** HEINRICH SIRK (*Monatsh.*, 1912, 33, 289—294).—Attempts were made to verify the existence of radio-uranium, the element supposed to intervene between uranium and uranium-X. A specimen of uranyl nitrate, subjected two years previously to a barium sulphate precipitation, was again similarly treated, and the barium sulphate subjected to various operations. No

substance the activity of which increased with the time was separated, and it is suggested that the original observations may have been due to secondary causes, such as diffusion, which are known to play a part in the variations of the activity of uranium-X. F. S.

**A Balance Method for Comparison of Quantities of Radium and Some of its Applications.** ERNEST RUTHERFORD and J. CHADWICK (*Proc. Physical Soc.*, 1912, 24, 141—151).—The method consists in balancing the saturation ionisation current due to the  $\gamma$ -rays against an opposite ionisation current due to a standard preparation of uranium oxide. The current due to the latter is kept fixed, and the standard radium preparation is moved until a balance is obtained. The standard is then removed and a balance obtained in the same way for a second radium preparation. Since the intensity of the  $\gamma$ -rays from a point source falls off nearly inversely proportional to the square of the distance, the relative  $\gamma$ -ray activity can be deduced from the measured distances of the radium preparations from the corresponding ionisation chamber. It is also shown that radium emanation may be estimated in this way by comparison of its  $\gamma$ -ray activity with that of a radium standard.

By means of the balance method, the half-value period for the transformation of the emanation was found to be 3.854 days. The time required for the development of the maximum  $\gamma$ -ray activity due to the emanation and its disintegration products was found to be 255 minutes, which agrees exactly with the calculated value. Exposure to a strong magnetic field was found to have no appreciable influence on the  $\gamma$ -ray activity of radium. H. M. D.

**Radium Standards.** HEINRICH MACHE and STEFAN MEYER (*Physikal. Zeitsch.*, 1912, 13, 320—322).—The heating effect of the  $\alpha$ -particles, calculated from present data as to their velocity and numbers, amounts to 127.7 calories per hour per gram of radium (element). The heat of the recoiling atoms increases this to 130 calories, that of the  $\beta$ -rays to 132.4, and of the  $\gamma$ -rays, if it were possible to absorb them all, to 138.

The experimental value found for the new Austrian standards, in which all the rays except 82% of the  $\gamma$ -rays were absorbed, is 132.3 instead of 133.4 as calculated. The calculation of the saturation current due to 1 curie of emanation, from the number of pairs of ions produced per  $\alpha$ -particle and the number of  $\alpha$ -particles expelled per second, is  $2.75 \times 10^6$  E.S.U. The total saturation current, in a vessel of infinite dimensions in which the active deposit in equilibrium with the emanation was deposited on the walls, is calculated to be  $6.10 \times 10^6$  E.S.U. The experimental values, extrapolated to vessels of infinite dimensions, are respectively 2.49 and 6.31 (Duane and Laborde), 2.75 and 6.10 (Rutherford), and 2.67 and 6.02 (Flamm and Mache) in terms of E.S.U.  $\times 10^6$ . This shows that the Manchester, Paris, and Vienna standards are in agreement within these limits of difference, a deduction which the International Radium Standards Committee at Paris have since confirmed at their Paris meeting 1912. F. S.

**The Distribution of the Active Deposit of Radium in an Electric Field.** E. M. WELLISCH and HOWARD L. BRONSON (*Phil. Mag.*, 1912, [vi], 23, 714—729; *Amer. J. Sci.*, 1912, [iv], 33, 483—498).—The percentage activity due to the active deposit of radium deposited on the positively charged case was compared to that deposited on the negatively charged central electrode in a testing vessel containing radium emanation under various conditions. For very small applied potentials, it was found that the percentage cathode activity was diminished somewhat when the ionisation in the testing vessel was increased by an extraneous source of ionisation, for example, X-rays.

For higher potentials there is no appreciable effect. In air at 1 atmosphere the percentage activity deposited on the cathode increased from 42.7% with 18 volts to 80% with 160 volts, and after that increased slowly and regularly to 91.3% with 4000 volts. For the latter part of the curve the percentage was independent of the amount of emanation. The curve strikingly resembles that of  $\alpha$ -ray ionisation under increasing potentials. The ratio of the ionisation currents is identical with the ratio of the percentage cathode activities at different potentials above that necessary to prevent "volume recombination" as distinguished from "columnar recombination." The experiments suggested that the proportion of the total activity deposited on the case was the same as the lack of saturation of the ionisation current. At a lower pressure (260 mm.) the percentage cathode activity was nearly constant at 82% for potentials from 80 to 2000 volts. Under greater pressures (up to  $3\frac{1}{2}$  atmospheres) the percentage cathode activity increased for a potential of 1100 volts as the pressure increased up to 2 atmospheres and then diminished. Under the most favourable conditions 10% of the total activity was not deposited on the cathode, but on the case the amount, however, appeared to diminish continuously as higher potentials were employed. The results at low pressures suggest that the percentage lack of saturation, which is proportional to the percentage activity escaping deposition on the cathode, is greater at low pressure than at high pressures, and that after the  $\alpha$ -particles have ceased to ionise, extra ionisation is produced by the electric field. The view is taken that "neutrons" or uncharged molecules capable of specially easy ionisation, for example, by collision with ions, are formed by the  $\alpha$ -rays, possibly as the result of a partial ionisation, whereby the molecule, although neutral, is left in an unstable electrical state. The active deposit particles which have been exposed at formation to the action of  $\alpha$ -particles are regarded as neutrons in this sense.

F. S.

**Decomposition of the Purines by the Action of Radium Emanation.** P. MESERNITSKY (*Le Radium*, 1912, 9, 145—147).—The action of radium emanation on sodium urate, xanthine, and hypoxanthine has been examined. The substances were suspended in an aqueous solution containing the emanation, and from time to time the amount of nitrogen in the solution was estimated. By this method it has been found that uric acid is readily decomposed, xanthine very slowly, whilst hypoxanthine is unaffected by the emanation. Other experiments have shown that the decomposition of the urate is

due to the  $\alpha$ -particles, the penetrating rays having no action. The decomposition occurs both in the presence and absence of oxygen, and ammonia appears as one of the decomposition products, about 34% of the nitrogen being found in this form. H. M. D.

**Action of Radium Emanation on Monosodium Urate.** ERICH VON KNAFFL-LENZ and WILHELM WIECHOWSKI (*Zeitsch. physiol. Chem.*, 1912, 77, 303—327).—Relatively large quantities of radium emanation have no effect either in decomposing or in increasing the solubility of monosodium urate. Radium-D is also entirely without action, and the amount of ozone formed in the air by the radium preparations is also insufficient to cause oxidation of uric acid, which is usually susceptible to ozone. These results are contrary to those obtained by Gudzent. Decomposition readily took place in impure preparations with an alkaline reaction. The possibility of the activation by the emanation of a uric acid oxydase, which is present only in traces in human organs, is discussed in order to explain the favourable action of the emanations in cases of gout. E. F. A.

**Action of Radium Emanation on Colloids. II.** WILLEM P. JORISSEN and H. W. WOUDESTRA (*Chem. Weekblad*, 1912, 9, 340—341. Compare Abstr., 1910, ii, 1024).—After the lapse of one and a-half years the colloidal solution of ferric hydroxide which was exposed to radium emanation had completely coagulated, so that the emanation brings about a slow coagulation of the colloid. A colloidal solution of chromium hydroxide, after exposure to the emanation, was found to have altered slightly in appearance, and to coagulate with a lower concentration of electrolyte than another portion which had not been exposed to the emanation. G. S.

**The Quantities of Radium and Thorium Emanations Contained in the Air of Certain Soils.** JOHN SATTERLY (*Proc. Camb. Phil. Soc.*, 1912, 16, 514—533).—Measurements on the quantity of radium emanation contained in the soil at various depths, continued over a year, gave for a depth of 100—150 cm. a mean value of  $2 \times 10^{-10}$  curie per litre, or 2000 times the usual amount in the atmosphere. From estimates of the relative volumes of air and soil and the quantity of soil necessary to supply the emanation, the apparent radium content of the underground soil is only  $1.7 \times 10^{-14}$  (gram of radium per gram), or seventy times less than the probable actual content, so that little of the radium emanation generated can escape.

The proportion of radium emanation to thorium emanation in soil air steadily increases with depth. At a depth of 150 cm., if the proportion of radium is assumed to be  $1.1 \times 10^{-12}$ , that of thorium is  $1.4 \times 10^{-5}$ , which is probably of the right order. F. S.

**The Chemical Action of Penetrating Radium Rays. II. The Influence of the Penetrating Rays on Alkali Iodides in Aqueous Solution.** ANTON KAILAN (*Monatsh.*, 1912, 33, 71—98).—Radium preparations of various strengths in closed tubes were

immersed in solutions of alkali iodides contained in opaque vessels kept at constant temperature, and the iodine liberated after a known time was titrated with thiosulphate. In similar circumstances the action increased with increasing concentration of the iodide less rapidly than the concentration, as in the analogous action of ultra-violet light. The action at  $25^{\circ}$  was less than at  $12^{\circ}$  and  $7^{\circ}$ . Addition of hydrochloric acid notably increased the action, making it appear probable that the alkali liberated exercises a retarding effect. Sodium iodide showed a smaller reaction velocity than potassium iodide, and with normal solutions in absence of acid no iodine could be detected after the action of over 100 mg. of radium for two days. Various explanations of the reaction are discussed. It is considered most probable that the rays decompose the undissociated iodide molecules, liberating iodine and hydrogen, both in acid and alkaline solutions.

F. S.

**Revision of the Atomic Weight of Radium and the Preparation of Standards of Radium.** OTTO HÖNIGSCHMID (*Monatsh.*, 1912, 33, 253—288).—The value obtained by Mme. Curie, recalculated as 226.34 in terms of  $\text{Ag}=107.88$  and  $\text{Cl}=35.47$ , is criticised on the grounds (1) that the radium chloride crystals may not have been completely dehydrated at  $150^{\circ}$ ; (2) that the crystals decompose rapidly in dry air with loss of chlorine, whereas the fused chloride is much more stable; (3) that the crystals are hygroscopic and rapidly absorb water during weighing; (4) that in the precipitation of the hot solutions with silver nitrate the rapid balling together of the silver chloride may cause adsorption of soluble salts, and (5) that the solubility of the silver chloride in hot water was not corrected for, which, it is estimated, may cause an error of  $+0.7$  unit in the atomic weight.

The raw material employed by the author contained about 1.5 grams of radium chloride, of which 0.82 gram was in the form of a nearly pure preparation which had been preserved in a stoppered quartz tube for two years. On heating in nitrogen to  $300^{\circ}$  scarcely any water was evolved, but on fusion in hydrogen chloride, it lost 5% of its weight and evolved chlorine and water. Freshly prepared radium chloride can be fused in hydrogen chloride without evolution of more than a trace of chlorine. Hence in the time since it was prepared oxygen had been absorbed and hypochlorite or chlorate produced. The fused chloride glowed brilliantly in the dark and during solution. It was found to give an atomic weight of 218.7 before purification, and about 220 after removing iron. On fractional crystallisation from aqueous hydrogen chloride the atomic weight rose rapidly to 225.9, and did not further increase. Repeating the crystallisation seventeen times and precipitating the aqueous solution with alcohol thirteen times did not change the atomic weight, and the material, about 1.35 grams of chloride in all, was considered as pure as these methods could produce. Any radium-*D* present was removed before fractionation by hydrogen sulphide. By means of the new apparatus of T. W. Richards the chloride in a platinum boat was stoppered in its weighing bottle in dry air before it was removed from the tube in

which it had been fused. The moist crystals in the boat were dried in a current of nitrogen below  $200^{\circ}$ , the nitrogen was displaced by dry hydrogen chloride, and the salt fused at  $900^{\circ}$ . On cooling, the hydrogen chloride was displaced by nitrogen, and, lastly, by dried air. The precipitation with silver nitrate was carried out in the cold in red light, the dissolved silver chloride in the wash-water being estimated for each precipitation by the nephelometer. It amounted to between 0.25 and 0.5 mg. Six estimations of the ratio  $\text{RaCl}_2/\text{AgCl}$  gave 225.95 as the mean atomic weight of radium with variations in the individual experiments of not more than  $\pm 0.03$ . About 1 gram of radium chloride was employed. Two determinations of the ratio  $\text{RaCl}_2/\text{Ag}$  by a gravimetric titration method with the help of the nephelometer gave also 225.95 for the atomic weight. At the end of the work the material was again crystallised twenty times out of hydrogen chloride solution, and an estimation showed no change of atomic weight.

In the preparation of radium standards containing a known weight of radium chloride, crystals dried at  $200^{\circ}$  were used, as experiment showed that these gave the same atomic weight as the fused salt. Glass tubes, 3 mm. wide and of wall thickness 0.27 mm., were quickly filled by a platinum funnel, and weighed in weighing tubes before sealing up. In this way five standards containing respectively 10.11, 31.17, 40.43, 236.91, 680.50 mg. of radium chloride were prepared, and also a standard solution containing 12.92 mg. in 500 c.c.

F. S.

**Absorption of Ultra-violet Light by Radioactive Elements, and the Degradation Products of these Elements.** NICOLAI D. ZELINSKY (*Bull. Acad. Sci. St. Pétersbourg*, 1912, 465—487).—The results of the author's measurements of the absorption spectra of radioactive and other substances show that the activity of elements obtaining their energy from some unknown source (probably from the internal, potential energy of the atom) is exhibited in the absorption of light both by the active materials themselves and by their emanations. This new method of detecting the presence of radioactive substances forms the fifth now available.

T. H. P.

**The Radioactive Properties of the Carlsbad Spring.** WERNER KOLHÖRSTER (*Ber. Deut. physikal. Ges.*, 1912, 14, 356—366).—The rate of decay of the emanation from the Carlsbad spring water shows that the emanation is almost entirely due to radium, although a slight initial fall in the activity after removal of the radium emanation by boiling appears to indicate that very small quantities of thorium are also present. The activity of the Gasteiner Lainer spring is equivalent to  $1.1 \times 10^{-11}$ , that of the Carlsbad spring to  $5.5 \times 10^{-11}$ , and that of the artificially concentrated spring water (Karlsbader Sprudellauge) to  $2.2 \times 10^{-9}$  gram of radium per litre. By addition of small quantities of barium chloride to the water acidified with sulphuric acid, the radium can be removed almost quantitatively. No separation is effected, however, by the addition of sodium thiosulphate to the acidified solution. Variable quantities are removed by the pre-

precipitation of carbonates and silicates, but the precipitation of ferric hydroxide which occurs when air is bubbled through the solution does not remove any of the radium salt. H. M. D.

**Radioactivity of the Thermal Springs of Saint Lucasbad (Hungary).** BÉLA SZILÁRD (*Compt. rend.*, 1912, 154, 982—984).—This group comprises twenty springs emitting the enormous volume of 40,000,000 litres of water *per diem*. The temperature varies from 24° to 68°, and the average total solids amount to 0·7 gram per litre. One spring gave  $33\cdot5 \times 10^{-10}$  international Curie units of radium emanation per litre, or  $90\cdot8 \times 10^{-10}$  units per litre of dissolved gas.

W. O. W.

**Radioactivity of the Waters of Monte Amiata and Experiments on the Atmospheric Dispersion of that District.** RAFFAELLO NASINI and C. PORLEZZA (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 316—324).—The authors record the results of measurements of radioactivity in the case of thirty-nine springs at this spot, as well as of a number of rocks of the locality. The radioactivity of many of the waters is high, reaching in one case 9·170 Mache units. The activity of the rocks examined was not unusually large.

R. V. S.

**The Radium Content of Rocks.** E. H. BÜCHNER (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 14, 1063—1066).—Fresh determinations of the radium content of rocks from the island of Borneo and the Moluccas, and also from the province of Limburg, Holland, confirm the average results previously obtained. The mean content of eighteen rocks, mainly from Central Borneo, was  $1\cdot73 \times 10^{-12}$  gram of radium per gram, which agrees with the mean found for the Sumatra rocks (1·65), and with the mean of 104 specimens of igneous rocks (1·4) found by other investigators, excluding Joly's results. Joly's results are four or five times higher than those found by other investigators, and give the mean value of 7 for 126 specimens. The Limburg rocks were from depths of 685 to 1397 metres from a bore near Baarlo, and consisted of very sandy shales and quartziferous sandstones. They did not reveal any regular connexion between radium content and depth. The mean content of this series excluding one exceptionally high result was 1·6. The provisional conclusion is drawn that there is no relation between radium content and depth.

F. S.

**The Emission of Electricity from Carbon at High Temperatures.** JOHN A. HARKER and G. W. C. KAYE (*Proc. Roy. Soc.*, 1912, [A], 86, 379—396).—The electrical properties of the atmospheres of carbon-tube resistance furnaces have been examined at temperatures from 1500° to 3000°. By the application of small potential differences (2 to 8 volts) to axially situated carbon electrodes, currents up to 10 amperes were obtained at the higher temperatures. The current intensity increases exponentially with the temperature. The current potential curves indicate that the current is proportional to the applied

potential at the higher temperatures, but at the lower temperatures saturation values appear to be reached even with the small voltages which were applied.

Without the application of any external potential difference, a current is obtained when one of the electrodes is kept permanently hot and the other cooled by a suitable method. The current flows from the cold to the hot electrode through the heated gas, and its magnitude is somewhat greater in hydrogen than in nitrogen. These currents (of the order of one ampere) appear to be associated with the transport across the electrode gap, firstly of the impurities in the carbon and afterwards of the carbon itself. The first of these stages is distinguished by a temporary current of greater intensity than that which is obtained when the steady state has been reached. Some of the effects described have also been found in experiments in which the high temperatures were produced by gas heating. H. M. D.

**Dielectric Constant of Liquid Arsenic Hydride.** HERMAN SCHLUNDT and O. C. SCHAEFER (*J. Physical Chem.*, 1912, 16, 253—254. Compare Abstr., 1911, ii, 458).—The hydride was prepared by Saunders' method by the action of dilute sulphuric acid on a sodium arsenic alloy. The dielectric capacity was measured at 15°, and at the boiling point, namely, about -70°.

The following table gives the dielectric capacities of the hydrides of the nitrogen group of elements:

	-50°.	+15°.
Ammonia .....	22.7	15.9
Phosphine .....	2.6	2.88
Arsenic hydride .....	2.58	2.05
Antimony hydride .....	2.58	1.81

R. J. C.

**Properties of Salt Solutions in Relation to the Ionic Theory. III. Electrical Conductivity.** ARTHUR A. NOYES and KAUFMAN G. FALK (*J. Amer. Chem. Soc.*, 1912, 34, 454—485. Compare Abstr., 1910, ii, 929; 1911, ii, 861).—Recent data on the conductivity of salt solutions have been selected and brought together in a table showing the equivalent conductivity at 18° and 0° at concentrations between 0 and 1000 milli-equivalents per litre. The viscosities of the solutions are also tabulated. The ionisation values have been calculated by means of the equation  $\gamma = \Lambda\eta/\Lambda_0\eta_0$ , where  $\eta$  is the viscosity of the solution, and  $\eta_0$  that of pure water. A study of these data has revealed certain relations between the degree of ionisation, the composition, and valence type of the salts, and has shown that, in general, ionisation is not an additive property with respect to the ion-constituents, and its value is not related to those of the mobilities of the ions. A comparison of the values at 0° and 18° has shown that the differences are so small that the ionisation values derived from the conductivity at 18° may be employed at 0° without incurring a greater error than is involved in making the determinations at 0°.

A study of the change of the equivalent conductivity with concen-

tration has indicated that, at fairly low concentrations, the functional relation between ionisation and concentration is independent of the number of ions into which the salt dissociates. The most general and satisfactory expression, so far discovered, of the relation between the conductivity and concentration of uni-univalent salts is given by the function:  $(C\Lambda)^2/C(\Lambda_0 - \Lambda) = K + D'(C\Lambda)^m$ , corresponding with  $(C\gamma)^2/C(1 - \gamma) = K + D(C\gamma)^m$ . In the case of salts of the uni-bivalent and higher types, the relation between ionisation and concentration is probably further complicated by the presence of the intermediate ion. The most probable assumptions which can be employed for estimating the concentration of the latter in solutions of uni-bivalent salts have been discussed by Harkins (this vol., ii, 29). E. G.

**Properties of Salt Solutions in Relation to the Ionic Theory. IV. Comparison of the Ionisation Values Derived from the Freezing-point Lowering and from the Conductivity Ratio.** ARTHUR A. NOYES and KAUFMAN G. FALK (*J. Amer. Chem. Soc.*, 1912, 34, 485—489).—A comparison of the ionisation values derived from freezing-point lowering (Abstr., 1910, ii, 929) and from the conductivity-viscosity ratio (preceding abstract) has shown that the two methods give values for most uni-univalent salts agreeing with each other within 2% up to concentrations of  $0.1N$ , and that the same is true of the uni-bivalent salts, potassium sulphate, and lead nitrate, even up to  $0.2N$ . The halides and sulphates of bivalent metals, as well as lithium chloride and sodium sulphate, on the other hand, show, as a rule, much larger deviations than this at concentrations of  $0.1$ — $0.2N$ .

A discussion is given of the causes underlying this agreement and of the effects of the presence of the intermediate ion and of the formation of double molecules, such as  $Mg_2(SO_4)_2$ , and of complex ions, such as  $Mg(SO_4)_2^-$ ,  $BaCl_4^-$ , or  $BaCl_3^-$ . E. G.

**Electrical Conductivity of Solutions of the Alcohols in Liquid Hydrogen Chloride.** EBENEZER H. ARCHIBALD (*J. Amer. Chem. Soc.*, 1912, 34, 584—592).—In earlier papers (Abstr., 1907, ii, 526, 840) an account has been given of the conductivity of solutions of the alcohols in liquid hydrogen bromide and of the organic acids in liquid hydrogen chloride and bromide. A study has now been made of the conductivity of solutions of methyl, ethyl and butyl alcohols, and resorcinol in liquid hydrogen chloride, and the temperature-coefficients have been determined at various concentrations.

It has been found that the molecular conductivity increases with the dilution in the case of dilute solutions of the three alcohols, and also in that of the more concentrated solutions of all four substances, but that for a wide range of dilution it decreases with the dilution. The increase in the molecular conductivity with dilution for the concentrated solutions is explained on the assumption that a considerable increase takes place in the viscosity of the solution as the concentration increases, and that this is accompanied by a corresponding decrease in the mobility of the ions. The decrease in molecular conductivity with dilution which occurs over a certain range is regarded

as due to a complex electrolyte containing  $n$  molecules of the solute; the molecular conductivity is then expressed by  $kv^n$  instead of  $kv$ . The best conducting solution for methyl and ethyl alcohols has a specific conductivity of 0.007 reciprocal ohms.

The temperature-coefficients for ethyl and butyl alcohols are very large and increase with the concentration. This is regarded as due to a large decrease in the viscosity of the solution with the temperature, the decrease being greater the more concentrated the solution. In the case of resorcinol, the effect of the decrease in the viscosity is sufficient to change a negative temperature-coefficient for a dilute solution into a positive coefficient for a concentrated solution.

The molecular conductivities of methyl and ethyl alcohols, resorcinol, and acetic acid in liquid hydrogen bromide and chloride are compared, and it is shown that the hydrogen chloride solutions are much the better conductors.

E. G.

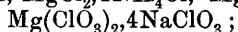
**The Becquerel Effect in Solutions of Uranyl Sulphate, Quinine Sulphate, and Chlorophyll.** ALEXANDER SAMSONOW (*Zeitsch. wiss. Photochem.*, 1912, 11, 33—60).—The conditions have been examined under which a potential difference is established between two electrodes immersed in the solutions when one of the electrodes is illuminated by the light from a quartz mercury lamp. The potential time curves can be interpreted most readily on the assumption that the ions, which result from the removal of electrons by the action of the light, diffuse to the electrodes at different rates. The maximum effect is obtained when the incident light corresponds with the region of maximum absorption. In the case of uranyl sulphate solutions, the presence of traces of uranous salts is necessary for the development of the phenomenon. In the continual action of the light rays, fatigue effects are exhibited, and when the light is removed, after-effects are observed.

It is supposed that the photo-electric effect is not a consequence of, but rather the preliminary stage in, the chemical changes which occur under the influence of the light. The assimilation of carbon dioxide by plants is supposed to be accompanied in the same way by a previous formation of electrically charged molecules.

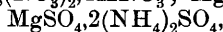
H. M. D.

**The Formation of Complex Compounds in Solution.** N. COSTĂCHESCU and TH. APOSTOI (*Ann. sci. Univ. Jassy*, 1912, 7, 101—131).—The relation between the conductivities or refractive indices and the concentration of the solution of an electrolyte, for example, of potassium chloride, is represented by a straight line. In the presence of another electrolyte, such as ammonium chloride, which does not form a complex with the potassium chloride, the relation is still a straight line, showing no break. If, however, the second electrolyte forms a complex compound with the first, a sharp break takes place at a point corresponding with the composition of the complex, the slope of the straight line being changed at the break. The position of the break depends only on the ratio of the concentrations of the two electrolytes, and not on the absolute concentration of the solution.

Using the method just indicated, the authors have been able to prove the existence of the following complexes in solution, all of which are of the type  $[\text{MgX}_6]\text{R}_4$ , where R is an alkali metal, hydrogen, or ammonium:  $\text{MgCl}_2, 4\text{KCl}$ ,  $\text{MgCl}_2, 4\text{NH}_4\text{Cl}$ ,  $\text{MgCl}_2, 4\text{HCl}$ ;



$\text{MgBr}_2, 4\text{KBr}$ ,  $\text{MgBr}_2, 4\text{NH}_4\text{Br}$ ,  $\text{MgBr}_2, 4\text{HBr}$ ;  $\text{Mg}(\text{NO}_3)_2, 4\text{KNO}_3$ ,  $\text{Mg}(\text{NO}_3)_2, 4\text{NH}_4\text{NO}_3$ ,  $\text{Mg}(\text{NO}_3)_2, 4\text{HNO}_3$ ;  $\text{MgSO}_4, 2\text{K}_2\text{SO}_4$ ,



$\text{MgSO}_4, 2\text{Na}_2\text{SO}_4$ . No compound is formed between magnesium sulphate and sulphuric acid, neither do magnesium salts form complexes with ammonia.

The conductivity method is the most sensitive one for indicating the formation of a compound; in the case of the compounds formed between the magnesium salts and the free acids, the refractive indices of the solutions afford no indication.

None of the above compounds has been isolated.

T. S. P.

**Relationship between Electrolytic Dissociation Constants and Chemical Constitution.** RUDOLF WEGSCHEIDER (*Zeitsch. Elektrochem.*, 1912, 18, 277—281).—The assertion of Derick (compare Abstr., 1911, ii, 712), that no general connexion between the chemical structure of organic electrolytes and their ionisation has been discovered, is incorrect, since Ostwald's well-known factor law formulates such a connexion, and has often found application in determining the constitution of organic electrolytes. It is shown that Derick's mode of representing the relationship between constitution and dissociation constants is more complicated and theoretically less well-founded than that of Ostwald, and it does not represent the observed results more accurately (in the case of the aromatic acids not so accurately) as the factor rule. There is, therefore, no reason to give up the use of Ostwald's rule in favour of that of Derick.

G. S.

**Electrochemical Behaviour of Iron.** GÜNTHER SCHULZE (*Zeitsch. Elektrochem.*, 1912, 18, 326—333. Compare Abstr., 1911, ii, 365; 1912, ii, 126).—The effect of polarising iron anodes with constant current in sulphuric acid of different concentrations has been examined. When the acid is less than 50% the iron is only rendered passive, but above 60% and a current of 3 milliamp./cm.<sup>2</sup> valve action occurs before the metal becomes passive. The valve action below 75% concentration of acid is unstable and slowly changes to passivity, but at higher concentrations is stable. The maximum potential varies according to the concentration of the acid between 40 and 70 volts. Below the maximum potential the residual current which flows through the cell is very small. Iron, both in concentrated and in fuming sulphuric acid, has, like aluminium, the property of partially transforming an alternating current into a direct current.

The electrostatic capacity of the active layer formed on iron is of the same order of thickness, and depends on the water content of the sulphuric acid in the same way, as does that on aluminium.

Nickel and cobalt behave similarly to iron, and other metals which show valve action and affect the direction of an alternating current

are aluminium, tantalum, magnesium, cadmium, zinc, antimony, bismuth, copper, and tin. G. S.

The Function of Interatomic Electrons in Catalysis and Electrolysis. NOE L. MÜLLER (*Compt. rend.*, 1912, 154, 1160—1161); PIERRE ACHALME (*ibid.*, 1161—1162).—A question of priority (compare Müller, *Abstr.*, 1909, ii, 112; Achalme, this vol., ii, 322, 340).

W. O. W.

The Electric Pressure Furnace. I. Construction of the Furnace and its Temperature-gradient Under Pressure. FRANZ FISCHER and HANS PLOETZE (*Zeitsch. anorg. Chem.*, 1912, 75, 1—9).—The furnace described may be used with oxygen under 100 atmospheres pressure up to 1000°. An unglazed porcelain tube, 36 cm. long, 15 mm. internal diameter, and 2 mm. thick, is wound with 0.5 mm. platinum wire on a paste of magnesia and alumina. After wrapping with asbestos, the tube is heated to redness to remove organic matter, and further coated when cool with alumina and magnesia. This process is repeated until the layers of asbestos and paste are 12 mm. thick, when it is coated with sodium silicate and placed in a mild steel tube with walls 1 cm. thick, provided with thick flanges to which the ends can be bolted. The leads pass through the flanges, and are insulated with asbestos. Oxygen is admitted through a copper tube passing through one of the caps, whilst the other is provided with an escape valve. The whole furnace is rendered water tight by suitable jointing material, and is cooled by immersion in a trough of water.

The temperature-gradient within the tube is much steeper under high pressures than under atmospheric pressure, and the difference between different parts of the interior may amount to nearly 200°, and the furnace is therefore only suitable for qualitative experiments.

The material to be examined is placed in a boat, and after closing the furnace and immersing it in the cooling trough, oxygen is admitted until the required pressure is reached, and heating is then begun. C. H. D.

Influence of Oxide Formation and Thermal Treatment on the Magnetism of Copper. J. G. GRAY and A. D. ROSS (*Physikal. Zeitsch.*, 1912, 13, 404—407. Compare *Abstr.*, 1909, ii, 208).—The explanation, suggested by Behnsen (this vol., ii, 17), of the author's previous observations is criticised adversely. Further observations relating to the influence of thermal treatment on the magnetic properties of various alloys lead to the view that the behaviour of nearly pure (non-electrolytic) copper is due to the special properties of the iron which is present in the form of a very dilute solid solution. This iron is supposed to form stable chains of elementary magnets which do not respond to an applied magnetic field in ordinary circumstances. Heating and subsequent rapid cooling afford conditions, however, which in all probability favour the breaking up of these chains, and this results in the development of permanent magnetic properties. The increased effect, which is obtained by cooling in

liquid air as compared with water, is attributed to the presence of traces of nickel, experiments having shown that the magnetic transition temperature is dependent on the proportion of nickel, and is very low in case traces only are present in the copper. H. M. D.

**The Magnetisation of Alloys of Nickel and Cobalt.** OTTO BLOCH (*Ann. Chim. Phys.*, 1912, [viii], 25, 5—22; *Arch. Sci. phys. nat.*, 1912, [iv], 33, 293—308. Compare Weiss and Bloch, this vol., ii, 17).—A more detailed account of work already published.

C. H. D.

**The Nitrogen Thermometer Scale from 300° to 630° with a Direct Determination of the Boiling Point of Sulphur.** ARTHUR L. DAY and ROBERT B. SOSMAN (*J. Washington Acad. Sci.*, 1912, 2, 167—176\*).—In order to avoid the uncertainty attaching to the distribution of temperature over the surface of the gas thermometer bulb when immersed in an air-bath, the authors have compared the indications of the nitrogen thermometer with those of thermocouples, when immersed in a fused mixture of sodium and potassium nitrates, at the boiling point of benzophenone and the melting points of zinc and antimony. The three temperatures, as measured in this way by the nitrogen thermometer, were found to be 305·85°, 419·3°, and 629·8° respectively. A determination of the boiling point of sulphur by the nitrogen thermometer gave 444·4°. H. M. D.

**Determination of the Ratio of the Specific Heats, and of the Specific Heat at Constant Pressure of Air and Carbon Dioxide.** H. W. MOODY (*Physikal. Zeitsch.*, 1912, 13, 383—388).—The specific heat ratio was obtained by the method of adiabatic expansion, the resulting change of temperature of the gas being determined by means of a copper-constantan thermocouple constructed of wire of 0·025 mm. diameter. The one junction was situated at the centre of the large spherical gas chamber of 60 litres capacity, and the other was placed so as to take up the constant temperature of the water-bath in which the gas bottle was immersed.

By making a series of experiments, in which the original excess of pressure in the gas chamber varied from 12 cm. to 12 mm. of mercury, it was possible to obtain by extrapolation a value of the specific heat ratio corresponding with zero excess pressure, and thus to eliminate the disturbing effects of the subsequent heat exchanges. The value thus obtained for the specific heat ratio is 1·4011 in the case of air, and 1·3003 for carbon dioxide at 20° and 760 mm. pressure. These numbers are utilised in the calculation of the specific heats at constant pressure, the values deduced being 0·24118 for air and 0·2008 for carbon dioxide, both at 20° and 760 mm. pressure. H. M. D.

**Specific Heat of Tungsten at High Temperatures.** O. M. CORBINO (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 346—351. Compare this vol., ii, 327).—By the adoption of certain modifications

\* and *Amer. J. Sci.*, 1912, [iv], 33, 517—533.

the author has been able to increase the accuracy of the results obtained by his method for the investigation of the thermal constants of a metallic filament. In regard to the thermal capacity of the tungsten filament employed, the new results confirm the conclusions previously reached. The proportionality between the thermal capacity at constant pressure and the variation of resistance with temperature is approximate only, but the proportionality is much closer when the thermal capacity at constant volume is concerned.

Actual weighing of the filament employed has shown, however, that a considerable error was made in the previous estimation of its weight, so that the agreement previously recorded between the observed value of the specific heat and the calculated value does not exist. The atomic heat at constant volume is 7.8.

R. V. S.

**Specific Heat of Binary Mixtures. III.** ALFRED SCHULZE (*Ber. Deut. physikal. Ges.*, 1912, 14, 344—355. Compare this vol., ii, 327, 428).—Measurements have been made of the specific heats of mixtures of ethyl ether and acetone, benzene and acetone, ethyl ether and carbon disulphide, and chloroform and carbon disulphide at different temperatures. In all cases the specific heat of the mixtures is less than that calculated from the simple mixture rule, and the deviations increase in magnitude with fall in temperature. The observed divergencies from the behaviour of an ideal pair of liquids is attributed to association of the acetone and the carbon disulphide. In all cases, the nature of the binary mixtures, which is indicated by the thermal behaviour, is in agreement with that suggested by the vapour pressure relationships.

H. M. D.

**Accurate Cryoscopic Determinations. I. Nitrates of Univalent Metals.** WALTER A. ROTH (*Zeitsch. physikal. Chem.*, 1912, 79, 599—620. Compare Abstr., 1903, ii, 467; Washburn and McInnes, Abstr., 1911, ii, 794; Biltz, this vol., ii, 242).—The freezing points of dilute aqueous solutions of potassium, sodium, silver, and caesium nitrates have been determined by the method already given. The "dissociation constant" of caesium nitrate in  $N/35$ - to  $N/10$ -solution increases with the concentration, and only becomes constant at higher concentrations. Potassium nitrate in  $N/50$  to  $N/3$  concentration and silver nitrate in  $N/100$  to  $N/8$  concentration behaves similarly to caesium nitrate. The view of Biltz, that caesium nitrate is exceptional, inasmuch as it follows the law of mass action, is, therefore, incorrect; the validity of the law within certain limits is ascribed to the compensating effect of two factors, namely, hydration, which increases the dissociation constant, and the formation of double molecules, which has the contrary effect. Sodium nitrate differs from the other three nitrates, inasmuch as the "dissociation constant" increases steadily from  $N/45$  to  $N/3$  dilution, and it is suggested that this salt does not polymerise in solution. This explanation also applies to the cryoscopic data for alkali chlorides and iodates due to Jahn (Abstr., 1905, ii, 145; 1907, ii, 433). The results are in accord with the views of a number of previous observers, that the degree of hydration diminishes with increasing atomic weight of the cation.

G. S.

**Freezing-point Determinations with Very Dilute Aqueous Solutions.** FRITZ FLÜGEL (*Zeitsch. physikal. Chem.*, 1912, 79, 577—591. Compare Hausrath, *Ann. Physik*, 1902, [iv], 9, 522).—As a mercury thermometer proved useless for measuring differences of temperature less than  $0.01^{\circ}$ , the author employed a thermocouple of copper and constantan, which, when carefully insulated and kept perfectly dry, gave results accurate to  $2.5 \times 10^{-5}$  degree. The freezing-point determinations were made by finding by analysis the concentration of the solution in equilibrium with ice.

Measurements were made with solutions of potassium and sodium chloride and sodium chlorate and bromate of concentrations 0.001 to about 0.1 normal. The experiments were designed to supplement the freezing-point determinations of Jahn (*Abstr.*, 1905, ii, 145 ; 1907, ii, 433) at higher concentrations, and are satisfactorily represented by the interpolation formula suggested by that observer. The electrical conductivity of solutions of sodium chlorate and bromate were measured at  $18^{\circ}$ , and it is shown that the differences between the degrees of ionisation calculated from cryoscopic and conductivity determinations is greater than the experimental error. Further, the law of mass action is not valid for the effect of dilution on the ionic concentration, whether calculated from cryoscopic or conductivity data.

Mannitol and carbamide both gave for the molecular freezing-point depression a value of about 1.86, but in the case of mannitol the factor in question increased slightly with increasing concentration.

G. S.

**Ethylene Dibromide in Cryoscopy.** ENRIQUE MOLES (*Anal. Fis. Quim.*, 1912, 10, 131—138).—Thorough desiccation by means of a current of dry air raises the m. p. of ethylene dibromide from  $9.61^{\circ}$  to  $9.975^{\circ}$ . The cryoscopic constant of the dry is 125 as against 118 for the moist compound.

G. D. L.

**Cryoscopic Behaviour of Quaternary Aromatic Ammonium Salts in Bromoform. Correction.** EDGAR WEDEKIND and F. PASCHKE (*Ber.*, 1912, 45, 1449—1450).—The molecular depression of the freezing point of bromoform is 144 (Walden, *Abstr.*, 1910, ii, 1036), not 151 (compare *Abstr.*, 1911, ii, 1060). The change in the constant yields values of the molecular weights of the quaternary ammonium salts which are in closer agreement with those required by the authors' theory.

C. S.

**Vacuum Sublimation Apparatus.** H. J. PRINS (*Chem. Weekblad*, 1912, 9, 343).—The apparatus consists of a short glass retort with a wide mouth, and provided with a narrow side-tube which can be connected to a filter pump. The retort is closed with a rubber cork carrying a glass tube with the closed end inside. This tube is kept filled with cold water, and when the arrangement is heated uniformly in an asbestos furnace, the whole of the sublimate collects on the cooled tube.

G. S.

**Sublimation, Vaporisation, and Liquefaction of Monatomic Elements.** EDUARD GRÜNEISEN (*Ber. Deut. physikal. Ges.*, 1912, 14, 322—334).—On the basis of Mie's theory of monatomic solid substances, formulæ are deduced for the heat of sublimation at absolute zero, the heat of vaporisation at the boiling point, the heat of liquefaction, and the constant in Nernst's vapour-pressure equation. H. M. D.

**Boiling Points of Metals.** HAROLD C. GREENWOOD (*Zeitsch. Elektrochem.*, 1912, 18, 319—326).—Most of the results given in the paper have already been published (compare Abstr., 1909, ii, 720; 1911, ii, 468). Measurements have also been made for pressures below and above that of the atmosphere, and the results are represented graphically. For the high pressure measurements the resistance furnace was enclosed in a high-pressure furnace of the type described by Hutton and Petavel (compare Abstr., 1907, ii, 432), the surface of the metal under examination being observed through a glass window. The boiling points of lead and bismuth were observed at pressures exceeding 10 atmospheres, that of zinc at 50 atmospheres. G. S.

**A Modified Form of the Landsberger Boiling-point Apparatus.** JOHN H. PATERSON (*Proc. Univ. Durham Phil. Soc.* 1912, 4, 142—144).—A measuring vessel of the usual Landsberger type is enclosed in an outer jacket provided with a wide-bore tap at the lower end. The vapour from the boiling flask enters the vessel by means of a side-tube, provided with an outlet at the top closed by a tap. In conducting an experiment, when the boiling point has become constant, using the pure solvent, the lower tap is opened, and the sudden cooling of the contents of the boiling flask causes the solvent in the inner vessel to be sucked back through the side-tube. The weighed solute is then introduced, and the lower tap closed to such an extent that some of the vapour continues to pass up through it and to warm the outer jacket, whilst the remainder passes up through the side-tube. When a sufficient quantity has condensed, the lower tap is opened, but to prevent sucking back, the upper small tap is opened. The volume and temperature are then read, and the experiment is then repeated at various dilutions. C. H. D.

**Pressure Regulators for Ebullioscopic Determinations.** ERNST BECKMANN [with WALTER WEBER and JULIUS VON BOSSE] (*Zeitsch. physikal. Chem.*, 1912, 79, 565—576).—An apparatus for keeping the pressure constant in the neighbourhood of that of the atmosphere is described and figured. The principle of the method is that an alteration of pressure forms an electrical connexion which actuates a relay and brings the enclosed air into contact either with a pump or with an arrangement for forcing in air. The making or interruption of the connexion between the pump and the air inside is effected by means of a glass tube surrounded at the closed end with a cork and an iron ring. It is inverted over a narrow tube leading to the pump, and in ordinary circumstances the open end dips in mercury and closes the connexion; when the relay works, however, it is pulled out of the mercury by an electromagnet, connex-

ion being thus established. For details, the original papers must be consulted.

The apparatus can be arranged to maintain constant low pressures (down to 55 mm.) or high pressures (up to 1350 mm.). G. S.

**Adiabatic Device for Bomb Calorimeter.** J. AUGUST FRIES (*J. Amer. Chem. Soc.*, 1912, 34, 643—652).—The application of a simple adiabatic device to a bomb calorimeter enables the heat of combustion to be determined with greater rapidity and accuracy, and obviates much tedious computation. Apparatus that has been previously described for the purpose cannot be adjusted to calorimeters which are already installed, and for this reason a new form has been devised which can be readily applied to any bomb calorimeter of the Atwater-Berthelot type. A full description is given of the apparatus and the mode of employing it. E. G.

**The Different Internal Energies of a Substance.** RICHARD D. KLEEMAN (*Proc. Camb. Phil. Soc.*, 1912, 16, 540—559).—On the assumption that the internal energy of a substance is divisible into three parts: (1) the kinetic energy of the translational motion of the molecules; (2) their internal molecular energy, and (3) the potential energy resulting from their mutual attraction, the author deduces formulæ for the intrinsic pressure, the internal heat of vaporisation of a liquid, the specific heat of a gas at constant volume and at constant pressure, and also the specific heat of a liquid. The temperature variation of the molecular attraction and the Joule-Thomson effect are also examined. The formula obtained for the intrinsic pressure of a liquid is  $P = -\alpha T/\beta$ , in which  $\alpha$  denotes the coefficient of expansion with rise of temperature, and  $\beta$  the coefficient of compression at constant temperature. The values so deduced are for ethyl ether — 2565 (at 25.4°), benzene — 4083 (at — 15.4°), chloroform — 2970 (at 20°), and pentane — 1337 atmospheres (at 20°). With rise of temperature the intrinsic pressure diminishes in all cases.

The considerations evolved in this method of treatment lead to the conclusion that the molecular attraction decreases with rise of temperature, and thus confirms the result arrived at in previous papers. H. M. D.

**The Function of Valency in the Stability of Binary Metallic Compounds.** CAMILLE MATIGNON (*Compt. rend.*, 1912, 154, 1164—1165).—If the heats of formation of three binary compounds of one atom of a bivalent metal with hydrogen, oxygen, and nitrogen respectively are  $q$ ,  $q_1$ , and  $q_2$  respectively, the heats of formation referred to one molecule of each of these gases will be represented by  $q$ ,  $2q_1$ , and  $3q_2$ . If these three numbers are of the same order of magnitude and the resulting compounds are solid at the moment of dissociation, these will show comparable stability. In other words, the gaseous non-metals unite with metals to form compounds of comparable stability when they combine with the same weight of the metal, developing amounts of heat inversely proportional to their valencies. The relative stability of the hydride, oxide, and nitride of calcium illustrate the truth of this statement. W. O. W.

**Affinity between Iodine and Silver.** ULRICH FISCHER (*Zeitsch. Elektrochem.*, 1912, 18, 283—288).—The heat of formation of silver iodide has been determined by three independent methods with fairly concordant results. The first method, based on the measurement of the temperature-coefficient of the *E.M.F.* of the cell: iodine | solution of potassium iodide | silver iodide | silver gave as mean value 15,170 cal. The first thermochemical method was based on the determination of the difference in the amount of heat given out when silver iodide, and free iodine and silver were dissolved in a concentrated solution of potassium cyanide, and gave a mean value of 14,820 cal. The third calorimetric method depended on the measurement of the difference of heat given out when silver iodide and silver chloride were dissolved separately in potassium cyanide solution, and gave a value of 14,980 cal. The mean of all the values is 14,990 cal., which is considerably higher than the old value of Thomsen, 13,800 cal. The new value agrees almost exactly with that calculated from the *E.M.F.* of the silver-iodine cell on the basis of Nernst's theorem (15,080 cal.), whereas there was a considerable discrepancy with the old value of Thomsen.

In the course of the work the heat of formation of silver chloride was recalculated as 29,940 cal. as compared with Thomsen's value, 29,400 cal. G. S.

**A New Method of Determining the Range of Molecular Action and the Thickness of Liquid Films.** MADISON M. GARVER (*J. Physical Chem.*, 1912, 16, 234—248. Compare Abstr., 1910, ii, 935).—It is assumed that the range of molecular interchange at the surface of a liquid extends to an equal depth,  $\epsilon$ , in vapour and liquid phases. If the surface is plane,  $n_1$  molecules of vapour are in equilibrium with  $n_2$  molecules of liquid, and  $n_1/n_2 = \sigma/\rho$ , where  $\sigma$  is the density of the vapour and  $\rho$  the density of the liquid in the respective active layers. If the liquid is in the form of a spherical drop of surface area,  $a$ , assuming the liquid density  $\rho$  to remain unchanged, but denoting the increased vapour density by  $\sigma'$ , the ratio  $\sigma'/\rho = n_1(a + \Delta a)/n_2(a - \Delta a)$ .

Taking the vapour pressures  $\omega'$  and  $\omega$  at spherical and plane surfaces as proportional to the vapour densities  $\sigma'$  and  $\sigma$  in the surface films:  $\omega'/\omega = \sigma'/\sigma = (a + \Delta a)/(a - \Delta a) = (r + \epsilon/r - \epsilon)^2$ , where  $r$  is the radius of the spherical drop.

Now according to Poynting and Kelvin's equation:  $\log_e \omega'/\omega = 2\gamma d/\omega r D$ , where  $\gamma$  is the surface tension and  $d$  and  $D$  the densities of vapour and liquid respectively. By combining the two equations for  $\omega'/\omega$  it is possible to calculate the value of  $\epsilon$ .

The assumption that the density of the liquid in the active film,  $\rho$ , remains unchanged when the surface changes from plane to spherical, breaks down when the thickness of the active film  $\epsilon$  is an appreciable fraction of the radius  $r$ . The error is less than 1% when  $\epsilon/r = 1/10$ , and is nearly 10% when  $\epsilon/r = 1/2$ .

The magnitude of the range  $\epsilon$  is calculated for a number of liquids. For water at 0°,  $\epsilon = 2.92 \times 10^{-8}$  cm.; ethyl ether at 20°,  $\epsilon = 3.65 \times 10^{-8}$  cm.; benzene at 80°,  $\epsilon = 3.42 \times 10^{-8}$  cm.

If the surface film may be supposed to be  $2\epsilon$  thick, the tension per sq. cm. of cross section  $=\gamma/2\epsilon$ , where  $\gamma$  is the surface tension in dynes per cm. The surface film of liquid water has about 1/8th the tensile strength of piano wire, or, weight for weight, about equal strength.

If the gas equation holds for the vapour of a given substance, it is deduced that  $\gamma/2\epsilon = \rho RT/m$ , where  $m$  is the molecular weight. Hence the degree of tension in the surface film is equal to the "intrinsic pressure" of the liquid as previously defined by the author (*loc. cit.*), referred to the density in the surface film,  $\rho$ . It is possible that the thickness of the surface film is less than  $2\epsilon$ , in which case  $\rho$  is greater than the density  $D$  of the bulk of the liquid.

With the equation  $\gamma/2\epsilon = \rho RT/m$ ,  $\epsilon$  may be computed from the surface tension instead of from the vapour pressure of the liquid. The two sets of values of  $\epsilon$  calculated by the author for a number of common liquids agree very closely.

R. J. C.

**Modification of V. Meyer's Vapour Density Apparatus.** MANUEL T. GIL (*Anal. Fis. Quim.*, 1912, 10, 82—83).—The bulb of liquid is placed on a wire carrier held in place by a side screw. When the apparatus is heated ready for use, the carrier and bulb are released by turning the screw.

G. D. L.

**Density of Solid Substances with Especial Reference to Permanent Changes Produced by High Pressures.** JOHN JOHNSTON and L. H. ADAMS (*J. Amer. Chem. Soc.*, 1912, 34, 563—584).—A method is described for the accurate determination of the density of solids, and a discussion is given of the effect of various factors on the density.

A type of pycnometer has been devised, consisting of a bottle with a thick, flanged neck, on to which the stopper fits by a plane ground joint. The two surfaces composing the ground joint must be optically flat, and great care must be taken to grind them properly. The stopper is placed firmly on the bottle by a sliding and slightly rotatory motion, and neither grease nor any other lubricant should be used. By means of this apparatus it has been found possible to determine the density of salts and other substances within 0.02%. In many cases such accuracy is unnecessary, as much greater variations occur due to the lack of homogeneity of the material.

It has been suggested by earlier observers that the density of a solid is increased by powdering it, but it is now shown that the density is almost, if not quite, independent of the size of the particles, provided that these are quite homogeneous and free from cracks or holes. In the case of strictly homogeneous substances, the change of density is usually less than 0.001, and, if real, is in the direction of a decrease.

The density of strictly homogeneous, crystalline compounds is not affected by the application of very high hydrostatic pressure. If, however, the pressure is not uniform, the density of a metal which has been thus compressed or deformed in any other way usually increases at first, probably owing to the filling up of pores or cracks,

and then decreases, sometimes attaining a final density of less than the original value. The density is increased by subsequent annealing. The change of density in bismuth on compression is in the same direction as that of other metals (compare Spring, *Abstr.*, 1904, ii, 313). These results are discussed in relation to the "flow" of metals, and are shown to be in harmony with the view that the "flow" or any deformation is a manifestation of a real melting produced by the unequal strains set up during the process.

Emphasis is laid on the fact that the density of most substances is somewhat variable owing to lack of complete homogeneity, and that, in consequence, slight changes of density, whether produced by compression or any other means, cannot be regarded as satisfactory evidence of the occurrence of a transformation or chemical reaction.

E. G.

**Equations of Condition in the Region of Small Volumes.** GUSTAV TAMMANN (*Ann. Physik*, 1912, [iv], 37, 975—1013).—From Amagat's data for the compressibility of ethyl ether, ethyl and methyl alcohol, and carbon disulphide, it is shown that the volume pressure relationships at pressures ranging from 500 to 3000 atmospheres can be represented by means of the equation:  $(v - v_{p=\infty})(K + p) = CT$ , in which  $v_{p=\infty}$  is the limiting volume for infinitely large pressure,  $K$  the pressure resulting from the attraction of the molecules, and  $C$  is a constant. This equation does not, however, furnish a satisfactory account of the volume pressure relationships at pressures less than about 500 atmospheres. If  $(v - v_{p=\infty})$  is regarded as the free volume of the liquid and  $(K + p)$  as the internal pressure, the relationship may be expressed in the form — (free volume)  $\times$  (internal pressure) =  $CT$ . This shows the existence of a close analogy between the behaviour of liquids under high pressures and that of ideal gases. Whereas, however, the gas equation has the same constant for molar quantities of different gases, the constant  $C$  in the high pressure equation varies with the nature of the liquid.

From the existence of the above relationship between pressure and volume at high pressures, it may be inferred that the molecular attraction ( $K$ ) is independent of the volume occupied by the molecules of the liquid, an inference which is not in accord with the assumptions made in the ordinary kinetic theory of the liquid state. In view of the close agreement of the high pressure equation of condition with experimental data, the conclusion may be drawn that these assumptions are not warranted.

It is further shown that an analogous equation will in all probability represent the pressure volume relationships of anisotropic substances at high pressures. The exact form of the equation cannot as yet be determined, however.

H. M. D.

**The Two Limiting Volumes of Liquids at the Absolute Zero of Temperature and at Infinitely Large Pressure.** FRIEDRICH KÖRBER (*Ann. Physik*, 1912, [iv], 37, 1014—1045).—With the object of determining by extrapolation the volume occupied by a liquid at absolute zero, dilatometric measurements of the expansion of various

liquids have been made at temperatures varying from  $0^\circ$  down to, or in some cases below, the freezing point. Over this range the volume change can be satisfactorily represented by the formula :

$$v_p = v_0 + aT + bT^2,$$

in which  $v_0$  is the volume at absolute zero, and  $a$  and  $b$  are constants. It is shown that this formula may be employed to calculate volumes at lower temperatures, although the extension to higher temperatures requires the introduction of another term involving  $T^3$ . The values of  $a$  and  $b$  and the extrapolated values of  $v_0$  are tabulated for ethyl ether, ethyl bromide, phosphorus chloride, carbon disulphide, acetone, and allyl, ethyl and methyl alcohols. Whereas the last three liquids are associated to a considerable extent, the first five are approximately normal, and this difference finds expression in the values of  $b$ , which are much smaller for the group of associated liquids than for the normal group.

Utilising Amagat's data for the compressibility of these liquids at high pressures, the author shows that the equation  $(v - v_{p=\infty})(K + p) = CT$  is also satisfied by the data for acetone, ethyl bromide and iodide, phosphorus chloride, and allyl alcohol. Values of  $v_{p=\infty}$ ,  $K$ , and  $C$  have been calculated for each of these liquids, and the corresponding values for ethyl ether, ethyl alcohol, methyl alcohol, and carbon disulphide have been recalculated in such a way as to utilise all the available experimental data in the deduction of the values. The pressure ( $K$ ) due to the molecular attraction has the following values : ethyl ether 2792, ethyl alcohol 2911, methyl alcohol 3050, allyl alcohol 3364, acetone 3574, ethyl bromide 3375, ethyl iodide 3333, phosphorus trichloride 3427, carbon disulphide 3691 atmospheres.

According to the equation of condition :  $(p + k)(v - v_{p=\infty}) = CT$ , the value of  $v_0$  should be equal to  $v_{p=\infty}$ . When these values are compared it is found that the former are in all cases greater than the latter, the difference being greater for the group of normal liquids than for the three alcohols. The divergences are discussed in reference to the form of the volume surface at very low temperatures.

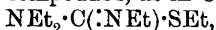
H. M. D.

**Physical Properties of Organic Sulphur Compounds.** MARCEL DELEPINE (*Ann. Chim. Phys.*, 1912, [viii], 25, 529—574).—The physical properties considered are volatility, density, colour, and refraction. The conclusions regarding volatility have been given already (*Abstr.*, 1911, ii, 1061). As regards density, it is pointed out that with the exception of hydrogen sulphide and thiophosphoryl chloride, sulphur compounds are heavier than their oxygen analogues. With the substitution of several oxygen atoms by sulphur atoms, the differences between the densities of the corresponding compounds increase, but this effect disappears as the molecules become more complex. Whilst oxygen ethers are generally less dense than the isomeric alcohols, the sulphur ethers have about the same density as the isomeric mercaptans, and the same is true for isomerides of the types  $X \cdot CS \cdot OR$  and  $X \cdot CO \cdot SR$ , but for compounds of the types  $X \cdot CS \cdot N$  and  $X \cdot CN \cdot S$  the former have higher densities than the latter.

As a general rule, compounds containing sulphur singly linked to carbon are not coloured, whilst those having sulphur doubly linked to

carbon are coloured if the molecule also contains an acid group acting as an auxochrome (compare von Braun and Stechele, *Abstr.*, 1903, i, 618, and Purvis, Jones, and Tasker, *Trans.*, 1910, 97, 2287).

Tables are given of the refractive indices and molecular refractions of a large number of sulphur compounds. Singly linked sulphur has a mean atomic refraction 7.84, except in the case of carbonyl joined to two atoms of sulphur. For sulphur doubly linked to carbon, the value may be 9.26 as in  $\text{CS}(\text{OMe})_2$ , or 9.68 as in  $\text{C}_2\text{H}_5\cdot\text{CS}\cdot\text{OEt}$ , and similarly constituted substances and further variations are introduced as the compounds considered become more complex. In the case of sulphur singly linked in nitrogen compounds, as in  $\text{C}_2\text{H}_5\cdot\text{S}\cdot\text{CN}$  or



the mean atomic refraction is about 8.00, but it shows considerable variation in the iminothiocarbonates and iminodithiocarbonates, and in the thiocarbamides becomes 10.75. In isomeric compounds containing sulphur similarly linked, the refractive indices are of about the same value, but an isomeride containing doubly linked sulphur always has a higher refractive index than one containing singly linked sulphur.

T. A. H.

**Adsorption of Dyes by Ochres.** A. BOUCHONNET (*Bull. Soc. chim.*, 1912, [iv], 11, 454—464. Compare *Abstr.*, 1911, ii, 495; this vol., ii, 165).—The author has investigated the adsorptive capacity of various ochres for organic dyes, and finds that whilst this is influenced in some cases by the composition, being proportional in some cases to the quantity of ferric oxide and alumina present, this is not always so, and the mechanical condition, molecular state, and origin of the ochres also exercise important influences.

The experiments were made by suspending a weighed quantity of the ochre in water, adding a solution of the colouring matter known to be insufficient, allowing to remain at least four hours with frequent shaking, and then adding more of the solution drop by drop until the suspending liquid remained slightly tinted. If the strength of the dye solution is known, the quantity of dye absorbed can then be calculated. For a more accurate determination, a distinct excess of the dye solution is added in the above operation, and the excess determined in an aliquot part of the suspending liquid, colorimetrically or gravimetrically. For ordinary commercial ochres, the amount of colouring matter absorbed varies from 0.67 to 1.92%, depending in part on the dye used, but in the case of impalpable ochres greater variation is shown. The results with the latter are tabulated in detail in the original.

T. A. H.

**Dissociation and Specific Heat of Water Vapour (I) and of Carbon Dioxide (II) at Very High Temperatures, Determined by the Explosion Method.** NIELS BJERRUM (*Zeitsch. physikal. Chem.*, 1912, 79, 513—536, 537—550).—I. The method adopted was that already used by Pier (*Abstr.*, 1908, ii, 352; 1909, ii, 542, 789), a correction being made for the loss of heat during the explosion (this vol., ii, 232). When hydrogen or nitrogen is added to electrolytic gas and the mixture exploded, the latter mixture gives smaller explosion pressures than the former, owing to the effect of the former gas in

diminishing the degree of dissociation of water vapour. If the thermal properties of nitrogen and hydrogen are the same under the conditions of the experiment, or if the slight differences compensate each other, the degree of dissociation of water vapour and the explosion temperatures can be calculated from the results. The thermodynamic agreement between the degrees of dissociation at different temperatures is better when it is assumed that the molecular heats of nitrogen and hydrogen are equal than on the assumption that the value for the former gas is 0.2 greater than for the latter.

In order to compare the dissociation of water vapour as determined at lower temperatures by Nernst and others with the present results up to 3000°, the specific heat of water vapour has been determined by the explosion method, hydrogen and argon respectively being added to electrolytic gas. Both series of experiments gave for the molecular heat the value of about 10.5 at 3000°. Finally, a complicated formula is deduced which gives the variation of the dissociation of water vapour with temperature; the observed and calculated results up to 3000° abs. are in good agreement. The degree of dissociation % up to 3000° abs. for 1 atmosphere pressure is as follows:

Temperature, abs.....	1705	2257	2642	2761	2834	2929
Dissociation % .....	0.108	1.79	4.3	6.6	9.8	11.1

In certain circumstances the membrane used in measuring the pressures was set in rapid vibration by the explosion.

II. The dissociation and specific heat of carbon dioxide at high temperatures were determined by the same method as for water vapour, and the results calculated on the same assumption as before. In this case no difficulties were met with owing to vibration of the membrane, as mixtures of carbon monoxide and oxygen inflame much less rapidly than electrolytic gas. The dissociation at a series of temperatures under 1 atmos. pressure is as follows:

Temperature, abs.....	1500	2640	2879	2945	3116
Dissociation % .....	0.04	21.0	51.7	64.7	76.1

The agreement of observed and calculated values at high temperatures is only moderate. G. S.

**Diffusion Phenomena.** RAPHAEL E. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 219—225).—When a glass plate is covered with a layer of gelatin containing sodium carbonate and litmus in solution and after solidification a drop of concentrated hydrochloric acid is added, a red circle is formed which spreads out at first, reaches a maximum at which it remains for some hours then slowly contracts in size and finally disappears. The diminution in the size of the red circle is due to the action of the reserves of alkali which slowly reach the zone by diffusion.

When a layer of gelatin containing sodium carbonate has solidified on a glass plate and a triangular section is cut out in the middle and filled with gelatin containing a little acid and litmus, the red colour again slowly spreads out, but instead of remaining triangular soon becomes circular. This is due to the fact that the reserves of acid

become exhausted most rapidly at the corners, thus allowing the alkali to push forward.

Analogous results are observed when a piece of jelly containing silver nitrate is immersed in a solution of potassium dichromate. Owing to the rapid exhaustion of the reserves of silver nitrate in the corners, the dichromate penetrates the jelly and causes a precipitate of silver chromate, whereas at other parts of the jelly the precipitate may occur only in the surrounding liquid. The bearing of these phenomena on reactions in the organism is discussed in detail. It is shown that differences of concentration in the surrounding liquid may cause a substance to be precipitated in one case in the colloidal system, in another case in the liquid in contact with it.

G. S.

**Principal Dates from the History of Osmotic Pressure and of the Osmotic Solution Theory.** PAUL WALDEN (*Bull. Acad. Sci. St. Pétersbourg*, 1912, 453—464).—Historical and polemical, Rosenstiehl's historical data (Abstr., 1911, ii, 588) being criticised.

T. H. P.

**Deformation of Jellies by Freezing.** RAPHAEL E. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 225—232. Compare Fischer, Abstr., 1909, ii, 545).—When gelatin gels are frozen, the changes of shape are not simply due to the displacement of the gelatin particles by ice crystals, but the mechanical work is done mainly by the drying gelatin. The crystals, however, sometimes localise the dehydration at definite points, thus leading to a special arrangement of the gelatin particles, to double refraction, and eventually to rupture and the formation of large pores. It is possible so to dry gelatin by cold that layers containing minute pores are formed, which may be used for filtration purposes. It is shown that there are many analogies between the phenomena just considered and the formation and arrangement of fibres in bones.

G. S.

**Electric Charges on Colloidal Particles.** NICOLA PAPPADA (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 242—248. Compare Abstr., 1911, ii, 1077).—A completely dialysed solution of a colloid differs in behaviour from an incompletely dialysed solution, and the author considers that when a colloid is dissolved in an electrolyte (for example, colloidal ferric hydroxide in ferric chloride solution), the colloid and electrolyte form a labile complex which is stable in the presence of excess of the electrolyte. As the latter is progressively removed by dialysis, the complexes become hydrolysed, forming true colloidal particles, which, it is suggested, are associated with the  $H^+$  or  $OH^-$  ions of water. The substance of the remainder of the paper, which deals with the mechanism of gelation and with the reciprocal coagulation of ferric hydroxide and silicic acid, has already been published (*loc. cit.*).

G. S.

**The Theory of Emulsification.** I. WILDER D. BANCROFT (*J. Physical Chem.*, 1912, 16, 177—233).—The paper consists mainly of extracts from the published work of Wo. Ostwald, Quincke, Donnan, Hillyer, Höber, and Freundlich.

Assuming that the drops in an emulsion are perfectly spherical and of uniform size, Ostwald deduces that any pair of non-miscible or partly miscible liquids will form two series of emulsions in which either dispersed phase may range up to 74.04% by volume. Pickering's emulsions containing 99% of kerosene as the dispersed phase prove that Ostwald's assumptions are not universally true, and the drops in an emulsion may be closer packed than he supposed. The author argues that two sets of emulsions are theoretically possible over the whole range of concentrations, although both sets have never been prepared for any one pair of pure liquids.

Probably a stable emulsion cannot be prepared from a pair of pure mobile liquids. A third substance is necessary as an "emulsifying agent." When an immediate emulsion is obtained on shaking oil with water or dilute alkali, the effect must be attributed to traces of free fatty acids in the oil.

The emulsifying agent must be a substance which lowers the surface tension of the dispersing phase and increases the viscosity of its surface film. The author does not commit himself to Höber's view, that the emulsifying agent in watery emulsions must be an "hydrophile colloid," and states that there is as yet no published theory connecting emulsification and foaming with the relative surface tensions of the pure liquids. R. J. C.

**The Alteration of the Chemical Equilibrium Point by the Energy of Motion.** FERDINAND RÖDER (*Biochem. Zeitsch.*, 1912, 40, 348—352).—The author calls attention to the fact that the influence of the energy of motion on chemical equilibrium has, so far, been but little studied, and considers that in systems with large capacity, such as exist in various biological processes, it may play an important part. He cites examples when the rate of action has been influenced by the motion of the system, including Engler and Frankenstein's researches on the peroxide of dimethylfulvene, and Metzger's observation on the destruction of pepsin by the agitation of the solution. He also cites the cases on geotropism, and the motion of the blood in the organism, which, he thinks, may influence the chemical equilibrium of the system  $\text{oxyhæmochrome} \rightleftharpoons \text{hæmochrome} + \text{oxygen}$ . S. B. S.

**Equilibrium in the Systems  $\text{CaX}_2\text{--MeOH--H}_2\text{O}$ .** S. CHUMANOFF (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 248—249). Compare this vol., ii, 349).—The phenomena observed when varying amounts of a solution of potassium hydroxide are added to an aqueous solution of calcium chloride, and when the reagents are mixed in the converse way, are described in tabular form. G. S.

**The System Water-Phenol-Hydrochloric Acid at 12°.** FRANZ A. H. SCHREINEMAKERS and J. L. M. VAN DER HORN VAN DER BOS (*Zeitsch. physikal. Chem.*, 1912, 79, 551—553).—The composition of the two layers in equilibrium at 12°, each containing water, phenol, and hydrochloric acid, and the composition of the solutions of the three components in equilibrium with solid phenol have been determined, and from the data thus available the equilibrium diagram of the

system has been constructed. Hydrochloric acid is much more soluble in the layer rich in water than in the layer rich in phenol. G. S.

**Velocity of Reactions between Gaseous Substances. False Equilibria.** E. BRINER (*J. Chim. phys.*, 1912, 10, 129—144. Compare Abstr., 1910, ii, 707).—The author has investigated the rates of synthesis of water and of sulphur trioxide and the rate of decomposition of nitrous oxide with a view to elucidating the disturbing influences which make these gaseous actions so erratic. The experiments lend support to the view that the surface of the containing vessel plays an important part in the chemical change, and that gaseous actions must therefore be regarded as occurring in heterogeneous systems.

The amount of water formed per day at 400° from a detonating mixture was 1.2% under 300 atm. pressure and 1.1% under 1 atm. pressure. The relatively large surface at the lower pressure almost compensated for the increased gaseous activity at the higher pressure.

Nitrous oxide at temperatures between 450° and 560° and pressures from 320 atm. to 570 atm. dissociates at a rate which undergoes a marked but irregular diminution in the early stages. In some cases the action almost ceased when about 20% of the nitrous oxide had been dissociated. In Hunter's experiments at a higher temperature (700°), the disturbing influence of the containing walls was not so marked (Abstr., 1905, ii, 805).

Mixtures of sulphur dioxide and oxygen, with and without platinised asbestos, were maintained at 211°, and the pressure (initially 600 mm.) was observed over a period of fifty-seven days. The velocity of the action diminished rapidly, and in the absence of the catalytic agent the action practically ceased at the end of thirty-seven days. The oxidation of carbon monoxide and the synthesis of hydrogen sulphide are reactions which may attain to a similar false equilibrium.

The view that all action ceases in these cases and the condition is a permanent one is incompatible with the kinetic hypothesis. According to the author's view the so-called "false equilibrium" is a temporary condition in which chemical change is retarded, because the containing walls have been rendered inactive by the condensation of the products of the change on them.

The effect of this surface condensation is more potent at high pressures where false equilibrium is most frequently observed. [The work of H. B. Baker is not alluded to.] R. J. C.

**Velocity of Reaction of Different Bases with Halogen-substituted Acids.** I. HJ. JOHANSSON (*Zeitsch. physikal. Chem.*, 1912, 79, 621—637. Compare Holmberg, this vol., ii, 443; Senter, Trans., 1907, 91, 460).—Mesodibromosuccinic acid is decomposed by barium hydroxide (mainly into bromide and bromomaleic acid) about ten times as quickly as by sodium hydroxide under equivalent conditions. The velocity coefficients, calculated for a bimolecular reaction, increase considerably as the reaction proceeds, and neutral salts with a common ion have an accelerating influence.

Dichlorosuccinic acid (m. p.  $210^{\circ}$ ) is decomposed by barium hydroxide five to six times as fast as by sodium hydroxide; the velocity coefficient in the first case is proportional to the square root, and with the sodium salt to the cube root of the cation concentration.

Monobromosuccinic acid is decomposed at approximately the same rate by barium hydroxide as by sodium hydroxide, and neutral salts accelerate the reaction. The ratio of the velocities of decomposition of monobromo- and monochloro-acetic acids by barium and by sodium hydroxide is about 5:3.

The phenomena are accounted for mainly on the assumption of catalytic acceleration by cations, advanced by Holmberg (*loc. cit.*).

G. S.

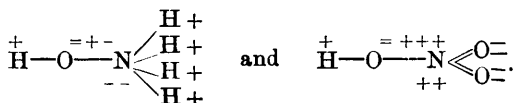
**Liquids Considered as Molecular Complexes.** PETRU BOGDAN (*Ann. Sci. Univ. Jassy*, 1912, 7, 139—164. Compare Abstr., 1906, ii, 274).—According to Stefan, the molecular diameter ( $d$ ) of a molecule can be calculated by means of the expression  $d = 2\gamma v/l$ , where  $\gamma$  is the surface-tension of the liquid,  $v$  is the molecular volume, and  $l$  the molecular latent heat of vaporisation. The author shows that in the case of various liquids, for example, methyl formate, ethyl acetate, carbon dioxide, etc., the values of  $2\gamma v/l$  decrease with rise in temperature. They do not, therefore, represent the molecular diameter, but rather the difference ( $c$ ) between the radius of the complex existing in the liquid and the radius of the molecule. The decrease with rise in temperature is then due to a breaking down of the complex, and if the law of this decrease is known, the value  $c$  at the critical point can be calculated.

Using the values of  $c$  so obtained, the author has been able to calculate superior limiting values for the molecular radius of various liquids at the critical temperature, the calculation being based on conceptions put forward by Drucker (Abstr., 1910, ii, 110).

The author further extends his theory to the calculation of the viscosity of certain liquids from a knowledge of the molecular radii, and to a discussion of the rules of Eötvös-Ramsay and of Longinescu.

T. S. P.

**Possible Explanation of Some Phenomena of Ionisation by the Electron Theory.** WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1912, 34, 663—664).—Although ammonium hydroxide and nitric acid both contain a hydroxyl group united directly to a nitrogen atom, the former yields hydroxyl and the latter hydrogen ions on ionisation. This fact is explained in accordance with the electron theory by the following formulæ:



In the case of ammonium hydroxide, the nitrogen atom with its three extra electrons (having gained four from the hydrogen atoms, but lost one to the oxygen atom) attracts the negative oxygen of the hydroxyl

but feebly, and the group can therefore easily separate by ionisation. In nitric acid, however, the nitrogen atom has lost five electrons and become strongly positive; it therefore holds the negative oxygen atom very firmly, but repels the positive hydrogen atom, thus enabling the latter to ionise readily.

Suggestions are also made with reference to the behaviour of sodium hydroxide and of hydrochloric acid. E. G.

**Critical Survey of Some Recent Applications of the Electron Conception of Valence.** HARRY SHIPLEY FRY (*J. Amer. Chem. Soc.*, 1912, 34, 664—673).—In accordance with the electron conception of valence, an atom or a univalent radicle may exert either a positive or a negative function. An element with a valence  $n$  may act in  $n+1$  different ways. Thus, it is shown that the quadrivalent carbon atom may function according to five different types, depending on whether its valencies are all positive, all negative, or some positive and some negative. These five types correspond with the successive stages of oxidation illustrated by the compounds methane, methyl alcohol, formaldehyde, formic acid, and carbon dioxide.

Falk's classification of the organic acids (*Abstr.*, 1911, ii, 711) is incomplete, since the direction of the valence which binds the  $\alpha$ -carbon atom to the carboxyl group is not taken into account. When this valence is considered, the theory demands eight classes of organic acids instead of only four as postulated by Falk. E. G.

**The Nature of Auxiliary Valencies. I. Metal Ammonias.** FRITZ EPHRAIM (*Ber.*, 1912, 45, 1322—1331).—The decomposition of molecular complexes, as, for example, hydrates, alcoholates, metal ammonias, etc., into their constituents is dependent on three factors, namely, pressure, temperature, and the so-called chemical affinity of the constituents, which are held together by auxiliary valencies. Assuming that the pressure is kept constant, the author puts forward the proposition that the temperature at which decomposition occurs is a measure of the energy of the auxiliary valencies, and proceeds to develop it by the following experimental evidence.

An examination of the temperature at which the hexamine chlorides of glucinum, nickel, cobalt, iron, copper, manganese, zinc, cadmium, and magnesium each has an ammonia pressure of 500 mm. shows that it decreases as the atomic volume of the metal increases, that is, the energy of the auxiliary valency is a function of the atomic volume of the central metal atom. A similar relation holds for the hexamine bromides, iodides, and sulphates. The atomic volume is not the only factor, however, since copper and iron, which have the same atomic volume, give hexamine chlorides possessing different dissociation temperatures. Glucinum, which has the least atomic volume, gives a hexamine chloride which is so stable that it decomposes before the dissociation pressure of 500 mm. is reached. Metals with an atomic volume greater than 14 do not give stable hexamine compounds at room temperature, although the chlorides of the alkaline earth metals give octamine compounds.

The influence of the atomic volume is all the less the greater the atomic volume. The expression  $\sqrt[3]{T} \cdot \sqrt[3]{v}$  is approximately constant for the compounds mentioned,  $T$  being the absolute temperature corresponding with a dissociation pressure of 500 mm., and  $v$  the atomic volume.

The anion has also an influence on the valency energy. It is found that the ratio of the absolute temperatures at which the hexammine chlorides and bromides have the same pressure is approximately constant, being independent of the central atom; for example,  $T_{\text{NiBr}_2} : T_{\text{NiCl}_2} = 1.073$ , and  $T_{\text{CoBr}_2} : T_{\text{CoCl}_2} = 1.086$ . This ratio is called the "tension modulus." Such a modulus also exists for the ratio  $\text{Cl/I}$ ,  $\text{Br/I}$ ,  $\text{SO}_4/\text{I}$ , etc., and varies between 1.08 and 1.10. The zinc hexa-ammonias form an exception.

When the absolute dissociation temperatures of, for example, the compounds  $\text{CdI}_2 \cdot 6\text{NH}_3$  and  $\text{CdBr}_2 \cdot 6\text{NH}_3$  are compared at a number of different pressures varying between 103 and 780 mm., it is found that the ratio  $T_{\text{iodide}} : T_{\text{bromide}}$  is a constant, 1.066, the extreme variations being respectively  $-0.001$  and  $+0.002$ . Also, when the absolute dissociation temperatures for pressures of 700 mm. and 200 mm. are compared for different compounds it is found that their ratio is constant and equal to 1.077. These results thus form a special case of the Ramsay-Young rule.

From the tension curves, the heat of formation ( $Q$ ) can be calculated by the expression  $Q = [(T_1 T_2) / (T_1 - T_2)] \log_e(p_2/p_1)$ , and Matignon (Abstr., 1899, ii, 273) has pointed out that for the same pressures the ratio  $Q/T$  is approximately constant, corresponding with Trouton's rule. The author finds this to be the case for the above compounds at a pressure of 500 mm., the value of the ratio varying between 0.030 and 0.036.

The various hexammine compounds investigated were prepared by treating the dehydrated salts with ammonia until no further increase in weight took place. The *hexammine* compounds of the following salts have not hitherto been described: glucinum chloride, magnesium chloride, magnesium iodide, cadmium bromide, zinc bromide, zinc iodide, ferrous bromide, manganese chloride, manganese bromide, and manganese iodide. Their properties are similar to those of the corresponding compounds which have been previously described. All the compounds are characterised by their low density.

The measurements of the ammonia pressures were made by heating the compound under investigation in a small flask with a narrow neck connected by lead tubing to a manometer. An oil-bath was used for heating, the temperature being regulated in a thermostat.

T. S. P.

**History of Alchemy.** EILHARD WIEDEMANN (*J. pr. Chem.*, 1912, [ii], 85, 391—392).—The author gives an extract from a manuscript of the India Office, from which it appears that the Arabian philosopher, Ibn Sinâ, recognised the possibility of the transmutation of metals.

F. B.

**A Combined Governor and Gauge for Maintaining a Regular Flow of Gas. A Thermostat with Delicate Adjustment and Long Range.** SYDNEY H. COLLINS (*Univ. Durham Phil. Soc.*, 1912, 4, 110—113).—Both these pieces of apparatus were used in the investigation of the production of hydrocyanic acid from linseed cake under digestive conditions (this vol., ii, 568). The governor and gauge in the course of 22 runs gave an average output of  $10.05 \pm 0.22$  litres of hydrogen per hour, when 10 litres per hour were required. The thermostat in over 200 trials gave an average of  $45.04^\circ \pm 0.10^\circ$  when the temperature required was  $45^\circ$ . Both are figured and described in the original. T. A. H.

**New Receiver for Vacuum Distillations.** ALADÁR GLASER (*Chem. Zeit.*, 1912, 36, 437).—The condenser opens in the usual way into a wide receiver fitted with four legs connecting with flasks to receive the various fractions. Just under the end of the condenser a funnel is supported by means of a glass rod passing through a rubber stopper in the top of the receiver. By turning the glass rod the funnel may be made to open into each of the flasks in succession, thus facilitating the collection of the various fractions. T. S. P.

**Modification of a Previously Described Experiment on the Migration of Ions.** E. E. CHANDLER (*J. Amer. Chem. Soc.*, 1912, 34, 662—663).—A lecture experiment has been described by Noyes and Blanchard (*Abstr.*, 1901, ii, 91) for illustrating the rates of migration of different ions. As the method has not proved quite satisfactory in certain respects, a modification has been devised which enables the experiment to be carried out in a simpler and more successful manner. E. G.

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### Inorganic Chemistry.

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**A Water-sealed Constant-pressure Hydrogen Gas Generator.** SYDNEY H. COLLINS (*Univ. Durham Phil. Soc.*, 1912, 4, 107—109).—The zinc is contained in an inverted glass cylinder and is held in position by a loose plug of copper wire. Two tubes pass to the top of the inverted cylinder, one for the delivery of dilute acid, the other for the exit of gas. The cylinder stands in a wide mouthed bottle, which serves as a receptacle for waste acid, which overflows into a trough in which the bottle stands. On the inverted cylinder is placed a wooden block surmounted by a Winchester quart bottle containing the acid, which is delivered on the zinc by a constant level siphon terminating in the acid delivery tube already referred to.

Rubber and cork pads are provided at required points to prevent breakage. The pressure at which the gas is delivered is determined by

the difference in levels of the liquids in the wide-mouthed bottle and the trough in which the latter stands, and can be adjusted by means of the constant level siphon. The apparatus is figured in the original. A mixture of mercuric chloride (three parts) with lime (one part), made into a paste, and then dried and powdered, was found to be a useful agent for removing the usual impurities in hydrogen. T. A. H.

**Preparation of Anhydrous Bromides.** MAURICE BARRE (*Bull. Soc. chim.*, 1912, [iv], 11, 433—440).—The author has applied Bourion's method for the preparation of chlorides (Abstr., 1907, ii, 690) from oxides, to the preparation of bromides, using sulphur bromide in place of sulphur chloride. The oxides begin to react at about 300° as a rule, but rapid formation of the bromide does not in general take place below 500°, and in some cases only at 700°. Oxides of the following metals give bromides under these conditions: lanthanum, cerium, cobalt, nickel, iron, chromium, aluminium, manganese, copper, tin, lead, zinc, cadmium, magnesium. Of the manganese oxides, the sesquioxide gave the best results. Litharge and red lead both yielded lead bromide. Thoria gave an oxybromide,  $\text{ThOBr}_2$ , and uranoso-uramic oxide gave uranyl bromide,  $\text{UO}_2\text{Br}_2$ . Stannous and stannic oxides both gave stannic bromide. Silica does not react even at 900°. T. A. H.

**Union of Iodine and Oxygen.** MARCEL GUICHARD (*Bull. Soc. chim.*, 1912, [iv], 11, 431—433. Compare Abstr., 1909, ii, 477).—It is shown on theoretical grounds that the direct combination of iodine and oxygen is not likely to be realised, and experimental trials in the generation of oxygen at high temperature and under high pressures in presence of iodine vapour showed that no combination occurred under these conditions. T. A. H.

**Preparation of Iodic Acid for the Estimation of Carbon Monoxide.** MAURICE NICLOUX (*Compt. rend.*, 1912, 154, 1166—1168. Compare Abstr., 1898, ii, 536).—Pure iodic acid suitable for use in the author's method for estimating carbon monoxide is obtained with a yield of 84.2% in the following manner: 70 c.c. of pure nitric acid (D 1.515—1.520) are heated to 70—73°, and 15 grams of iodine are then added in portions of about 0.5 gram, during thirty to forty-five minutes, with shaking. The temperature is slowly raised to 80—85° until nitrous fumes are no longer evolved. The crude product is dissolved in 50 c.c. of hot water, and the liquid boiled until milky in appearance. After dissolving the solid in 10 c.c. of water and evaporating to dryness, the residue is heated at 175—200° to remove nitric acid. The process is repeated using 7 c.c. of water. Finally the iodic acid is heated at 180—190° in a U-tube in a current of air. The product has the advantage of not liberating iodine when exposed to pure air. The yield may be increased to 92.8% by working up the nitric acid mother liquors. W. O. W.

**Atomic Weight of Fluorine.** D. J. MCADAM, jun., and EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1912, 34, 592—599).—Determinations

of the atomic weight of fluorine have been made by converting sodium fluoride into sodium chloride by passing dry hydrogen chloride over the salt at a temperature of about  $450^{\circ}$ . The sodium fluoride was carefully prepared by heating sodium hydrogen fluoride in a current of dry nitrogen, the temperature being gradually increased from  $300^{\circ}$  to  $500^{\circ}$ . The results of two experiments gave values for the atomic weight, 19.0176 and 19.0133 ( $\text{Na}=23.000$ ). It was found that on heating the salt in hydrogen chloride, a perfectly constant weight could not be obtained, and this may have been due to the presence in the interior of the granules of particles of sodium fluoride which could not be reached. In future work, the process will be modified so as to ensure the absolute removal of the whole of the fluorine.

E. G.

**Mixed Crystals of Sulphur and Tellurium.** EDOARDO BILLOWS (*Zeitsch. Kryst. Min.*, 1912, 50, 503—504; from *Riv. Min. Crist. Ital.*, 1909, 38, 91—94).—Red crystals of sulphur containing 0.56% Te were obtained by evaporating a carbon disulphide solution; they are orthorhombic with  $a:b:c=0.8132:1:1.8693$ . Koksharoff's values for native sulphur are  $0.8131:1:1.9034$ ; hence the presence of tellurium has the effect of shortening the vertical axis. These mixed crystals are analogous to the red sulphur from Japan containing 0.17% Te. When the carbon disulphide solution was completely evaporated, a rare form of reddish-yellow, monoclinic crystals was obtained, but the amount of tellurium in these was not determined; these crystals become transformed into orthorhombic sulphur. Similar orthorhombic and monoclinic crystals were also obtained from a warm solution of methylene bromide.

L. J. S.

**The Conversion of Sulphur Dioxide into Sulphuric Acid in Presence of Positive and Negative Catalysts.** A. E. LANGE (*Zeitsch. Ver. deut. Zuckerind.*, 1912, 555—559).—It is known that sulphuric acid is not formed in appreciable quantity when sulphur dioxide is passed into a sucrose solution. If a stream of sulphur dioxide mixed with air free from carbon dioxide is passed through a flask containing a copper or iron salt as a positive catalyst, and then through a second flask containing the same salt together with a 25% solution of sucrose, the formation of sulphuric acid, as determined by estimations of sulphurous acid and total acidity, is greatly diminished by the presence of sucrose. Unexplained irregularities are sometimes observed.

C. H. D.

**Theory of Sulphuric Acid Manufacture.** WILLIAM C. REYNOLDS and WILLIAM H. TAYLOR (*J. Soc. Chem. Ind.*, 1912, 31, 367—369).—After an experimental examination of the statements made by Raschig (compare Abstr., 1911, ii, 200, 272), the authors, for reasons which are fully explained, come to the following conclusions: (1) Nitrososulphonic acid has no existence. (2) The evolution of nitric oxide in Raschig's experiments is due to the action of nitrous acid on hydriodic acid (liberated from the potassium iodide which is present as an indicator). (3) That chamber crystals can exist in 60% sulphuric

acid. (4) That the "violet" acid can be formed only in solutions which contain chamber crystals. W. P. S.

**Comparative Investigations on the Oxidation of Nitrogen in the High Tension Flame.** MAX TAUSENT (*Zeitsch. Elektrochem.*, 1912, 18, 314—319).—Simple arrangements are described for the oxidation of nitrogen in the electric arc and the influence of varying conditions on the yield was determined. As anticipated, vertical arcs with alternating current were more stable, and gave a better yield of nitric acid than horizontal arcs under the same conditions. No originality is claimed for the results described in the paper. G. S.

**Preparation of Pure Nitric Oxide by an Electrolytic Method.** FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 244362).—Pure nitric oxide is readily obtained by the electrolysis of a mixture of nitric and nitrous acids with a current of 5—10 amperes at the ordinary temperature. The concentration of the nitric acid should be about 20—30%, whilst the amount of nitrous acid may vary from 1—1.9% according to the electrodes and other conditions employed. At higher temperatures nitrogen peroxide is simultaneously produced, whilst by varying the conditions other reduction products can also be obtained. F. M. G. M.

**Crystallographic Determination of Some New Compounds.** UGO PANICHI (*Zeitsch. Kryst. Min.*, 1912, 50, 495—496; from *Riv. Min. Crist. Ital.*, 1909, 36, 88—92).—Hydrazine perchlorate,  $2\text{N}_3\text{H}_5\text{ClO}_4 \cdot \text{H}_2\text{O}$ , prepared by R. Salvadori; monoclinic,  $a : b : c = 1.1572 : 1 : 2.0441$ ;  $\beta = 99^\circ 12'$ .

*l*- $\alpha$ -Aminophenylacetic acid *d*-camphorsulphonate,  $\text{C}_{18}\text{H}_{25}\text{O}_6 \cdot \text{NS}$ , prepared by M. Betti and M. Mayer (*Abstr.*, 1908, i, 639); orthorhombic,  $a : b : c = 0.4527 : 1 : 1.1333$ . L. J. S.

**Comparative Experiments on Certain Methods of Preparing Perborates.** E. BOSSHARD and K. ZWICKY (*Zeitsch. angew. Chem.*, 1912, 25, 938—943. Compare von Girssewald, *Abstr.*, 1909, ii, 312).—The authors have studied the methods of preparing perborates, which have been patented by von Girssewald (D.R.-P. 204279), Deutsche Gold und Silber-scheideanstalt (compare *Abstr.*, 1908, ii, 689), L. Blumer (D.R.-P. Anm. 49641), Jaubert (D.R.-P. 193559), and by Stolle and Kopke (French Pat. 384967), determining the yield and recovery of active oxygen employed in the perborate obtained by the several methods.

It is found that the loss of "active" oxygen is smallest in the methods of Blumer and of Stolle and Kopke. This loss is no doubt to be attributed to the unavoidable production of heat when the sodium peroxide is added to the borate solution; attempts to obtain better results by using the hydrate of sodium peroxide, however, were not successful. W. H. G.

**Devitrification of Silica Glass.** SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1912, A, 86, 406—408).—When a perfectly clear and transparent silica tube was heated at  $1300^\circ$  for twenty hours,

devitrification occurred, and air was found to have leaked through the walls of the previously exhausted tube. Further observations showed that leakage of air through the devitrified silica occurs at the ordinary temperature. Micro-photographs of the surface of the devitrified material are given, which exhibit hexagonal cell structure. A similar appearance was presented by a silica dish after being employed for the evaporation of a solution of radium bromide.

H. M. D.

**Melting Point of Silicates.** EMIL DITTLER (*Zeitsch. Elektrochem.*, 1912, 18, 281—282); ROBERT MARC (*ibid.*, 282).—Polemical. Dittler states that silicates do not melt sharply within  $1^\circ$ , but show a pronounced melting-point interval. Marc replies that the melting points of silicates given by Dittler differ considerably from those given by Day, and the latter investigator has shown that a definite silicate melts within a range of one or a very few degrees.

G. S.

**Development of Heat by a Mass Separated from Iron, Containing Graphite, Silicon, and Phosphorus.** THEO GRZESCHIK (*Chem. Zeit.*, 1912, 36, 505).—A piece of cast iron was attacked for fifty hours with dilute hydrochloric acid (1:3). After washing and drying, the outer spongy layer was scraped off, and when 7—10 grams of the mass was packed round the bulb of a thermometer, a rise of temperature of  $100$ — $120^\circ$  was observed. Fresh particles scraped off and added to the hot mass burnt with incandescence. If left attached to the iron, the mass lost its power of heating when kept in air, but preserved it if kept under water. The mass was much richer in impurities than the original iron:

	Total C.	Graphite.	Si.	Mn.	P.	S.
Original iron .....	3.51	—	2.39	0.63	0.78	0.08
Mass dried at $110^\circ$ ...	14.15	12.24	8.98	0.88	2.71	0.116

The product after incandescence is magnetic, and is a mixture of oxides.

C. H. D.

**The Proportion of Potassium Chloride Contained in Potassium Chlorate and its Estimation by the Nephelometer; Atomic Weight of Silver.** PHILIPPE A. GUYE (*J. Chim. Phys.*, 1912, 10, 145—153. Compare Stähler and Meyer, *Abstr.*, 1911, ii, 881).—Guye and Gazarian have stated that potassium chlorate purified according to Stas' method by recrystallisation still contains 0.027% of potassium chloride. Stähler and Meyer in their recent work on the ratio  $\text{KClO}_3 : \text{KCl}$  claim to have reduced the potassium chloride to 0.000053% by centrifugalising the crystals of chlorate.

The optical method of estimating chloride used by Stähler and Meyer, depending on the opalescence produced with silver nitrate, is open to criticism on the ground that the particles of silver chloride may be of an unusual size and possess an abnormal solubility when precipitated in presence of excess of potassium chlorate. The method used by Guye and Gazarian, namely, titration with silver nitrate, using

chromate as an indicator, is not sufficiently delicate for the estimation of minute quantities, but the method devised by Dutoit and von Weise (Abstr., 1911, ii, 1130), making use of the contact potential of the solution instead of potassium chromate as an indicator, should give trustworthy results.

The author finds by this method that recrystallised potassium chlorate contains roughly 0.001% of chloride, and he holds that, in view of the care taken by Stähler and Meyer in purifying their chlorate, the proportion of chloride in it did not exceed the amount stated by them.

The ratio  $\text{KCl}:\text{KClO}_3=0.60834$  found by Stähler and Meyer is less than the earlier results of Stas, Marignac, Gerhardt, Pérouze and others, approximating most closely to the 0.60839 found by Marignac.

When combined with the ratio  $\text{KCl}:\text{Ag}=0.691073$  found by Richards and Stähler it gives as the atomic weight of silver  $\text{Ag}=107.88$ , a value in accord with other recent estimates.

The work of Stähler and Meyer is of importance as bringing the earlier methods of estimating the atomic weight of silver into agreement with modern work.

R. J. C.

**The Electric Pressure Furnace. IV. Alkali Peroxides from Alkali Hydroxides and Oxygen.** FRANZ FISCHER and HANS PLOETZE (*Zeitsch. anorg. Chem.*, 1912, 75, 30—40).—Potassium hydroxide, heated to  $375^\circ$  in oxygen in a pressure furnace (this vol., ii, 530), yields a coloured product which evolves oxygen on contact with water. The product obtained by heating dry potassium hydroxide in a silver boat under 100 atmospheres pressure is transferred to a special form of closed apparatus in which the volume of oxygen evolved on decomposition with cold water is measured. The potassium is then estimated in the solution by titration with acid. The maximum yield of potassium peroxide obtained is 70%. The yield under 96 atmospheres pressure in air is equal to that under 20 atmospheres pressure in oxygen, the partial pressure of the oxygen being about the same in both cases. Nitrogen compounds are not formed when air is used.

Rubidium and caesium hydroxides give a still larger yield of peroxide, amounting to 95% in the case of caesium at  $350^\circ$ . The products are dark green in colour. Lithium and sodium hydroxides give entirely negative results.

C. H. D

**Some Compounds of Nitrates and Sulphates.** FRANS A. H. SCHREINEMAKERS and A. MASSINK (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 14, 1042—1044. Compare Schreinemakers and Hoenen, Abstr., 1909, ii, 236).—The formation of double salts between the nitrates and sulphates of lithium, sodium, and potassium have been investigated.

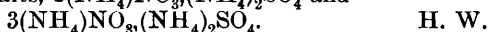
The solid phase in contact with the saturated aqueous solution of lithium nitrate and lithium sulphate at  $35^\circ$  contains  $\text{LiNO}_3$ ,  $\text{Li}_2\text{SO}_4$ ,  $\text{LiNO}_3, \frac{1}{2}\text{H}_2\text{O}$ ,  $\text{Li}_2\text{SO}_4, \text{H}_2\text{O}$ , and the double salts  $\text{LiNO}_3, 9\text{Li}_2\text{SO}_4, 27\text{H}_2\text{O}$  and  $\text{LiNO}_3, 11\text{Li}_2\text{SO}_4, 17\text{H}_2\text{O}$ .

In the system  $\text{NaNO}_3\text{--Na}_2\text{SO}_4\text{--H}_2\text{O}$  at  $20^\circ$ , besides  $\text{NaNO}_3$  and

$\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , the double salt  $\text{NaNO}_3 \cdot \text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$  occurs as a solid phase, whilst at  $35^\circ$ , in addition to the two anhydrous salts  $\text{NaNO}_3$  and  $\text{Na}_2\text{SO}_4$ , the double salts  $3\text{NaNO}_3 \cdot 2\text{Na}_2\text{SO}_4$  and  $3\text{NaNO}_3 \cdot 4\text{Na}_2\text{SO}_4$  are found.

As solid phase of the system  $\text{KNO}_3\text{--K}_2\text{SO}_4\text{--H}_2\text{O}$  at  $35^\circ$ , only the anhydrous components  $\text{KNO}_3$  and  $\text{K}_2\text{SO}_4$  have been found.

In the system  $\text{NH}_4\text{NO}_3\text{--}(\text{NH}_4)_2\text{SO}_4\text{--H}_2\text{O}$ , besides the two anhydrous salts,  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ , there occur also at  $0^\circ$ ,  $30^\circ$ , and  $70^\circ$  the two anhydrous double salts,  $2(\text{NH}_4)\text{NO}_3 \cdot (\text{NH}_4)_2\text{SO}_4$  and

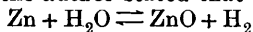


**Double Salts of Rubidium and Cæsium Chlorides with Ferrous Chloride.** ERNST WILKE-DÖRFURT and GERHARD HEYNE (*Ber.*, 1912, 45, 1012—1015).—The following double salts have been obtained:  $2\text{RbCl} \cdot \text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ : clear, monoclinic crystals, efflorescing in the air, owing to oxidation;  $D^{23}$  2.850.  $2\text{CsCl} \cdot \text{FeCl}_2 \cdot 2\text{H}_2\text{O}$ : colourless, monoclinic, efflorescent crystals;  $D^{20}$  3.275.  $\text{RbCl} \cdot \text{FeCl}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{CsCl} \cdot \text{FeCl}_2 \cdot 2\text{H}_2\text{O}$  both form pale green, efflorescent crystals; the former has  $D^{20}$  2.711, and the later  $D^{17}$  2.907. T. S. P.

**Portland Cement Clinker. The Hypothetical Compound**  $8\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ . GEORGE A. RANKIN and FRED E. WRIGHT (*Zeitsch. anorg. Chem.*, 1912, 75, 63—67).—The compound  $3\text{CaO} \cdot \text{SiO}_2$ , although not observed by Day and Shepherd (Abstr., 1906, ii, 770), was detected by Shepherd and Rankin (Abstr., 1911, ii, 725) in the binary system as well as in the ternary system lime—silica—alumina. Jänecke (this vol., ii, 159) has described a ternary compound,  $8\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ . It is now shown that the supposed compound is really a mixture, containing at the ordinary temperature  $3\text{CaO} \cdot \text{SiO}_2$ ,  $2\text{CaO} \cdot \text{SiO}_2$ , and  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ . The same compounds are recognised in mixtures of this composition quenched in mercury from  $1391^\circ$ , whilst quenching from  $1432^\circ$  gives glass and the di- and tri-calcium silicates, and quenching from  $1475^\circ$  gives only glass and the trisilicate. Jänecke's error is explained by the liability of these mixtures to undercooling, and by the nearly identical refractive indices of the three compounds present. C. H. D.

**The Electric Pressure Furnace. II. Strontium Peroxide from Strontium Oxide and Oxygen.** FRANZ FISCHER and HANS PLOETZE (*Zeitsch. anorg. Chem.*, 1912, 75, 10—14).—When strontium oxide is heated in oxygen at 100 atmospheres pressure in the pressure furnace (this vol., ii, 530), strontium peroxide is formed, the maximum yield being at  $410^\circ$ , when the product contains 16%  $\text{SrO}_2$ . It has not been found possible to obtain a product which gives a peroxide reaction with titanous acid by heating lime in oxygen at different temperatures under 100 atmospheres pressure, even when the lime is previously heated with other substances as catalytic agents. C. H. D.

**Reduction of Zinc Oxide by Hydrogen.** CAMILLE GILLET (*Bull. Soc. Chim. Belg.*, 1912, 26, 106—107).—In a previous paper (Abstr., 1910, ii, 381) the author stated that the action:



is reversible. Doubt having been cast on this statement, experimental evidence has been obtained showing that zinc oxide is completely reduced on heating it in a stream of dry hydrogen. W. G.

**The Structure of Ternary Alloys.** GILBERT H. GULLIVER (*Proc. Roy. Soc. Edin.*, 1912, 32, 36—39).—An examination of micro-sections of alloys of lead, tin, and bismuth, containing primary crystals of bismuth, shows the presence of skeletal crystals of tin in the fringe of eutectic surrounding each crystal of bismuth. During the solidification of a binary eutectic in a ternary alloy, the temperature is not constant, and liquid is always present. The particles are therefore free to migrate, and instead of forming a fine-grained eutectic, the crystals grow and have the same appearance as primary crystals. Similarly, in an alloy of 66% of lead, 24% of antimony, and 10% of copper, primary forms of both antimony and the compound  $\text{Cu}_2\text{Sb}$  are observed.

C. H. D.

**The Electric Pressure Furnace. III. Preparation of Lead Peroxide from Lead Oxide, and the Dark Brown Compound,  $\text{Pb}_5\text{O}_8$ .** FRANZ FISCHER and HANS PLOETZE (*Zeitsch. anorg. Chem.*, 1912, 75, 15—29).—Lead peroxide has not been obtained by directly heating lead oxide in air. When lead oxide is heated in oxygen in a pressure furnace (this vol., ii, 530) oxidation proceeds until a maximum of 4.2% of active oxygen, estimated by heating with a solution of oxalic acid and titrating with permanganate, is obtained. This corresponds with the formula  $\text{Pb}_5\text{O}_8$ . The product is dark brown, resembling lead peroxide. The maximum yield is obtained at 100 atmospheres pressure between  $400^\circ$  and  $450^\circ$ , and the same product results when lead carbonate or lead peroxide is used as the starting-point.

The new oxide may be regarded as lead pyroplumbate,  $\text{Pb}_2(\text{Pb}_3\text{O}_8)$ , red lead being lead orthoplumbate, and the oxide  $\text{Pb}_2\text{O}_3$ , lead metaplumbate.

A mixture of lead peroxide and dry potassium hydroxide, when heated in oxygen under pressure at  $375^\circ$ , yields a product which evolves oxygen on treatment with water. Other catalytic agents do not raise the percentage of active oxygen above 4.2. C. H. D.

**The Effect of Organic and Inorganic "Addition Agents" on the Electro-deposition of Copper from Electrolytes Containing Arsenic.** CHING YU WEN and EDWARD F. KERN (*Trans. Amer. Electrochem. Soc.*, 1911, 20, 121—176; Summarised, *Chem. News*, 1912, 105, 218—219).—The anodes used contained arsenic and antimony, and were prepared from copper-arsenic and copper-antimony alloys which had been specially made for these experiments. The electrolyte used contained 15% of copper sulphate pentahydrate, 10% of free sulphuric acid, and percentages of arsenic (present as arsenic acid) varying from 1.5 to 8%. The current density used in all the experiments was 40 amperes per sq. foot.

With electrolytes containing no "addition agents," much arsenic

and antimony were deposited with the copper, even when the electrolytes contained 1.5% of arsenic; with 2—3% of arsenic, dendrite "trees" were formed. At temperatures between 50° and 60°, and with more than 6% of arsenic, the arsenic acid appeared to act as an addition agent, preventing, to some extent, the deposition of impurities (arsenic and antimony) and the formation of trees; at temperatures below 40°, 8% of arsenic was required for the same effect.

Hydrochloric acid, copper chloride, aluminium chloride, sodium chloride, sodium sulphate, sodium nitrate, sodium chlorate, sodium borate, and aluminium sulphate, when present in small amounts, each cause a distinct improvement of the deposited copper, both chemically and physically. The best and most effective of these is sodium chloride; hydrochloric acid, cupric chloride and cuprous chloride being effective to a slightly less degree.

The results appear to show that the salts of those metals which stand far higher in the potential series than copper are generally satisfactory addition-agents. An excess of chloridion in the electrolyte causes the deposit to become brittle and less pure; the amount of chlorine present as chloride should not exceed 0.01%, and should be present preferably as sodium chloride.

Temperature plays an important part; at higher temperatures the ductility of the copper is increased, and the potential between the electrodes decreases. Sodium sulphate is the more effective as an addition agent the higher the temperature.

Gelatin, glue, and tannin are satisfactory organic addition-agents. At the beginning of the electrolysis the presence of either gelatin or glue causes the formation of small, fern-like "trees," but after a time the formation of these trees ceases, and the deposits become smooth and ductile. Peptone exerts a detrimental influence on the deposits.

The deposits of copper obtained from electrolytes containing both organic and inorganic addition-agents were all satisfactory, particularly when the combinations gelatin and sodium chloride, glue and sodium chloride, or glue and cuprous or cuprous chloride were used; the first-mentioned combination gives the best results.

The authors finally develop a theory to explain the beneficial effects of the sodium and chloride ions. The paper is illustrated by photographs of all the copper deposits, and full analytical details are given.

T. S. P.

**The Preparation and Properties of Basic Copper Nitrate and the Hydrates of Copper Nitrate.** ALEXANDER C. CUMMING and ALEXANDER GEMMELL (*Proc. Roy. Soc. Edin.*, 1912, 32, 4—11). —The trihydrate of copper nitrate is best obtained by dissolving copper oxide in concentrated nitric acid, recrystallising from hot concentrated nitric acid, and drying on a porous tile over potassium hydroxide. The insoluble, green basic nitrate described by Graham has not been obtained by the use of concentrated acid. If the acid is distilled from sulphuric acid in a current of carbon dioxide, it reacts with copper oxide at 70—75° with evolution of oxygen and nitrogen peroxide according to the equation:  $\text{CuO} + 6\text{HNO}_3 = \text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O} +$

$4\text{NO}_2 + \text{O}_2$ . Liquid or solid nitrogen pentoxide is without action on copper oxide.

Copper nitrate hexahydrate readily loses water in a vacuum over phosphoric oxide, leaving the trihydrate. No nitrogen compound is lost at this stage. After some weeks, the trihydrate loses nitrogen oxides, and the residue is a basic nitrate, but the reaction is incomplete even after seven months. The compound  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$  is prepared by heating the trihydrate to  $100^\circ$ , or by boiling a concentrated solution of copper nitrate with copper oxide. This appears to be the only basic nitrate of copper.

The transition temperature between copper nitrate hexahydrate and trihydrate is found by the dilatometric method to be  $24.66^\circ$  (corr.), and by the thermometric method to be  $24.65^\circ$  (corr.).

C. H. D.

**Theory of the Mercury Ammonia Compounds.** EDWARD C. FRANKLIN (*Amer. Chem. J.*, 1912, 47, 361—397).—In earlier papers (Abstr., 1905, ii, 582; 1907, ii, 264; this vol., ii, 451) it has been shown that the mercury ammonia compounds may be arranged in three classes: (1) normal mercuric salts with ammonia of crystallisation, comprising compounds of the type of the fusible white precipitate; (2) ammonobasic mercuric salts, including those of the type of the infusible white precipitate and Nessler's precipitate, and (3) mixed hydrobasic ammonobasic mercuric salts, represented by Millon's base. This scheme of classification is now discussed in detail.

It is shown that all other suggestions which have been made with reference to the constitution of these compounds are inadequate, and arguments are adduced to establish the validity of the author's theory.

E. G.

**Cerium-Aluminium Alloys.** RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1912, 75, 41—57).—Cerium and aluminium may be melted together at  $1100^\circ$ , when combination occurs and the temperature rises to  $1600$ — $1700^\circ$ . Repeated re-melting is necessary in order to obtain a homogeneous mixture. The development of heat is a maximum at the composition  $\text{CeAl}_4$ . Alloys rich in aluminium are fused in carbon tubes, and the remainder in porcelain tubes, which are very little attacked at  $1100^\circ$ . Many of the thermal changes in the system are indistinct, and the diagram has been completed from microscopical observations.

The freezing-point curve has two maxima, at  $614^\circ$ , corresponding with the compound  $\text{Ce}_3\text{Al}$ , and at  $1460^\circ$ , corresponding with  $\text{CeAl}_2$ . There are also breaks at  $595^\circ$ ,  $780^\circ$ , and  $1250^\circ$ , corresponding with the formation of the compounds  $\text{Ce}_2\text{Al}$ ,  $\text{CeAl}$ , and  $\text{CeAl}_3$ , respectively. The last compound undergoes a transformation at  $1005^\circ$ . There are three eutectic points, and solid solutions are not formed.

The alloys, with the exception of those containing more than 75 atomic % Ce, are stable towards air and water. The compound  $\text{CeAl}_2$  is hardly attacked by concentrated hydrochloric, nitric, or sulphuric acid, but burns vigorously when heated in a Bunsen flame. Only the alloys richest in cerium give sparks when filed. The maximum hardness, 6, is given by the compound  $\text{CeAl}_2$ .

The compound  $\text{CeAl}$  forms characteristic lozenge-shaped crystals, whilst  $\text{CeAl}_2$  forms skeletons, and  $\text{CeAl}_4$ , large prisms. Alloys containing carbon are less stable, and exhibit an altered structure.

C. H. D.

**Action of Mercury and its Salts on Aluminium.** PAUL NICOLARDOT (*Bull. Soc. chim.*, 1912, [iv], 11, 410—413).—Kohn-Abrest (Abstr., 1910, ii, 506) has shown that aluminium foil is scarcely affected by solutions of mercuric chloride of less than 0.01% strength, but that the action increases as the concentration of the solution in mercuric chloride is increased. The author finds that moderately pure aluminium (99.2%) is more sensitive than this, and that hydrogen is produced when such material is immersed in mercuric chloride solution of 0.001% strength, and that if the foil is carefully cleaned, action is perceptible in still weaker solutions. Aluminium alloyed with 3% of copper is not attacked. Aluminium foil painted with a solution (0.1%) of mercuric chloride develops white filaments on its surface, whilst an aluminium-copper alloy remains apparently unaffected, although the surface, examined microscopically, shows slight change. In this action of mercuric chloride on aluminium, the latter is converted into alumina, whilst any alkali or alkaline earth metals present as impurities pass into solution and may be estimated in the latter.

T. A. H.

**Passivity of Iron.** FR. FLADE and HANS KOCH (*Zeitsch. Elektrochem.*, 1911, 18, 335—338).—The two current views as to the nature of the passivity of iron are: (1) the oxygen hypothesis, according to which pure iron is active and the passivity is due in some way to the presence of oxygen; (2) the hydrogen hypothesis, according to which pure iron is passive and the activity is due to the presence of hydrogen (compare Grave, Abstr., 1911, ii, 896). A decision between these alternatives seems possible: (a) by strongly heating an active specimen of iron in a vacuum, which must remove all the hydrogen; (b) by heating a passive electrode in a reducing gas, which will remove oxygen, but not affect hydrogen. Experiments by the first method showed that the electrode remained active in spite of the removal of the hydrogen, which supports the oxygen hypothesis. The second criterion did not lead to so conclusive results, since a passive electrode remained passive and an active electrode became passive on heating in carbon monoxide. The last result can be interpreted in terms of the oxygen hypothesis on the assumptions that in the heated gas there is an equilibrium between carbon, oxygen, and carbon monoxide and dioxide, and that even in such small concentration oxygen exerts a polarising action.

G. S.

**Corrosion of Steel in Water.** G. J. BURROWS and CHARLES E. FAWSITT (*J. Roy. Soc. New South Wales*, 1912, 45, 67—75).—The authors believe that the first stage in the process of rusting is the solution, to a limited extent, of iron in water, with the formation of ferrous ions. The hydrogen so produced, in the absence of free oxygen, polarises the iron surface; the function of oxygen is then the

removal of the layer of polarising hydrogen. If this is so, contact with a more electronegative metal, like platinum, should increase the velocity of rusting. Experiments made to test this, using uniform steel strips fully immersed in unstirred distilled water, showed that such strips when connected with platinum rusted more rapidly than in ordinary circumstances. The steel used had the composition: C, 0.35%; Mn, 0.61%; P, 0.06%; Si, 0.01% and S, 0.01%.

Experiments to test the influence of the composition of steel on the velocity of rusting in water containing 2.64 grams of sodium hydrogen carbonate, 0.113 gram of magnesium sulphate, and 0.166 gram of sodium chloride per litre gave irregular results, from which few exact conclusions could be drawn. It was noticeable, however, that the initial rate of corrosion is very different from the rate which sets in after a few weeks, and that a steel containing 0.9–1% of carbon rusts to a lesser extent than steels containing a smaller percentage of carbon.

Magnetisation has no noticeable effect on the corrosion of a steel of the composition given in the first paragraph.

Experiments with Woodlands Bore water, containing 0.03% of total solids, chiefly sodium hydrogen carbonate, and Coonamble No. 2 Bore water, containing 0.04% total solids, chiefly calcium and sodium hydrogen carbonates, showed (1) that they were not noticeably more corrosive than distilled water; (2) that moderate stirring has an accelerative effect on the rusting process, and (3) that the initial rate of corrosion does not stand in any simple relation to the rate which sets in after some time has elapsed. Distilled water gave a uniform corrosion, whereas the bore water corroded the steel in patches.

In discussing the work of Heyn and Bauer on corrosion, the authors state that the accelerative effect of salts on corrosion is explained by the greater conducting power of the solution, and that the decrease in the velocity of rusting with higher concentrations is probably due to the decreased solubility of oxygen in the solution.

The water from Coonamble No. 2 bore processes a radioactivity corresponding, on Boltwood's scale, with an initial activity of  $90 \times 10^{-4}$  grams of uranium per litre of water. The activity is due to radium emanation. The addition of radioactive salts to water did not affect the rate of corrosion of steel.

T. S. P.

**The Influence of Carbon and Other Elements on the Corrosion of Steel.** JOHN O. ARNOLD, WILLIAM E. S. TURNER, W. PALMER WYNNE, A. MCWILLIAM, C. CHAPPELL, and F. HODSON (*Brit. Assoc. Report*, 1911, 83–91).—Experiments with pure carbon steels show that the corrosion by sea-water of rolled or annealed specimens increases with the carbon-content up to 0.89%, diminishing with the appearance of free cementite. In hardened and tempered specimens the corrosion increases continuously, without showing any maximum. The minimum corrosion is shown by steels containing laminated pearlite. The rate of attack by 1% acid solutions is a maximum at 0.22% C and a minimum at 0.30–0.40% for annealed specimens, whilst

hardened specimens show a rapid increase in the higher percentages of carbon. The curves of solution pressure in acids show two maxima.

C. H. D.

**Chromyl Chloride I.** ENRIQUE MOLES and L. GÓMEZ (*Anal. Fis. Quim.*, 1912, 10, 43—64).—Pure chromyl chloride was prepared by the action of fuming sulphuric acid on a mixture of potassium dichromate and sodium chloride, and repeated fractionation after agitation with mercury. The boiling point at 760 mm. is  $116.63^\circ$ , and those observed at various pressures agree well with the figures calculated by means of Cauchy's formula. The compound has m. p.  $-96.5 \pm 0.5^\circ$ , and  $D_4^{47}$  2.0528—2.0515,  $D_4^i$  1.9591—1.9582, and  $D_4^{25}$  1.9124—1.9113. The vapour is not dissociated at  $181^\circ$ . The molecular magnitude is normal in phosphoryl chloride, and in glacial acetic acid there is association, whilst dilute solutions in nitrobenzene and ethylene dibromide show dissociation passing on increasing concentration of the solute into association.

G. D. L.

**Crystallographic Constants and Isomorphous Relations of the Double Chromates of the Alkalis and Magnesium.** ALFRED E. H. TUTTON and MARY W. PORTER (*Min. Mag.*, 1912, 16, 169—196).—Detailed morphological and optical determinations were made for ammonium magnesium chromate ( $D_4^{20}$  1.832.  $a:b:c = 0.7517:1:0.4924$ ;  $\beta = 106^\circ 7'$ ), rubidium magnesium chromate ( $D_4^{20}$  2.466.  $a:b:c = 0.7526:1:0.4953$ ;  $\beta = 104^\circ 49'$ ), and caesium magnesium chromate, ( $D_4^{20}$  2.747.  $a:b:c = 0.7431:1:0.4888$ ;  $\beta = 106^\circ 4'$ ). These three salts belong to the isomorphous series,  $R'_2M''[(S,Se,Cr)O_4]_2 \cdot 6H_2O$ . The caesium salt is more stable than the rubidium salt, whilst the corresponding potassium salt could not be prepared. The ammonium salt stands outside the eutropic set, including the two former. The chromates, although isomorphous with the corresponding sulphates and selenates, do not fall into the same eutropic set, since the series shows no progression in characters with the atomic weights.

L. J. S.

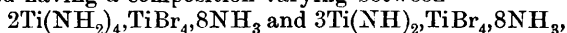
**Isomorphism of Complex Molybdates of the Rare Earths.** EDOARDO BILLOWS (*Zeitsch. Kryst. Min.*, 1912, 50, 500—503; from *Riv. Min. Crist. Ital.*, 1909, 38, 82—90).—The salts examined were prepared by G. A. Barbieri (Abstr., 1908, ii, 595), and have the general formula  $(NH_4)_6R_2Mo_{14}O_{28} \cdot 24H_2O$ , where  $R = Ce, La, (Ce, La), Nd, Pr$ , and  $Sa$ . They are all triclinic and perfectly isomorphous.

L. J. S.

**The Melting Point of Tungsten and Molybdenum.** MARCELLO VON PIRANI and ALFRED R. MEYER (*Ber. Deut. physikal. Ges.*, 1912, 14, 426—428. Compare Abstr., 1911, ii, 899).—The melting point of tungsten has been determined in four different ways involving optical and electrical measurements, the mean value obtained being  $3100^\circ \pm 60^\circ$ . The melting point of molybdenum, determined by optical measurements, was found to be  $2450^\circ \pm 30^\circ$ .

H. M. D.

**New Titanium Compounds. Titanium Nitrides.** OTTO RUFF and OSKAR TREIDEL (*Ber.*, 1912, 45, 1364—1373. Compare Abstr., 1908, ii, 700; 1909, ii, 406).—When the compound of titanium tetrabromide with ammonia,  $\text{TiBr}_4 \cdot 8\text{NH}_3$ , is washed with liquid ammonia (compare Abstr., 1908, ii, 700), an orange-coloured, insoluble bromide is obtained having a composition varying between



according to the duration of the washing. The attempt to remove the bromine from this substance by treatment with a solution of the equivalent amount of potassium amide in liquid ammonia led to the formation of a mixture containing about 20% of the original bromide, 10% of *potassium hydrogen titanium di-imide*,  $\text{Ti}(\text{NH})\text{NK}$ , and 70% of a *titanic nitride*,  $\text{Ti}_3\text{N}_4$ , which must be distinguished from titanous nitride,  $\text{TiN}$ . In contradistinction to titanous nitride, the titanic compound is decomposed by water, hydrated titanium dioxide and ammonia being formed. It has a brown colour, and decomposes on heating into titanous nitride and nitrogen. It was not obtained pure.

When the potassium amide is used in excess, potassium hydrogen titanium di-imide is obtained in a fairly pure condition as a brownish-red salt. On exposure to the air, it immediately takes fire, with the formation of potassium titanate and potassium oxide. Titanium di-imide possesses amphoteric properties, since the reaction products of potassium hydrogen titanium di-imide with potassium iodide or ammonium sulphide are apparently the hydrogen iodide and hydrogen sulphide salts respectively of titanium di-imide. T. S. P.

**The Volatilisation of Vanadic Acid by means of Hydrofluoric Acid.** WILHELM MANCHOT (*Ber.*, 1912, 45, 1154).—A claim for priority over Prandtl and Manz (Abstr., 1911, ii, 990), based on the author's work with H. Fischer (Abstr., 1908, ii, 46).

T. S. P.

**The Action of Calcium Fluoride on Vanadium Pentoxide.** WILHELM PRANDTL and HERMANN MANZ (*Ber.*, 1912, 45, 1343—1344).—A reply to Manchot (preceding abstract), in which the authors maintain that their observation is new, and that volatile vanadium oxyfluorides are formed when a dry mixture of calcium fluoride and vanadium pentoxide is heated. The observations made by Manchot and Fischer (Abstr., 1908, ii, 46) were not new, having been made as far back as 1876 by Guyard. T. S. P.

**Solubility of Sodium Metavanadate.** D. J. McADAM, jun., and C. A. PIERLE (*J. Amer. Chem. Soc.*, 1912, 34, 604—609).—During a study of the atomic weight of vanadium (McAdam, Abstr., 1911, ii, 117), it was observed that on recrystallising sodium metavanadate the crystals obtained seemed to vary considerably in solubility and appearance. A study has therefore been made of the solubility of the salt.

A method is described for the preparation of pure sodium metavanadate. The solubility experiments have shown the existence of the anhydrous salt,  $\text{NaVO}_3$ , and the dihydrate,  $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$ . The

anhydrous salt is soluble to the extent of 21.10% at 25°, 26.23% at 40°, 32.97% at 60°, and 38.83% at 70°. The solubilities of the dihydrate, expressed in terms of the anhydrous salt, are about 15.23% at 25°, 29.93% at 40°, and 68.36% at 60°. On attempting to determine the solubility of the latter salt at 75°, a value was obtained which showed that the solid phase had changed into the less soluble modification.

E. G.

**Oxysulphides of Antimony.** E. QUERCIGH (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 415—419).—The author has applied the method of thermal analysis to the study of the system  $\text{Sb}_2\text{O}_3$ — $\text{Sb}_2\text{S}_3$ . The two substances are miscible in the fused state in all proportions. They form a compound,  $\text{Sb}_4\text{OS}_5$  (that is,  $5\text{Sb}_2\text{S}_3, \text{Sb}_2\text{O}_3$ ), which does not melt unchanged, but decomposes at 522° into crystals of  $\text{Sb}_2\text{S}_3$  and a liquid phase. Mixed crystals of  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_4\text{OS}_5$  exist between certain concentrations (0—18%  $\text{Sb}_2\text{S}_3$  and 16.66—23%  $\text{Sb}_2\text{O}_3$ ). The eutectic of  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_4\text{OS}_5$  has the concentration of kermesite (about 33.33% of  $\text{Sb}_2\text{O}_3$ ; 489°), and this mineral cannot be obtained, therefore, from fused mixtures of its components. Of Schumann's two oxysulphides (compare *Annalen*, 1877, 187, 312), only  $\text{Sb}_4\text{OS}_5$  is really formed in the crystallisation of the fused mixture, whilst the formation of solid solutions in the system is very limited (compare Rose, *Ann. Phys. Chem.*, 1853, [i], 89, 316).

R. V. S.

**Carnot's Reagent and the Preparation of Sodium Bismuth Thiosulphate.** JEAN A. SANCHEZ (*Bull. Soc. chim.*, 1912, [iv], 11, 440—443).—Carnot's reagent, employed in the estimation of potassium, is a slightly acid solution of sodium-bismuth thiosulphate in alcohol. The double salt has been prepared crystalline by the following method: Bismuth oxynitrate, 1 gram, is dissolved in acetic acid, 10 c.c., the solution boiled during one minute, cooled, and 10 c.c. of a 20% solution of sodium thiosulphate added drop by drop. To this liquid forty drops of aniline are added, and then twenty to twenty-five times its volume of alcohol of 95°. On shaking, a crystalline precipitate of sodium bismuth thiosulphate separates, which is purified by washing with alcohol.

T. A. H.

**Gold Silver Alloys.** U. RAYDT (*Zeitsch. anorg. Chem.*, 1912, 75, 58—62).—A determination of the liquidus and solidus curves of the system gold-silver confirms the results of Jänecke (*Abstr.*, 1911, ii, 1089). The crystallisation interval is small, and the crystals are nearly homogeneous, but cores, when present, are not removed by short periods of annealing.

C. H. D.

**Device for the Complete Precipitation of Gold.** EDUARD PŘIWOZNIK (*Oesterr. Zeitsch. Berg. Huttenw.*, 1911, 59, 639—641).—Gold can be precipitated with reducing agents, such as glycerol, by the following procedure: 300 c.c. of glycerol (D 1.27) are mixed with an equal quantity of water and 400 c.c. of a moderately concentrated solution of sodium carbonate added, the mixture is raised to its boiling point and slowly treated with a cold solution of gold chloride, and, if

necessary, rendered alkaline with a further quantity of sodium carbonate. The mixture turns black, but the colour slowly disappears, whilst the gold separates as a dark brown, spongy mass, which, after prolonged boiling and frequent washing (by decantation), assumes a paler colour, and finally by gentle heating after separation from the liquid has the yellow colour of ordinary gold. F. M. G. M.

**Volatility of Metals of the Platinum Group.** SIR WILLIAM CROOKES (*Proc. Roy. Soc.*, 1912, *A*, 86, 461—477).—The volatility of the metals at 1300° has been investigated by heating the metals in a small electric furnace and determining the losses of weight after successive two-hour periods of heating.

At this temperature, platinum was found to lose weight at a constant rate, the loss after thirty hours amounting to 0.245%. The character of the metal surface was not appreciably altered as a result of the loss in weight.

Palladium lost weight to the extent of 0.745% after heating for thirty hours. The loss of weight was more rapid in the earlier stages, and the blistered appearance of the metal indicated that this was probably due to the liberation of occluded gas. The surface of the metal changed gradually, and had a crystalline moiré appearance at the end of thirty hours. The metallic nature of the surface was, however, unimpaired, and no oxidation could be detected.

Iridium volatilises very quickly, and a loss of weight of 7.297% was found after twenty-two hours' heating. The surface gradually became crystalline, and showed a beautiful moiré effect at the conclusion of the experiment. Observations made at temperatures between 1000° and 1400° showed that the rate of loss of weight is approximately proportional to the temperature.

Rhodium was found to have lost 0.131% after heating for thirty hours. The rate of loss of weight was constant, and the surface appeared to be unchanged, showing no evidence of crystalline structure.

Ruthenium lost 25% of its weight after eight hours' heating at 1300°. The polished metal became dull black in appearance, and was covered with a coating of oxide.

Similar experiments at 900° showed that platinum and rhodium are non-volatile at this temperature. Palladium decreased in weight to the extent of 0.1827% after thirty hours, and iridium lost 0.092% after twenty-two hours.

In the case of platinum the metal appears to be volatile per se at 1300°, whereas the loss in weight of iridium is probably due to the formation of a volatile oxide. The gradual wearing out of the platinum heating coils of resistance furnaces is attributed to the volatility of the platinum, and examination of the metallic dust which collects on the porcelain tubes has shown that this consists of minute hexagonal plates of metallic platinum which have been formed by sublimation of the heated metal. H. M. D.

## Mineralogical Chemistry.

**Natural Gas in the Neighbourhood of Pisa.** TORQUATO GIGLI (*Chem. Zeit.*, 1912, 36, 511).—Natural gas, which is used for lighting and heating, is obtained at two places situated a few kilometres from Pisa; the pressure of the gas is about 2 atmospheres, the depth of the borings being 18 and 24 metres respectively. An analysis of the gas from one boring showed that it consisted of methane, 80·7%; ethane, 6·0%; nitrogen, 6·7%; carbon dioxide, 3·8%, together with small quantities of heavier hydrocarbons, oxygen, and carbon monoxide.

W. P. S.

**Rare Earths in Spain. Spectra of the Cathode Phosphorescence of the Fluorites of Aulestia and Mañaria (Biscay).** ANGEL DEL CAMPO CERDÁN (*Anal. Fis. Quim.*, 1912, 10, 93—104).—The fluorites of these localities are identical, and are shown to contain terbium, dysprosium, and samarium.

G. D. L.

**Analysis of Aragonite from Molina de Aragon.** RÁMON LLORD Y GAMBOA (*Zeitsch. Kryst. Min.*, 1912, 50, 473; from *Bol. R. Soc. Españ. Hist. Nat.*, 1909, 9, 110).—Rose-red crystals from the original locality for this mineral contain:  $\text{CaCO}_3$ , 97·36%;  $\text{SrCO}_3$ , 1·61%; ferruginous clay, 0·000480%. Magnesia is absent.

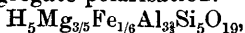
L. J. S.

**Mineral Occurrences in Fossils of the Tyrolese Limestones.** AUGUST HAAS (*Jahrb. Min.*, 1912, i, 1—20).—A description is given of various crystallised minerals (quartz, fluorite, calcite, dolomite, brown-spar, anhydrite, celestite, and an aluminium silicate) occurring in cavities and often in the interior of fossils, in the Muschelkalk, and the Wetterstein limestone to the north of Innsbruck. Small rhombohedra of dolomite gave analysis I, corresponding, not with normal dolomite, but with  $7\text{CaCO}_3, 4\text{MgCO}_3$ . Analysis II of brown-spar gives the molecular ratios  $4\text{CaCO}_3, 4\text{MgCO}_3, \text{FeCO}_3$ .

	$\text{CaCO}_3$ .	$\text{MgCO}_3$ .	$\text{FeCO}_3$ .	Total.
I.	66·41	33·075	—	99·485
II.	49·00	36·58	13·91	99·49

The celestite contains  $\text{SrSO}_4$ , 96·35;  $\text{BaSO}_4$ , 3·20%.

The aluminium silicate (anal. III) is soft and earthy, and dull green to brownish in colour. Under the microscope it shows irregular particles with feeble aggregate polarisation. In composition,



it approximates to pyrophyllite and especially to gümbelite, but it appears to differ from these in its physical characters.

	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{MgO}$ .	$\text{HgO}$ .	Total.
III.	52·99	32·88	2·45	4·06	7·75	100·13

L. J. S.

**Occurrence of Ankerite in Coal.** THOMAS CROOK (*Min. Mag.*, 1912, 16, 219—223).—The white mineral frequently observed as thin seams along the joint-planes of coal has usually been assumed to be calcite. It is, however, shown by the following analyses to be ankerite. Analysis II corresponds closely with normal ankerite,  $2\text{CaCO}_3, \text{Fe}(\text{Mn})\text{CO}_3, \text{MgCO}_3$ , but in I there is an excess of 9.6%  $\text{CaCO}_3$ .

	$\text{CaCO}_3$ .	$\text{FeCO}_3$ .	$\text{MnCO}_3$ .	$\text{MgCO}_3$ .	Total.	Sp. gr.
I.	54.91	24.70	1.86	18.84	100.31	3.01
II.	51.26	25.21	1.46	22.55	100.48	3.05

Other minerals sometimes present in these miniature mineral-veins are calcite, iron-pyrites, zinc-blende, and galena. L. J. S.

**Identity of Neocolemanite with Colemanite.** ARTHUR HUTCHINSON (*Min. Mag.*, 1912, 16, 239—246).—By a simple change in the orientation of the crystals (namely, a rotation of  $180^\circ$  about the normal to the basal cleavage), it is shown that the angles and optics of neocolemanite (Abstr., 1911, ii, 901) are in complete agreement with those of colemanite. L. J. S.

**Composition of Minerals of the Apatite Group.** AUSTIN F. ROGERS, with analyses by G. E. POSTMA (*Amer. J. Sci.*, 1912, [iv], 33, 475—482).—A calcium carbonato-phosphate referred to dahllite (= podolite, Abstr., 1910, ii, 1076) occurs as a white drusy coating of minute hexagonal crystals with iodyrite, quartz, etc., at Tonopah, Nevada. Analysis I. agrees with  $3\text{Ca}_3(\text{PO}_4)_2, \text{Ca}(\text{CO}_3, \text{F}_2, \text{O})$ . The interior of the crystals is opaque, but the outer portions show a division into optically biaxial sectors.

	Ca.	$\text{PO}_4$ .	F.	Cl.	$\text{CO}_3$ .	O.	Insol.	Total.
I.	32.56	47.03	0.29	—	2.48	1.07	12.72	—
II.	39.83	57.07	1.20	—	0.23	0.92	—	99.55
III.*	38.81	46.82	nil	trace	6.46	—	3.22	—

\* Also  $\text{Fe}_2\text{O}_3$ , 1.93;  $\text{Al}_2\text{O}_3$ , 3.93; organic matter, 1.87.

Apatite from several localities effervesces with hot nitric acid, and therefore contains the carbonate radicle. Again, many published analyses of apatite show a deficiency in fluorine and chlorine, and also in the carbonate radicle. This deficiency is taken to represent oxygen, and in the analyses of Voelcker (1883) of apatite from Kragerö, Norway, it amounts to 1.30 to 1.48% oxygen. The presence of this is also shown in analysis II of a large, white tabular crystal from the Zillertal, Tyrol. These and other analyses suggest the existence of the compound  $3\text{Ca}_3(\text{PO}_4)_2, \text{CaO}$ , or oxy-apatite, for which the name *voelckerite* is proposed. The isomorphous members of the apatite group are then:

Fluor-apatite.....	$3\text{Ca}_3(\text{PO}_4)_2, \text{CaF}_2$
Chlor-apatite .....	$3\text{Ca}_3(\text{PO}_4)_2, \text{CaCl}_2$
Dahllite (carb-apatite).....	$3\text{Ca}_3(\text{PO}_4)_2, \text{CaCO}_3$
Voelckerite (oxy-apatite)	$3\text{Ca}_3(\text{PO}_4)_2, \text{CaO}$

Certain ill-defined minerals of the apatite group as well as phosphorite and rock-phosphates may be regarded as mixtures of these compounds.

Analysis III, of a dark brown, egg-shaped nodule from Volhynia, Russia, corresponds with  $3\text{Ca}_3(\text{PO}_4)_2 \cdot \text{CaCO}_3$ , with an excess of calcium carbonate.

The following analysis of pyromorphite from Lower Sugar Loaf Creek, Marion Co., Arkansas, shows that here, also, chlorine may be replaced by the carbonate radicle. This pyromorphite is of the polysphærite variety, and occurs as a grey or greenish-grey alteration crust on galena.

Pb.	Ca.	$\text{PO}_4$ .	$\text{CO}_3$ .	Cl.	Insol.
66.73	4.02	23.82	1.93	2.55	0.42

L. J. S.

**Petrography of the Colony Eritrea.** ERNESTO MANASSE (*Zeitsch. Kryst. Min.*, 1912, 50, 510—511; from separate publication, Siena, 1909, 168 pp.).—Various minerals are described. Alunite occurs as concretionary masses, and also finely disseminated through a reddish schistose rock which is regarded as an altered phyllite; analysis gave (after deducting 4.78% quartz):

$\text{SO}_3$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{K}_2\text{O}$ .	$\text{Na}_2\text{O}$ .	$\text{H}_2\text{O}$ .	Total.
38.20	37.93	trace	7.33	2.25	[14.29]	100.00

Analcite occurs abundantly together with other zeolites in augite-teschenites at Hamasat, Massaua;  $n = 1.4837$ ; analysis gave:

$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3$ .	$\text{Fe}_2\text{O}_3$ .	$\text{CaO}$ .	$\text{MgO}$ .	$\text{Na}_2\text{O}$ .	$\text{K}_2\text{O}$ .	$\text{H}_2\text{O}$ .	Total.
56.24	21.68	trace	0.33	trace	13.30	0.42	8.40	100.47

L. J. S.

**Tungsten Minerals from Spain.** CONR. GRANELL (*Zeitsch. Kryst. Min.*, 1912, 50, 472; from *Bol. R. Soc. Españ. Hist. Nat.*, 1909, 9, 81).—A description is given of the several occurrences of wolframite in Spain; these are, for the most part, at the contacts of granite with schists and slates, and are often associated with tin ores. One analysis of wolframite shows no manganese, this material being pure iron tungstate or ferberite; two show 0.46 and 0.95%  $\text{MnO}$ , whilst in fourteen others  $\text{MnO}$  ranges from 1—14.4%. In only one analysis is any tin shown ( $\text{SnO}_2$ , 0.22%); alumina and lime never reach 1%. Scheelite occurs at many of the localities in association with the wolframite. Cuproscheelite is found in small amount together with scheelite in the Sorpresa wolfram mine at Montoro; it contains:

$\text{WO}_3$ .	$\text{CaO}$ .	$\text{CuO}$ .	$\text{FeO}$ .	$\text{SiO}_2$ .	$\text{Al}_2\text{O}_3, \text{K}_2\text{O}, \text{Li}_2\text{O}, \text{SO}_3$ .	Loss on ignition.
78.69	10.91	2.57	0.03	7.91	traces	1.24

Here the ratios are not normal, but are  $\text{WO}_3 : \text{CaO} + \text{CuO} = 3.39 : 2.25 = 1.5 : 1$ . The silica is probably present as admixed quartz.

L. J. S.

**Strüverite from the Federated Malay States.** THOMAS CROOK and S. J. JOHNSTONE (*Min. Mag.*, 1912, 16, 224—231).—The

material examined consisted of coarse, angular grains separated from a tin-bearing alluvium on the Sebantun river, Kuala Kangsar district, Perak. It is black and lustrous, and gives a greenish-black streak. Very small particles allow the passage of some light, and are seen to be strongly pleochroic; the material appears to be optically uniaxial. In the analysis the mineral was dissolved by heating for several days with concentrated sulphuric acid. After precipitating tin, the titanium, tantalum, and columbium were precipitated with excess of sodium thiosulphate. This precipitate was ignited, mixed with about its own weight of pure sugar-carbon, and strongly heated in a current of chlorine which had passed through carbon tetrachloride; the less volatile tantalum and columbium chlorides were thereby separated from the titanium chloride. The results of the analysis are as follows. Scandium was also detected with the spectroscope:

TiO <sub>2</sub> .	Ta <sub>2</sub> O <sub>5</sub> .	Cb <sub>2</sub> O <sub>5</sub> .	FeO.	MnO.	SnO <sub>2</sub> .	SiO <sub>2</sub> .	H <sub>2</sub> O.	Total.	Sp. gr.
45.74	35.96	6.90	8.27	trace	2.67	0.20	0.50	100.24	5.30

These results support the view that strüverite (Abstr., 1908, ii, 398; 1911, ii, 499) is an isomorphous mixture or a solid solution of tapiolite [Fe(Ta,Cb)<sub>2</sub>O<sub>6</sub>] in rutile (TiO<sub>2</sub>). Calculations of the density suggest that the strüverite from Piedmont is considerably richer in tantalum than indicated in the original analysis. L. J. S.

**Radioactive Uraniferous Columbotantalotitanites from Pegmatites of Madagascar; their Frequent Association with Bismuth Minerals.** ALFRED LACROIX (*Compt. rend.*, 1912, 154, 1040—1046).—Except as autunite, uranium only occurs in the pegmatites of Madagascar as more or less altered and hydrated columbotantalates. These are met with as orthorhombic species (euxenite, etc.), and with blomstrandite as a new cubic species. The minerals are all radioactive, and are often associated with native bismuth and bismuth minerals, otherwise rarely found in pegmatites. Two members of the cubic species are described; with blomstrandite they form a group approaching pyrochlore in general characteristics. *Betafite*, D 4.17, is dark green, and shows rudimentary cubic faces. *Samiresite* occurs in very fragile octahedra, resembling rubber in appearance.

I. Blomstrandite associated with beryl at Tongafeno. II. Betafite from Ambolotora. III. Samiresite from Samiresy. IV. Ampanga-beite from Ampangabé near Miandrarivo.

	Nb <sub>2</sub> O <sub>5</sub> .	Ta <sub>2</sub> O <sub>5</sub> .	TiO <sub>2</sub> .	SnO <sub>2</sub> .	ThO <sub>2</sub> .	UO <sub>2</sub> .	Bi <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .
I.	23.30	28.50	10.87	0.30	—	18.10	0.40	—	—
II.	34.80	trace	18.30	0.30	1.30	26.60 (U <sub>2</sub> O <sub>3</sub> )	—	2.10	2.87
III.	45.80	3.70	6.70	0.10	—	21.20	—	0.74	—
IV.	34.80	8.90	4.90	—	2.50	19.40	—	2.10	8.60

	FeO. (CeLaDi) <sub>2</sub> O <sub>3</sub> .	(YEr) <sub>2</sub> O <sub>3</sub> .	MnO.	MgO.	CaO.	PbO.	K <sub>2</sub> O.	H <sub>2</sub> O.	Total
I.	1.35	2.50	0.30	0.50	0.20	4.00	—	9.60	99.85
II.	—	0.60	0.90	—	0.40	3.45	—	7.60	99.22
III.	1.06	0.20	—	—	—	7.35	0.30	12.45	99.60
V.	—	0.60	4.00	—	—	1.50	—	12.40	100.50

*Ampangabeite* occurs in large, brownish-red, elongated, rectangular crystals, D 4.29. It seems to resemble Brögger's "ännerödite," but, unlike this mineral, is homogeneous. Large crystals of monazite occur in the same veins, together with enormous quadratic crystals of a mineral resembling strüverite crystallographically. W. O. W.

**Solid Solution in Minerals : Composition of Analcite.** HARRY W. FOOTE and W. M. BRADLEY (*Amer. J. Sci.*, 1912, [iv], 33, 433—439).—The formula usually accepted for analcite is  $\text{Na}_2\text{Al}_2(\text{SiO}_3)_4 \cdot 2\text{H}_2\text{O}$ , but the published analyses exhibit a considerable deviation from this. Those quoted by Dana give the molecular ratios :

$\text{SiO}_2$	: $\text{Al}_2\text{O}_3$ , etc.	: $\text{Na}_2\text{O}$ , etc.	: $\text{H}_2\text{O}$ .
3.57—5.35	: 0.93—1.23	: 1.00	: 1.62—2.37

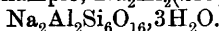
The following new analyses, each the mean of two, were made on carefully selected crystallised material, which in all cases, except in No. III, was clear and glassy.

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{MgO}$	$\text{K}_2\text{O}$	$\text{Na}_2\text{O}$	$\text{H}_2\text{O}$	Total.	Sp. gr.
I.	55.90	22.40	0.11	—	0.03	12.91	8.35	99.70	2.254
II.	54.41	23.62	0.12	—	0.12	13.36	8.24	99.87	2.260
III.	54.68	23.33	0.14	—	0.02	13.47	8.46	100.10	2.257
IV.	55.06	22.85	0.15	0.17	—	13.18	8.38	99.79	2.219
V.	56.48	22.13	—	0.21	0.11	13.04	8.39	100.36	2.223
VI.	56.84	22.81	0.22	—	0.19	12.69	8.27	101.02	2.231

These analyses give the following ratios :

	$\text{SiO}_2$	: $\text{Al}_2\text{O}_3$ , etc.	: $\text{Na}_2\text{O}$ , etc.	: $\text{H}_2\text{O}$ .
I. Two Islands, N.S. ...	4.46	1.06	1.00	2.24
II. Cyclopean Is. ....	4.16	1.07	1.00	2.12
III. Kerguelen Is. ....	4.18	1.05	1.00	2.17
IV. Victoria, Aust. ....	4.29	1.05	1.00	2.19
V. Michigan, U.S.A. ....	4.45	1.02	1.00	2.21
VI. Montreal, Can. ....	4.61	1.09	1.00	2.25

Here  $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$  is nearly 1 : 1, and further  $\text{H}_2\text{O} : \text{SiO}_2$  is very close to 1 : 2, but there is no simple ratio between alumina (or soda) and silica (or water). The case is thus similar to that of nephelite (Abstr., 1911, ii, 122), and in the same way the variations in composition can be explained by assuming the solid solution of some other compound with the analcite molecule. The formula may be written  $\text{Na}_2\text{Al}_2(\text{SiO}_3)_4 \cdot 2\text{H}_2\text{O} + x\text{H}_2\text{Si}_2\text{O}_5$ ; but other components could of course be chosen, for example,  $\text{Na}_2\text{Al}_2(\text{SiO}_3)_4 \cdot 2\text{H}_2\text{O}$  and



The fact that the water in analcite does not behave like ordinary water of crystallisation (the vapour pressure at a given temperature not being constant) gives some support to this view. L. J. S.

**Rocks and Minerals from Beaume, Piedmont.** LUIGI COLOMBA (*Zeitsch. Kryst. Min.*, 1912, 50, 497—500; from *Riv. Min., Crist. Ital.*, 1909, 38, 35—82).—A detailed description is given of the several minerals (albite, glaucophane, ilmenite, mohnite, anatase, rutile, hæmatite, quartz, pyrites, barytes, calcite, dolomite, rhodochrosite,

chalybite, and chlorite) occurring at the contact of limestones and schists in the valley of the Upper Doro Riparia. The albite forms small veins (anal. I), and occurs also in the altered limestones (anal. II) :

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	CaO.	Na <sub>2</sub> O (with traces of K <sub>2</sub> O).	Total.
I.	67·96	20·62	0·40	10·95	99·93
II.	67·38	20·50	0·45	11·21	99·63

Mohsite, with the axial ratio  $a:c = 1:1.3455$  and  $D\ 4.4-4.5$ , is not decomposed by hydrochloric acid. This is held to be distinct from ilmenite, and to be geometrically isomorphous with eudialyte, catapleiite, and senaite, with the general formula  $R^{II}O_2R^{IV}O_2$ . The ilmenite from this locality has  $a:c = 1:1.3681$ , and gave on analysis : Fe<sub>2</sub>O<sub>3</sub>, 85·06; FeO, 7·07; TiO<sub>2</sub>, 7·86%, corresponding with the formula  $2FeTiO_3, 11Fe_2O_3$ . Dolomite gave : CaCO<sub>3</sub>, 57·21; MgCO<sub>3</sub>, 42·75, corresponding with  $10CaCO_3, 9MgCO_3$ ; the angle (111):(100) =  $43^\circ 59'$  also differs from that of normal dolomite.

L. J. S.

The Behaviour of Spodumene on Heating. ALBERT BRUN (*Zeitsch. anorg. Chem.*, 1912, 75, 68. Compare Endell and Riecke, this vol., ii, 266).—The author has previously shown (Abstr., 1902, ii, 461) that spodumene undergoes a change at  $1010^\circ$ , expanding largely whilst retaining its external form, and becoming very friable. This point is to be distinguished from the melting point.

C. H. D.

Composition of Nephelite. HARRY W. FOOTE and W. M. BRADLEY (*Amer. J. Sci.*, 1912, [iv], 33, 439—441).—A reply to Schaller (Abstr., 1911, ii, 992) and Bowen (this vol., ii, 176). Whilst explaining the excess of silica in nephelite by solid solution, the authors do not commit themselves as to the exact form in which this is present. Analyses of nephelite occurring in intimate association with albite show that the "saturation ratio" of the silica is 2·2.

L. J. S.

An Iron-poor Epidote (Clinzoisite-Epidote) from S. Barthélemy, Aosta Valley, Piedmont. FEDERICO MILLOSEVICH (*Zeitsch. Kryst. Min.*, 1912, 50, 492—493; from *Atti Soc. Ligustica Sci. nat. geogr. Geneva*, 1909, 19).—Epidote occurs together with calcite, diopside, and garnet at a serpentine contact at Bois Noire and Issologne, near S. Barthélemy. It is colourless, greenish, or pale rose-red. Analyses of pale yellowish-green crystals with feeble negative birefringence gave :

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MnO.	CaO.	MgO.	H <sub>2</sub> O.	Total.	Sp. gr.
38·92	29·57	5·25	trace	23·37	0·98	2·03	100·12	3·341

corresponding with a mixture of 88—89% of  $H_2Ca_4Al_6Si_6O_{28}$  with 11—12% of  $H_2Ca_4Fe_6Si_6O_{28}$ . Colourless crystals with feeble positive birefringence contained 3·25% Fe<sub>2</sub>O<sub>3</sub>, corresponding with 7% of  $H_2Ca_4Fe_6Si_6O_{26}$ . (The clinzoisite from Rothenkopf, Tyrol, with 3·52% Fe<sub>2</sub>O<sub>3</sub> is optically negative, while that with less iron is positive.)

L. J. S.

**Analysis of the Gases Spontaneously Liberated in the Spring San Jose (Bath of La Aliseda). Radioactivity of the Gases.** FAUSTINO DIAZ DE RADA (*Anal. Fis. Quim.*, 1912, 10, 113—121).—The gas contains carbon dioxide 6·3, and nitrogen 93·7%. Of the nitrogen, 1·08% is composed of rare gases in the relative proportions of neon and traces of helium 0·246, and argon with traces of krypton and xenon 99·754. In every twenty-four hours, 406·4 litres of rare gases are disengaged from the spring.

Ten litres of the spring water contain on issuing at least 0·113 mg.-minutes of emanation, and 10 litres of the gas similarly showed 0·377 mg.-minutes. G. D. L.

**Sinter from the Wiesbaden Thermal Springs.** FERDINAND HENRICH and GÜNTHER BUGGE (*Chem. Zeit.*, 1912, 36, 473. Compare Henrich, *Abstr.*, 1907, ii, 150)—A specimen of sinter from the Kochbrunnen, Wiesbaden, contained  $\text{SiO}_2$  12·44,  $\text{As}_2\text{O}_5$  0·22,  $\text{Fe}_2\text{O}_3$  6·83,  $\text{Al}_2\text{O}_3$  2·95,  $\text{MnO}$  0·22,  $\text{ZnO}$  0·37,  $\text{CaO}$  49·27, organic matter 0·30%. A comparison with specimens of sinter at some distance from the spring shows that a high percentage of iron accompanies high radioactivity, but that there is no exact proportionality. C. H. D.

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## Physiological Chemistry

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**Function of Respiratory Pigments in the Oxidation Processes of Plants and Animals.** WLADIMIR I. PALLADIN (*Bull. Acad. Sci. St. Pétersbourg*, 1912, 437—451; partly in *Ber. Deut. bot. Ges.*, 1912, 30, 104—107).—Consideration of the author's previous results and of those of Bach and Chodat, Bertrand, etc., leads to the following conclusions.

The function of respiratory pigments in oxidation processes consists in the extraction of hydrogen from the substance undergoing oxidation. Oxydases are both pigment-forming and water-forming enzymes. During respiration, the whole of the hydrogen of dextrose is oxidised to water solely by atmospheric oxygen, the water formed during respiration being of aerobic origin. Oxidation of dextrose by means of a respiratory pigment takes place with co-operation of the water, the oxidation of the carbon present in the dextrose being effected to the extent of one-half by the oxygen of the sugar and, for the rest, by the oxygen of the water assimilated during respiration. Water is not only separated, but also assimilated, during respiration. The complete decomposition of dextrose during respiration proceeds as follows: (1) Anærobic resolution of the dextrose, with assimilation of water, by zymase and perhydridase. (2) Transference of hydrogen from the intermediate, labile product to the respiratory pigment. (3) Removal of hydrogen from the reduced respiratory pigment and its oxidation to water with the help of the system peroxydase + oxygenase.

T. H. P.

**The Action of Acids on the Respiratory Centre.** T. BRAILSFORD ROBERTSON (*Pflüger's Archiv*, 1912, 145, 329—334).—If dilute acids are applied directly to the medulla oblongata of decerebrate frogs, respiration is stimulated. Potassium cyanide applied in the same way brings about complete arrest of breathing in a few minutes.

W. D. H.

**Expired Air.** II. WOLFGANG WEICHARDT and H. STÖTTER (*Arch. Hygiene*, 1912, 75, 265—289. Compare Abstr., 1911, ii, 993).—The presence of physiologically active substances in expired air may be missed if the air is passed through water, because aqueous solutions soon lose their activity; but if the air is passed through glycerol, this is avoided. The experiments were performed with the expired air of guinea pigs and men. The toxic material in low concentration increases, but in higher concentration inhibits, the guaiacum reaction. Various products of protein cleavage act in the same way, but pure carbohydrates, certain salts, and carbon dioxide do not.

W. D. H.

**The Dependence of the Number of Heart Beats on the Partial Pressure of Oxygen.** JACQUES LOEB and HARDOLPH WASTENEYS (*Biochem. Zeitsch.*, 1912, 40, 277—295).—The authors show that the number of heart beats in a given time (20") in a fundulus embryo is diminished by one-half to one-third by diminishing the partial pressure of the oxygen. The limiting value of the oxygen tension cannot be accurately ascertained. The action has been observed when the volume of the air has been diminished from one-fourth to one-tenth by mixing it with hydrogen. The heart can continue to beat with diminished frequency for several days. The addition of sodium cyanide also diminishes the frequency of the heart beats, and the rate of beating is a function of the amount of cyanide in solution.

S. B. S.

**The Causation of the Heart Beat.** E. G. MARTIN (*Amer. J. Physiol.*, 1912, 30, 182—191).—Ventricular tissue cut off from the circulation relaxes steadily for several hours in moist air, 0.7% sodium chloride solution, and in Ringer's solution. The improvement in beat following treatment with oxygen, sodium carbonate, or calcium chloride is not necessarily dependent on the tonus-increasing powers of these substances, since improvement in tone and beat do not always go together. Sodium chloride "exhaustion" cannot be due to excessive loss of tone; it is not the result of any specific action of the salt, so much as an effect due to separation from the circulation.

W. D. H.

**The Influence of Temperature and Blood-pressure on the Isolated Mammalian Heart.** F. P. KNOWLTON and ERNEST H. STARLING (*J. Physiol.*, 1912, 44, 206—219).—The method used is to leave the lungs as well as the heart intact, so that the blood is naturally aerated. The rate of beat then varies directly as the temperature, being unaltered within wide limits of change either in arterial or venous pressure. Within wide limits the cardiac output is

independent of arterial resistance or temperature. Up to a certain point the output is proportional to the venous inflow; beyond that venous pressure rises and the lungs become œdematous. W. D. H.

**The Size and Growth of the Blood in Rabbits.** ARTHUR E. BOYCOTT (*J. Path. Bact.*, 1912, 16, 485—501).—A full account of a research of which a preliminary account has already appeared (*Abstr.*, 1911, ii, 1108). W. D. H.

**The Dissociation of Oxyhæmoglobin at High Altitudes.** ERNEST H. STARLING, JOSEPH BARCROFT, and WILLIAM B. HARDY (*Brit. Assoc. Report*, 1911, 153—154. Compare Barcroft, *Abstr.*, 1911, ii, 211).—In the course of ascents from Pisa (sea-level) to Col d'Olen (10,000 feet) and Capanna Margherita (15,000 feet), the acidity of the blood, exclusive of that due to carbon dioxide, was determined by measuring the degree of saturation with oxygen, and comparing with blood to which definite quantities of lactic acid had been added. The increase of lactic acid was about 0.025% at Col d'Olen, and twice as much at Capanna Margherita, but immediately after ascending the latter, was found to be as high as 0.8%. The acid is not immediately excreted on descending. This leads to a lower carbon dioxide tension in the alveolar air at Col d'Olen after a descent from Capanna Margherita than before the ascent.

C. H. D.

**The Physiology of Water and Salt.** OTTO COHNHEIM, G. KREGLINGER, L. TOPLER, and O. H. WEBER (*Zeitsch. physiol. Chem.*, 1912, 78, 62—88).—The authors, who spent a few days on Monte Rosa, failed to detect either in themselves or in the dogs (using several methods of estimation) any increase in red corpuscles or hæmoglobin, such as had been observed by numerous other investigators. They attribute their loss of weight to the unhygienic conditions of the hut where they lived. Great sweating was found to lead to a marked retention of chlorine in the body. The influence of varying amounts of sodium chloride and water in the food is also discussed.

W. D. H.

**The Fat-splitting Properties of Blood and Plasma Under Various Conditions.** EMIL ABDERHALDEN and ARNO ED. LAMPÉ (*Zeitsch. physiol. Chem.*, 1912, 78, 396—401).—The blood and serum of well-nourished dogs have little or no action in causing the fission of tributyrin. In inanition, the power appears and increases as the fast goes on. The fat therefore remains longer as fat in the blood under normal conditions of feeding.

W. D. H.

**Glycolysis.** J. EDELMANN (*Biochem. Zeitsch.*, 1912, 40, 314—325).—The intensity of glycolytic action in normal blood is strongest in the first six hours; after twenty-four hours hardly any more sugar can be detected. Hæmolyse blood is also active; within the first two or three hours in this case there is an apparent weakening of the glycolytic action, due to the setting free of sugar from the substance of

the corpuscles. In dogs deprived of the pancreas, the glycolytic action is diminished, and actually entirely disappears after a long interval after the operation. In dogs deprived of thyroids and parathyroids the glycolysis within the first six hours is diminished; after twenty-four hours, however, the glycolysis has proceeded as far as in normal blood; this result, again, appears to be due to the setting free of sugar from the substance of the corpuscles. S. B. S.

**The Isolation of Oöcytase, the Fertilising and Cytolysing Substance in Mammalian Blood Sera.** T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1912, 11, 339—346).—Eggs of sea-urchins are induced to form fertilisation membranes by immersing them in sera and various tissue extracts, especially if the eggs are first sensitised by exposure to a temperature of 30—31°, or immersion in a solution of strontium or barium chloride approximately isotonic with sea-water. Calcium chloride is much less powerful in this direction. The same agent which sensitises for fertilisation also sensitises for agglutination. The fertilising agent itself is termed oöcytase, and is probably derived from the breaking down of corpuscles in shed blood. It is thermostable, resisting exposure to a temperature of 58° for nineteen hours. The view that the sensitising is due to the precipitation of the oöcytase on the egg is supported by experiments. W. D. H.

**Chemical Composition of Horse Lymph.** FRANZ ZARIENICKY (*Zeitsch. physiol. Chem.*, 1912, 78, 327—332).—The sample of lymph contained 95% of water, 4.9% of solids, 4.3% of coagulable protein, 3.5% of globulin, 0.68% of inorganic substances. Dextrose, carbamide, uric acid, and xanthine bases were not present. The constituents of the ash agree closely in amount with the determinations made by Zeynek and by Ludwig on lymph from other sources. E. F. A.

**The Amylolytic Property of Saliva.** C. LOVATT EVANS (*J. Physiol.*, 1912, 44, 191—202).—A method which in general terms consists in the estimation of maltose is described which gives accurate comparisons of the amylolytic power of saliva. Later in hydrolysis dextrose is formed, but at the start when the ratio of substrate (starch) to enzyme is large, the reaction (maltose formation) is linear. The optimum concentration of the starch solution is about 3%, and the optimum temperature for salivary amylase (ptyalin) is 46°.

W. D. H.

**Method for the Determination of Amylolytic Activity.** C. LOVATT EVANS (*J. Physiol.*, 1912, 44, 220—224).—The author's method of determining amylolytic activity is far superior as regards accuracy to either the "achromic point" or Wohlgemuth's method. Of the two last, the former is the more accurate. W. D. H.

**The Cleavage of the Milk Proteins by Gastric Juice under Various Conditions.** EMIL ABDERHALDEN and FRIEDRICH KRAMM (*Zeitsch. physiol. Chem.*, 1912, 77, 462—470).—The quantity of amino-nitrogen is greater when milk previously curdled by rennin is digested than in cases where rennetic action is prevented by sodium oxalate,

but the differences are small. Any inhibitory influence excited by the oxalate was excluded by adding the same amount to the gastric juice employed. A much greater effect is produced by boiling milk, the yield of amino-nitrogen being decreased by this procedure.

W. D. H.

**The Fate of Protein Cleavage Products in the Intestine. The Occurrence of Individual Amino-Acids in Different Parts of the Intestinal Canal.** EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1912, 78, 382—395).—The experiments recorded do not contradict the theory that the cells of the intestinal wall can synthesise protein from the amino-acids present. The cleavage of proteins and peptones occurs in the same way in all parts of the small intestine, and there is no localisation in individual regions of different stages in the cleavage. Trypsin and erepsin work as well at the end as at the beginning of the intestinal canal.

W. D. H.

**The Cleavage of Proteins in the Intestinal Canal.** EMIL ABDERHALDEN and FRIEDRICH KRAMM (*Zeitsch. physiol. Chem.*, 1912, 77, 425—434).—Physiologists have drawn the conclusion that in the intestine the proteins are broken down almost entirely into their ultimate cleavage products. They have done so in spite of the fact that in vitro the reaction occurs so slowly. Experiments in vitro, however, differ considerably from natural digestion; during digestion in vivo the products are removed by absorption, and are therefore no longer present to inhibit enzymic activity; in the body, also, the proportions and order of action of the different proteolytic juices are adjusted to give an optimum effect. In the present experiments after peptone feeding, the contents of the intestine were removed and transferred to flasks, kept warm, and the natural chyme examined at short intervals for amino-nitrogen. These experiments do not provide for the removal of the final products, such as occurs in the intestine, but they at any rate demonstrate that the action is very rapid, as compared with purely artificial mixtures.

W. D. H.

**Chemical Equilibrium and End Conditions in Metabolism.** LEOPOLD LICHTWITZ (*Zeitsch. physiol. Chem.*, 1912, 77, 402—419).—In cases of enzymes which have a reversible action, there is a certain state in which the two actions balance each other; but in addition to this an enzyme may stop activity and a "false equilibrium" be obtained, because the products of its action have a specific inhibiting or paralysing influence on the enzyme. Urea formation is regarded as an instance of true equilibrium; von Lang stated that liver emulsion has quite a small power of splitting off ammonia from urea. The deamidation of amino-acids, however, is, as Knoop and others have shown, a reversible reaction. The present experiments on dogs and men show that if urea is given by the mouth (or in dogs also subcutaneously), an increase occurs in the excretion of ammonia and amino-acids (that is, nitrogen titratable with formaldehyde), and a drop in the amount of urea eliminated.

W. D. H.

**The Part Played by Methyl and Ethyl Alcohols in the General Metabolism of the Animal Organism.** WILHELM VÖLTZ and WALTER DIETRICH (*Biochem. Zeitsch.*, 1912, 40, 15—28).—The amount of methyl alcohol excreted in the expired air and in the urine was estimated. It was found that after administration of 2 c.c. of methyl alcohol per kilo. of body-weight to a dog, 24·3% was excreted in forty-eight hours, of which 21·5% was in the expired air, and 2·8% in the urine. As 36·8% was found in the body, it follows that only 39% was oxidised in the body. If the caloric value of the methyl alcohol oxidised is calculated, it will be found that this represents only 3% of the total metabolism of the body. These results are in marked contrast to those obtained with ethyl alcohol under analogous conditions. In this case 2 to 4% of the quantity administered was found in the expired air and 0·4 to 3·8% in the urine within ten to fifteen hours. After fifteen hours only 3 to 12% was found in the body. Of the foodstuffs degraded within ten hours, the ethyl alcohol (calculated on the caloric values) formed 42%, and in fifteen hours 35%.  
S. B. S.

**Carbohydrate Metabolism.** MAX KLOTZ (*Arch. exp. Path. Pharm.*, 1912, 67, 451—480).—Baumgarten and Grund (*Deutsch. Arch. klin. Med.*, 104) found in phloridzinised dogs that feeding on oatmeal produced fatty livers, and that fatty liver can be prevented by feeding on wheat. The cause of the discrepancy between these statements and those of the author is discussed. One most important factor, hitherto much neglected in a study of carbohydrate metabolism, is the character of the intestinal flora; the relative number of sugar-destroying organisms varies on different diets, and thus starch feeding may lead to the formation either of fat or of glycogen. Another important distinction between starches of the same chemical composition is their physical state, and this determines in large measure the effect of bacteria on them. The paper contains a large amount of analytical data in relation to various flours, and discusses at length the rationals of so-called "carbohydrate cures" for diabetes; here the conditions of flora, etc. are so uncertain and variable that the effect is largely a matter of chance.  
W. D. H.

**Purine Metabolism of Man. I. Are the Purine Substances Intermediary or Final Products of Metabolism?** V. O. SIVÉN (*Pflüger's Archiv*, 1912, 145, 283—297).—The purine substances excreted by human beings are terminal products of metabolism. The exogenous purine (that is, that in the diet) undergoes, to the extent of 50%, a break up in the digestive canal; another portion is absorbed with the purine nucleus intact; this part is not further destroyed, but is excreted within twelve to fifteen hours by the kidneys. The purine compounds in the blood-stream, whether they are of endogenous or exogenous origin, suffer no further cleavage; in other words, uricolytic action is not present.  
W. D. H.

**Feeding Experiments with the Amino-acids Derived from Protein, and with Ammonium Salts.** EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1912, 78, 1—27).—The conclusion is drawn from

experiments on dogs that when the sole source of nitrogen is in the form of ammonium salts added to a due supply of fat and carbohydrate, nitrogenous metabolism is influenced in such a way as to lead to retention of nitrogen. Ammonium salts, like amino-acids, may lead to synthesis of protein. W. D. H.

**Fasting Studies. IX. Differential Leucocyte Count During Prolonged Fasting.** PAUL E. HOWE and PHILIP B. HAWK (*Amer. J. Physiol.*, 1912, 30, 174—181).—The observations were made on dogs and men. The proportions of the different kinds of leucocyte are given in tables. In dogs the departures from the normal were different in different dogs, and different also in the same dog in different fasts or different periods of a fast. In the men, two in number, the fast lasted a week; here there was an increase in polynuclear leucocytes at first, followed by a fall below normal; the opposite conditions held for the lymphocytes, and one subject showed a rise in eosinophile cells throughout the whole period. On the resumption of food, both in men and dogs, normal conditions were soon re-established. W. D. H.

**The Balance of Acid-forming and Base-forming Elements in Food, and its Relation to Ammonia Metabolism.** HENRY C. SHERMAN and A. O. GETTLER (*J. Biol. Chem.*, 1912, 11, 323—338).—This balance was estimated in ash analyses of forty-seven kinds of food. Meats, including fish, show a predominance of acid-forming elements; the same is true for eggs, although in smaller degree; grain products show a still smaller predominance. Milk shows a slight predominance of base-forming elements, and this is increased in vegetables and fruits. If the acid-forming elements are increased in the diet of man, a rise in the ammonia excreted accounts only for from one-quarter to one-half of the acid involved. W. D. H.

**Absorption of Metallic Salts by Fish in their Natural Habitat. I. Absorption of Copper by *Fundulus heteroclitus*.** GEORGE F. WHITE and ADRIAN THOMAS (*J. Biol. Chem.*, 1912, 11, 381—386).—The fish took up a considerable amount of copper, and it is especially found in the vascular system; it therefore probably enters through the gills. Analytical details are given in full. W. D. H.

**Fat Absorption.** W. R. BLOOR (*J. Biol. Chem.*, 1912, 11, 429—434).—None of the impure isomannide dilaurate employed passes unchanged into the chyle, although large amounts are digested and absorbed. This agrees with Frank's work with the ethyl esters of fatty acids, and emphasises the probability that readily saponifiable fatty acid esters do not escape saponification under the favourable conditions obtaining in the normal intestine (excess of lipase and rapid removal of the products). Whether fatty substances of any kind may pass into the chyle unchanged remains to be proved. W. D. H.

**The Occurrence of Peptolytic Enzymes.** EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1912, 78, 344—348).—Various tissue juices

decompose polypeptides or silk peptone into their amino-acids. Evidence is adduced in aseptic experiments that this is due to peptolytic enzymes in the extracts, and not to micro-organisms. The condition in various diseased states is of interest, and it was found that in pneumonia before the crisis, the peptolytic power is slight or absent, and is increased markedly at the crisis. W. D. H.

**The Combined Action of Muscle-plasma and Pancreas Extract on Some Mono- and Di-saccharides.** PHÆBUS A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1912, 11, 347—352).—Muscle-plasma combined with pancreatic extract has the power to cause condensation of only two closely related hexoses, dextrose and *d*-lævulose. It has no action on mannose, xylose, ribose, and lactose. The same mixture also has the power of bringing about the hydrolysis of maltose, but not of lactose. W. D. H.

**The Action of Various Tissues and Tissue-juices on Dextrose.** PHÆBUS A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1912, 11, 353—360).—In the presence of antiseptics, and when oxygen is not excluded, animal tissues or their juices, aided or unaided by auxiliary substance, fail to bring about a destruction of dextrose. Any fall in reducing power is due to condensation of the dextrose. Whether glycolysis may occur under other conditions has yet to be settled. W. D. H.

**The Action of Leucocytes on Dextrose.** PHÆBUS A. LEVENE and G. M. MEYER (*J. Biol. Chem.*, 1912, 11, 361—370).—Leucocytes were obtained from the pleura of the dog after injections into it of turpentine. Under the influence of these cells, dextrose loses part of its reducing power, and this cannot be restored to the normal by boiling with mineral acid. The rate of glycolysis is inversely proportional to the sugar concentration. If distilled water is used instead of a phosphate mixture, the leucocytes have no such action. As a product of the action, sarcolactic acid was discovered, but no volatile acids; the amount of lactic acid found did not account for the total loss of the sugar. The experiments were conducted aseptically. Toluene inhibits the change. W. D. H.

**The Action of Tissue Extracts containing Nucleosidase on  $\alpha$ - and  $\beta$ -Methyl Pentosides.** PHÆBUS A. LEVENE, WALTER A. JACOBS, and FLORENTIN MEDIGRECEANU (*J. Biol. Chem.*, 1912, 11, 371—380).—The experiments recorded fail to contribute to the knowledge of the structure of the nucleosides, but furnish new information regarding the nature of nucleosidases, showing that they possess a greater degree of specificity than is known to be the property of many glycosidases. W. D. H.

**The Relationship between Cell Structure and Bio-chemical Reactions.** OTTO WARBURG (*Pflüger's Archiv*, 1912, 145, 277—282).—The question whether oxidation processes in the animal body are due to enzymatic action can be answered to some extent by examining what happens to cells of which the structure has been completely destroyed by

mechanical means. The answer given by the present research is that complete destruction of the cells (including their nuclei) leads to complete abolition of oxidative power. The red corpuscles of birds were used in the research; these were crushed by the apparatus of Barnard and Hewlett. This apparatus is a particularly effective one, and the crushing is not accompanied with any serious rise of temperature.

W. D. H.

The Physiological Permeability of Cells. IV. The Permeability and the Partition Coefficient of Gland Cells for Dyes, and a New Method of "Vital" Observation. ANTONIUS GARMUS (*Zeitsch. Biol.*, 1912, 58, 185—236).—The cells of the type of those found in the glands of the nictitating membrane of the frog take up the "vital staining" pigments of Ehrlich, and the staining is really "vital." The granules so obtained are not artifacts. The capacity to undergo vital staining has no relationship to the solubility of the dyes in lipoids. The basicity of the dyes is important, but not absolutely necessary. Another series of pigments do not stain the gland cells, but the epithelium of the membrane, here again, however, no relationship to lipid solubility is observable. The intensity and rate of the staining is increased by pilocarpine and lessened by atropine. This shows a relationship between physiological activity and the power to take up the vital stain; that is to say, when the activity of the cells in their uptake of water and salts is greatest, then also their permeability for dyes increases. Poisons, such as saponin, sodium fluoride, and ether, which affect lipoids do not affect the vital staining.

W. D. H.

The Relation between Oxydase and Tissue Respiration. HORACE M. VERNON (*J. Physiol.*, 1912, 44, 150—168).—The indophenol oxydase of mammalian tissues (kidney, heart, brain, liver) is extremely thermolabile, being largely destroyed at 50°, and completely at 60°; the gaseous metabolism of the tissues is affected by temperature in the same way.

Perfusion of a kidney for eleven hours at 17—35° with oxygenated Ringer's solution leads to no loss of oxydase, although its gaseous metabolism sinks to one-third of the normal, and much tissue protein (28%) is washed away. If the Ringer's solution contains lactic acid or phenol, destruction of respiratory activity and oxydase are parallel. Methylamine and chloroform act less destructively on the latter than the former; ammonia, mercuric chloride, nitric acid, and formaldehyde are still less destructive. Minced kidney is more sensitive to poisons than the intact organ. The various poisons (except sodium fluoride and formaldehyde) used cause tissue disintegration and a washing out of variable amounts of tissue protein.

Indophenol oxydase is insoluble in water and in saline solution. It is a true enzyme. The "peroxydase" which activates it is not an enzyme, and can be heated to 100° with impunity.

W. D. H.

Relation of the Liver to the Fibrinogen Content of the Blood. WALTER J. MEEK (*Amer. J. Physiol.*, 1912, 30, 161—173).—A full account of a research of which a preliminary notice has already appeared (this vol., ii, 273).

W. D. H.

**The Action of the Liver on the Simpler Sugars.** IDA SMEDLEY (*J. Physiol.*, 1912, 44, 203—205).—An enzyme is present in the liver which transforms glyceraldehyde into substances which are non-reducing, but is incapable of acting on dextrose. W. D. H.

**Histozyeme.** N. MUTCH (*J. Physiol.*, 1912, 44, 176—190).—Histozyeme is the enzyme which can be extracted from the kidney which hydrolyses hippuric acid, and is probably also responsible for the synthesis of that substance in the body, because (1) its power of hydrolysing sodium hippurate is incomplete, an equilibrium point being reached when the proportion of hippuric acid hydrolysed to that unchanged is 97:3; (2) by reacting on concentrated solutions of sodium benzoate and glycine, it produces in small amount a substance with the solubilities of hippuric acid; and (3) because its hydrolytic action is retarded by sodium benzoate, one of the end-products. The enzyme can still exert its hydrolytic action when benzoyl-alanine is substituted for hippuric acid, the benzoyl group remaining unaltered. W. D. H.

**The Relation of the Adrenal Glands to Blood Pressure.** R. G. HOSKINS and C. W. McCCLURE (*Amer. J. Physiol.*, 1912, 30, 192—195).—In eleven dogs under anæsthesia, ligaturing off the adrenal glands caused no immediate fall of blood pressure, although the animals were sensitive to minute doses of adrenaline, and under the existing conditions this substance was quickly destroyed after injection. The vaso-constrictor and supposedly other sympathetic fibres, therefore, had not been under a tonic influence exerted by the adrenal glands. W. D. H.

**The Thyroid Gland.** VIII. WALTER EDMUNDS (*J. Path. Bact.*, 1912, 16, 481—484).—Early death from tetany which usually follows total excision of thyroid and parathyroid glands in dogs can often be prevented by the administration of calcium salts in large doses. Pituitary extract has no such effect. If the calcium is stopped, the animals die, but even if it is continued the animals eventually die. W. D. H.

**The Influence of Muscular Rigidity on the Carbon Dioxide Output of Decerebrate Cats.** HERBERT E. ROAF (*Quart. J. exp. Physiol.*, 1912, 5, 31—54).—The muscular rigidity produced by removal of the cerebrum in cats differs from ordinary muscular (tetanic) contraction in that it is not accompanied by any increase in the output of carbon dioxide. W. D. H.

**The Ash of Smooth Muscle.** EDWARD B. MEIGS and L. A. RYAN (*J. Biol. Chem.*, 1912, 11, 401—414).—A full account of a research of which a preliminary notice has already appeared (this vol., ii, 274). W. D. H.

**The Formation of Glycine in the Animal Organism.** EMIL ABDERHALDEN and PAUL HIRSCH (*Zeitsch. physiol. Chem.*, 1912, 78, 292—305).—The fact that animal tissues possess marked synthetic

properties has recently received abundant confirmation. The formation of hippuric acid from glycine and benzoic acid is the instance which has been known longest. In the present experiments on rabbits, the amount of hippuric acid excreted was in excess of that which could be accounted for by the glycine in the food, and the conclusion is drawn that this animal is capable of forming large quantities of glycine in its body, by direct synthesis from ammonia. The same conclusion is drawn from experiments on dogs fed on caseinogen which is free from glycine. W. D. H.

**The Components of Animal Fats.** ISIDOR KLIMONT (*Monatsh.*, 1912, 33, 441—446).—The fat of *Lepus vulgaris* had the following constants:  $D^{50}$  0.9134, acid number 15.3, saponification number 204.9, iodine number 107.0, m. p.  $35^{\circ}$ , temperature of solidification  $29^{\circ}$ . The crude fat was melted, filtered, and cooled. The solid portion, after repeated recrystallisation from acetone and from a mixture of acetone and chloroform, had m. p.  $61.5^{\circ}$ , and was nearly pure tripalmitin. The liquid portion, in which the presence of linolic acid has been proved, did not appear to contain linolenic acid. H. W.

**The Behaviour of the Fat of Torpedo During Pregnancy.** FELIX REACH [and, in part, VIKTOR WIDAKOWICH (*Biochem. Zeitsch.*, 1912, 40, 128—137).—The estimations of fat were made on the organs, eggs, and embryos of *Torpedo ocellata* obtained in different seasons of the year. The iodine and neutralisation numbers of the fatty acids were also determined when sufficient material was available. From the tabulated results of the analyses, it would appear that the liver stores up the characteristic fat, the storage commencing even in embryonal life. During the period of nutrition, the fat increases so as to form a source of energy during periods of starvation. It afterwards passes into the eggs, first in the ovaries and then in the uterus, and forms the source of energy for the development of the embryo. S. B. S.

**Influence of Freezing on the Composition of Milk.** CARL MAI (*Zeitsch. Nahr. Genussm.*, 1912, 23, 250—254).—When milk is partly frozen the solid and liquid portions have different compositions; the results given in the following table show the composition of these portions obtained by keeping 10 litres of milk in a churn at  $-15^{\circ}$  for thirty hours.

	D.	Refracto- meter number.	Fat, per cent.	Solids, not fat, per cent.	Acidity.
Original milk .....	1.0318	38.6	3.7	8.94	6.2
Upper spongy ice (0.6 litre) ...	1.0256	40.2	11.6	8.30	8.2
Fluid portion (2.5 litres).....	1.0534	53.5	3.3	14.17	11.0
Hard ice on sides of churn (7 litres) .....	1.0201	30.1	2.9	5.75	3.8
Milk, thawed and re-mixed.....	1.0320	38.7	3.6	8.97	7.0

W. P. S.

**The Time of Excretion of Nitrogen, Sulphur, and Carbon After Ingestion of Proteins and Their Hydrolysis Products.** I. The Time of Excretion After Protein Ingestion. II. The Time of Excretion After Ingestion of the Degradation Products. CHARLES G. L. WOLF and EMIL ÖSTERBERG (*Biochem. Zeitsch.*, 1912, 40, 193—233, 234—276).—The experiments were carried out with the object of determining the degradation time of the various forms of protein. They were carried out on the person of a single individual who was kept in nitrogenous equilibrium on a standard diet which was ample for the caloric needs of the organism. From time to time nitrogenous additions were made to this diet, for which the following materials were employed: veal cutlets, plasmon, gelatin, alanine, cystine, egg-white (cooked and uncooked), urea, ammonium chloride, ammonium nitrate, degradation products of egg-white which yielded no biuret reaction, acid amides, and asparagine. Furthermore, the excretion was investigated after periods of fasting and after addition of fats and carbohydrates to the diet. During the period of investigation, the urine was collected hourly for sixteen hours after the ingestion of the added diet, and the following analyses of the same were made: total nitrogen, urea, ammonia, total sulphur, sulphates, neutral sulphur, and carbon. The last-named factor was determined by a wet method, which is described in some detail, and does not differ in any essentials from the usual methods. The apparatus used for the purpose is figured in the text. It was found that the curves representing the nitrogen and carbon excretions are practically parallel. The same holds true in many cases for the nitrogen and sulphur excretion, but this is by no means always the case, for example, the maximum excretion times in the case of unboiled egg-white differ by no less than twenty-four hours. In many cases it appears as if the sulphur part of the protein molecule is attacked first, the formation of sulphates taking place before that of urea. This fact is especially noticeable in the case of boiled and unboiled egg-white. This early metabolism of sulphur is not due to the presence of the cystine group, as it is also observed in the case of gelatin, in which the cystine group is absent. The method employed in these investigations has not led to the determination of the true time of deamidisation of proteins. In the preliminary stages of excretion, the acid excretion products are not combined with ammonia, but with fixed alkalis derived either from the body or the food. After ingestion of ammonia, either as citrate or chloride, its excretion follows very rapidly. With small doses, the excretion reaches the maximum in the second hour after ingestion, but with larger doses the excretion commences almost immediately after ingestion, and reaches its maximum even in the first hour. Urea formation from ammonia is a reversible process, for after ingestion of large doses of this substance, ammonia is excreted.

Uncooked egg-white seems to be degraded only slowly, which fact the author ascribes to the presence of antiferments which it contains. In the case of digested egg-proteins, there is not the great want of parallelism between the nitrogen and sulphur excretion curves such as was observed in the cases of both cooked and uncooked egg-albumin. In

this case, furthermore, the ammonia excretion reaches its maximum before that of either carbon, nitrogen and sulphur. This fact can be explained partly by the presence of free ammonia, and partly by the rapid deamidisation of the digestion products. The ingestion of fats and carbohydrates causes an increase in the nitrogen and carbon excretion, but this is possibly due only to increased diuresis. It is very difficult, if not impossible, to draw any very definite conclusions from experiments of the character described as to the time occupied in degrading proteins through their various stages, until the final end-product, urea, is formed. Some of the results, such as those obtained with alanine and urea, are due probably, not to increased time of resorption, but to retention in the organism. S. B. S.

**Undialysable Urinary Substances.** HENRI LABBÉ and G. VITRY (*Compt. rend.*, 1912, 154, 1189—1191).—The non-dialysable substances excreted by a normal subject in the urine of twenty-four hours amount to 1·5—2 grams. The material is highly nitrogenous, but free from amino-acids, and appears to consist of polypeptides or higher degradation products of proteins. W. O. W.

**The Reducing Substances in the Urine of Women during the Lying-in Period.** HELGA GRÖNVALL (*Biochem. Zeitsch.*, 1912, 40, 145—151).—The total reduction (by Bang's method) of the urine both before and after fermentation was estimated. From the average of twenty cases, it was found that the urine contained 0·17% of sugar, which is about six times the normal quantity. The daily variations and also the creatinine and uric acid were determined in several cases. The sugar was found to account for 44·2 to 55·6% of the total reduction, the uric acid 5·1—7·9%, and the creatinine 5·5 to 12%. The creatinine excretion is less than normal, and the uric acid about normal. The amount of sugar secreted daily shows considerable variations, as also does the creatinine; the uric acid variations, on the other hand, are somewhat small. S. B. S.

**Calomel Diuresis.** RUDOLF FLECKSEDER (*Arch. exp. Path. Pharm.*, 1912, 67, 409—450).—Mercury acts as a diuretic only in the ionised, not in the colloidal, condition. Its effect on the kidney is mainly secondary to its effect in producing hydræmia, and this in its turn largely depends on increased absorption of water from the alimentary canal. Atropine, which lessens this, acts antagonistically to calomel in its diuretic effect. Opium inhibits calomel diarrhoea, but by lessening peristalsis increases the possibility of water absorption from the large intestine. Diuresis therefore is usually observed with a combination of calomel and tincture of opium. W. D. H.

**Certain Reactions of the Blood in Carcinoma.** JOHN A. SHAW-MACKENZIE (*Proc. Roy. Soc. Med.*, 1912, 5; Therap. Section, 152—161).—The serum of the blood taken from cases of carcinoma manifests two important properties: (1) an increased antitryptic value, and (2) a power to accelerate the action of pancreatic lipase which is far in excess of what is found in normal serum. These

two reactions when present together furnish a valuable aid in the diagnosis of malignant disease, and their absence excludes the diagnosis of cancer. After recovery or improvement, or during a period of quiescence, the accelerating action on lipase remains high or may even increase; but under the same conditions the antitryptic value falls to normal. Such reactions serve therefore to control treatment and to indicate progress towards recovery or the reverse. The lipoclastic acceleration is possibly a natural factor in resistance to disease in carcinoma and other conditions. If this is admitted, serum and other substances which increase this protective mechanism are indicated in treatment. Already beneficial results in malignant disease, both in mice and men treated on such lines, have been noted, but the cases are as yet too few to yield decisive results. W. D. H.

**Does an Abnormal Composition of Fat Play Any Part in Cancer?** LEONHARD WACKER (*Zeitsch. physiol. Chem.*, 1912, 78, 349—364).—An abnormal composition of the body fat, such as a high content of olein or oleic acid, does not occur in carcinoma. W. D. H.

**The Respiratory Exchange of Diabetic Patients on Different Forms of Diet.** ALFRED LEIMDÖRFER (*Biochem. Zeitsch.*, 1912, 40, 326—340).—The Zuntz-Geppert apparatus was employed in these researches. It was found that in severe cases on a rigid diet there was an increase in the oxygen consumption as compared with the normal without any marked increase of carbon dioxide output. There was no marked deviation from the normal in moderately severe cases. In the severe cases the oxygen consumption diminished to the normal, without any marked change in the carbon dioxide output, when the patients were put on an oat or vegetable diet. The increase of oxygen consumption in severe cases on a rigid diabetic diet is to be ascribed to the increase in the intermediary metabolism, such as the formation of sugar and acetone-substances from proteins and fats, and as these are not oxidised, the fact that there is no increased carbon dioxide output can be accounted for. The increased respiration of diabetic patients, furthermore, can be explained by the acidosis and the stimulating action of the acid metabolism products, such as the acetone substances, on the breathing centres. S. B. S.

**The Diminution of the Antitryptic Power of the Blood in Diabetes.** KURT MEYER (*Biochem. Zeitsch.*, 1912, 40, 125—127).—As it has been stated that in diabetes there is a diminution of the antitryptic action of the blood, experiments were carried out to ascertain whether this is due to the sugar. A rabbit was rendered hyperglycæmic by the injection of adrenaline, and it was found that in spite of the marked increase of sugar, there was no change in the antitryptic value. The conclusion is drawn that in cases of diabetes, side by side with the destruction of pancreas and diminution of trypsin production, there is also a diminution of antitrypsin formation. S. B. S.

**The Resorption of Drugs from Ointments made from Different Bases.** F. SAUERLAND (*Biochem. Zeitsch.*, 1912, 40, 56—82).—Iothione, methyl salicylate, spirosal, and saligenin were made up into ointment containing 25% of the drug with the following media as bases: lard, vaselin, and lanolin. The conditions of application in the various experiments were made as nearly similar as possible, and the resorption was determined by estimating the time and rate of excretion, in one set of drugs of iodine, and in the other of salicylic acid in the urine. The results, which are chiefly of technical pharmaceutical interest, show marked differences of the rate of resorption of the various drugs, according to the medium in which they are mixed.

S. B. S.

**The Rapidity of Absorption of Drugs Introduced into the Cerebro-spinal Fluid.** WALTER E. DIXON and WILLIAM D. HALLIBURTON (*Proc. physiol. Soc.*, 1912, vii; *J. Physiol.*, 44).—Small doses of drugs with easily recognisable physiological actions, such as atropine and adrenaline, when introduced into the cerebro-spinal fluid produce their typical effects in a very short time, usually within a few seconds, in fact almost as rapidly as if introduced intravenously. They are, therefore, probably absorbed directly into the blood, and not *via* the lymph stream. This view is supported by experiments with methylene-blue; no traces of blood colour can be seen in the thoracic lymph during half an hour after it is placed in the cerebro-spinal space.

W. D. H.

**The Relationship between Chemical Constitution and Pharmacological Action of Preparations of Antimony.** OTTO BRUNNER (*Arch. exp. Path. Pharm.*, 1912, 68, 186—208).—A number of experiments on animals are recorded, in which many compounds of antimony were given by various methods. The main outcome of the research is that all the powerfully acting compounds contain trivalent, and all the feebly acting ones contain quinquevalent, antimony. No evidence of habituation to either group was obtained.

W. D. H.

**The Concentration of Ethyl Chloride in the Blood of Warm- and Cold-blooded Animals at the Onset of Narcosis.** ERNST FREY (*Biochem. Zeitsch.*, 1912, 40, 29—35).—The concentration was determined by finding the concentration of ethyl chloride in the air just necessary to produce narcosis, and ascertaining the amount of gas which could be dissolved by water under these conditions. The concentration of this aqueous solution was assumed to be the concentration of ethyl chloride in the plasma at the onset of narcosis. It was found that this onset takes place in the case of a frog when the air contains 1.8% of the chloride. Water at the temperature of air dissolves 0.5679% when in contact with pure ethyl chloride. When ethyl chloride forms only 1.8% of the atmosphere in contact with water, the latter dissolves 0.01022%. The narcosis experiments were carried out under a pressure slighter higher than atmospheric. Under these conditions, water dissolves 0.0104% of ethyl chloride, and this is assumed to be the concentration of the gas in frog's blood at the onset

of narcosis. A mouse is narcotised in an atmosphere containing 3·6% of ethyl chloride. The solubility of the gas in water at the body temperature of the mouse when water is in contact with undiluted gas is 0·2709%. From these numbers it is calculated that onset of narcosis takes place in a mouse when the blood contains 0·0101% of ethyl chloride, a number hardly differing from that found in the case of the frog. S. B. S.

**Pharmacology and Therapeutics of Lecithin and Phytin.** WILLIAM BAIN (*Lancet*, April 6th, 1912; Reprint 12 pp.).—Lecithin is a valuable drug in anæmia and debility; it acts as a metabolic stimulus, for it is impossible to conceive that the small extra amount of nitrogen and phosphorus given in a few grains of lecithin can act as a tissue-former in any substantial degree. Its good effect on the nervous system is secondary to improvement in general nutrition, and not because it is a "brain food." Its most striking effect is on the blood, red and white corpuscles (especially lymphocytes) and hæmoglobin being all increased. Illustrative experiments on rabbits are given in detail. The effects with phytin on animals were so unsatisfactory that it was not tried clinically. The paper also discusses such questions as the comparative therapeutic value of inorganic and organic compounds of phosphorus, and the possible ways in which minute quantities of certain constituents of the food may influence nutrition. W. D. H.

**Hypotensive Action of Guanine.** ALEXANDRE DESGREZ and DORLÉANS (*Compt. rend.*, 1912, 154, 1109—1111).—Experiments on dogs and rabbits show that guanine diminishes the arterial blood pressure when administered by intravenous injection. As guanine arises in the pancreas, the antagonistic effects of this organ to those of the suprarenal secretion are probably due, in part, to the action of this substance. W. O. W.

**Formation of Homogentisic Acid After the Administration of Large Quantities of *l*-Tyrosine by the Mouth.** EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1912, 77, 454—461).—Hitherto efforts to produce alkaptonuria by the administration of tyrosine and phenylalanine have failed. Similar experiments on dogs and rabbits by the author, even with large doses, also gave a negative result, largely because these substances are badly absorbed and may produce vomiting. Doses of 30 grams of tyrosine and 25 grams of phenylalanine in man also proved ineffectual. In one man, however, a positive result was obtained: the laboratory attendant took 50 grams of tyrosine within twenty-four hours, and homogentisic acid was separated from his urine. W. D. H.

**Action of Atropine in the Organism.** RENE METZNER (*Arch. exp. Path. Pharm.*, 1912, 68, 110—159).—Rabbit's blood or serum destroys atropine both in vivo and in vitro, so that it no longer dilates the pupil or paralyses the organs; 5 mg. may be destroyed per c.c. of blood in twenty-four to forty-eight hours. The actual power is variable, but no relationship to thyroid disease, such as Fleischmann

described, was found. This power of the blood explains the variable doses of the alkaloid necessary to paralyse the vagus in different rabbits. It is destroyed by heating the serum to 60°, but not by extraction with ether; the atropine is broken up into tropine and tropic acid.

W. D. H.

**The Behaviour of Atropine in the Organism of the Rabbit.** ARTHUR HEFFTER and G. FICKEWIRTH (*Biochem. Zeitsch.*, 1912, 40, 36—47).—There is no storing up of atropine in the organism of a rabbit after prolonged dosage per os. A part is secreted unchanged in the urine, together with very small quantities of tropine and a small quantity of an unknown base. The total quantity of bases recovered is about half that of the atropine ingested. A considerable amount of tropine is burnt up in the organism. Atropic acid is also burnt up. The disappearance of atropine can be explained on the assumption that it is first hydrolysed and the hydrolytic products are then oxidised. Atropine is also hydrolysed when left in contact with putrefying urine. The total bases in the urine are estimated by extracting for several days with ether, dissolving out from an aliquot part of the solution with excess of *N*/100-hydrochloric acid, and titrating the excess of acid with *N*/100-alkali in the presence of iodoeosin. Tropine and atropine could be separated by a fractional crystallisation of the aurichlorides.

S. B. S.

**The Resistance of the Rabbit to Atropine.** ARTHUR HEFFTER and G. FICKEWIRTH (*Biochem. Zeitsch.*, 1912, 40, 48—55).—In comparing the toxic doses of atropine when administered per os, subcutaneously, and intravenously, it was found that the intravenous toxic dose was about one-tenth of that of the subcutaneous. The greater resistance to atropine of the rabbit as compared with the dog was found to exist only when the drug was administered subcutaneously. In this case about twice as much more atropine is necessary to kill the rabbit than is toxic to the dog. This is due to the fact that rabbit's blood can render atropine non-toxic. When injected directly into the blood-stream, however, the atropine rapidly disappears therefrom, and is taken up by the tissues.

S. B. S.

**Rate of Evolution of Hydrocyanic Acid from Linseed Under Digestive Conditions.** SYDNEY H. COLLINS (*Univ. Durham Phil. Soc.*, 1912, 4, 99—106. Compare Henry and Auld, *Abstr.*, 1908, ii, 619).—The results show that under normal conditions hydrocyanic acid is not likely to be liberated in dangerous quantity in the stomach of an animal fed on linseed cake.

A regulated current of hydrogen, provided by the apparatus described elsewhere (this vol., ii, 548), was passed through a weighed quantity of linseed cake, mixed with water and kept at a definite temperature by a special thermostat (this vol., ii, 548). The hydrocyanic acid formed was thus removed, absorbed in sodium hydroxide solution, and estimated colorimetrically. It was found that the production of hydrocyanic acid is greatly retarded by the presence of acid in much less amount than is normally present in the stomach of a

healthy animal. The amount of hydrocyanic acid formed is also dependent on the amounts of glucoside and enzyme present, and on the temperature and various other factors. It is possible that poisoning by linseed cake might occur in animals suffering from indigestion of such a character that the food is not rendered acid, but such cases are probably very rare.

T. A. H.

**The Toxicity of Sugar Solutions to *Fundulus* and the Apparent Antagonism between Salts and Sugars.** JACQUES LOEB (*J. Biol. Chem.*, 1912, 11, 415—420).—*Fundulus* lives longer in solutions of sucrose and dextrose made up in a  $M/5$ -solution of the chlorides of sodium, potassium, and calcium than when the salts are absent. In these solutions, bacteria cause acid formation, and the apparent antagonism between sugar and salt is really antagonism between acid and salt. The fatal effect of the sugar solutions can be prevented by renewing the solution every twenty-four hours. Greater concentrations of sugar than  $M/4$  are, however, toxic in themselves.

W. D. H.

**Adrenaline-like Actions of Cobra Venom.** JAMES A. GUNN (*Quart. J. exp. Physiol.*, 1912, 5, 67—82).—Without going so far as to assert that the active principle of cobra venom is adrenaline, many resemblances in the action of the two substances in stimulating sympathetic nerve-endings and in the comparative resistance of different animals towards both materials are pointed out.

W. D. H.

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## Chemistry of Vegetable Physiology and Agriculture.

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**The Chemical Composition of Tubercle Bacilli.** THEODOR PANZER (*Zeitsch. physiol. Chem.*, 1912, 78, 414—419).—The fat extracted from tubercle bacilli contains no cholesterol (digitonin method). Evidence was found of the presence of a gelatinising material (pectin) and of a carbohydrate-yielding substance, which is probably chitin.  
W. D. H.

**Fermentative Degradation of Cellulose.** HANS PRINGSHEIM (*Zeitsch. physiol. Chem.*, 1912, 78, 266—291).—Cellulose is exposed to the action of bacteria for a certain time, and when decomposition is vigorous an antiseptic is added. This checks the development of gas, but allows the action of the endo-enzymes to continue. After a short period of action of these, it is possible to show the presence of cellobiose and of dextrose in the degradation products. This result was obtained with denitrifying bacteria, with bacteria which produce methane or hydrogen, and with thermophil bacteria, the last being especially active in causing decomposition. Other non-reducing carbohydrates are not formed. The range of activity of the cellulase is

from 20° to 70°. It is very stable towards antiseptics. Iodoform was found to be the best antiseptic for arresting the bacterial action, which is only temporarily stopped by the other antiseptics.

Deductions are drawn from the intermediate formation of cellobiose from cellulose by digestion as to the behaviour of cellulose in the animal stomach.

E. F. A.

**The Effect of Lecithin on the Fermentation of Sugar by Bacteria.** ALBERT A. EPSTEIN and H. OLSAN (*J. Biol. Chem.*, 1912, 11, 313—322).—The tendency of lecithin is to increase fermentation, but there are differences between different sugars, although no relationship between this difference and the chemical composition of the sugars was made out.

W. D. H.

**The Surface Tension of the Living Plasma Membranes of Yeasts and Moulds.** BRUNO KISCH (*Biochem. Zeitsch.*, 1912, 40, 152—188).—The cells were treated with various solutions, and the injury was investigated (*a*) by ascertaining whether invertin had escaped from the cells when the latter, after centrifugalisation from the liquid under investigation, were treated with a sucrose solution; (*b*) by ascertaining whether the cells were capable of germinating when transferred after treatment to a normal culture medium. It was found that yeast cells were permanently injured when treated with a liquid of which the surface tension was less than half of that at the inter-surface water-air. Acids of a concentration higher than *N*/9 also permanently injured the cells. Various moulds behave in the above respects like yeast. Spores and conidia are more resistant. The changes produced by acids and liquids of low surface tension are irreversible.

S. B. S.

**Proteolysis of Yeast.** ALBERT J. J. VANDEVELDE (*Bull. Soc. chim. Belg.*, 1912, 26, 107—112).—A study of the proteolysis of yeast cells under the influence of different reagents, namely, hydrochloric acid, sodium carbonate, pepsin, trypsin, and tartaric acid, an admixture of chloroform and acetone being used to prevent putrefaction during prolonged incubation (compare Abstr., 1907, i, 372).

W. G.

**Fermentative and Proteolytic Phenomena of Yeast Cells in the Presence of Iodoform, Bromoform, Chloroform, and Acetone.** ALBERT J. J. VANDEVELDE (*Biochem. Zeitsch.*, 1912, 40, 1—4).—Yeast cells in the presence of acetone and an acetone solution of iodoform were capable of fermenting sugar, although the amount of carbon dioxide evolved was less than normal. The cells when sown afterwards in a normal fermentation liquid produced normal fermentation. In presence of acetone solutions of bromoform and chloroform, the fermentation was much less, and the cells when sown afterwards in a normal liquid produced no fermentation. The proteolysis of yeast cells in presence of chloroform and acetone under varying conditions was also investigated, and the distribution of the nitrogen amongst the coagulable proteins, proteoses, peptones, and amino-acids was determined, the results being tabulated.

S. B. S.

**Alcohol, a More or Less Excellent Food for Different Fungi.** PAUL LINDNER and STEFAN CZISER (*Woch. Brauerei*, 1912, 29, 1—7; *Zeitsch. Spiritusind.*, 1912, 73—75).—An account of numerous experiments which demonstrate that many yeasts (especially mould yeasts) increase vigorously when kept in a 2—4% solution of alcohol, a portion of the alcohol being employed for the production of new cells. In some cases the growth in alcohol was equal to (or greater than) that in ammonium sulphate-dextrose solutions. Numerous illustrations of the cultures, with the tabulated results of the experiments, are given in the original. F. M. G. M.

**Fermentation by Yeast. II.** HANS VON EULER and HELMER BÄCKSTRÖM (*Zeitsch. physiol. Chem.*, 1912, 77, 394—401).—The sodium salt of hexosephosphoric acid accelerates fermentation of dextrose by living yeast, but is itself not fermented by the yeast. The addition of double the quantity of the ester salt has no further effect on the rate of fermentation. An equivalent quantity of sodium dihydrogen phosphate causes a slight acceleration of fermentation.

Well-washed dry yeast together with sodium hexosephosphate is unable to cause fermentation in dextrose solutions, but on the addition of the washings, fermentation takes place. The hexosephosphate is therefore not the co-enzyme; this is a confirmation of the view expressed by Harden and Young (*Abstr.*, 1910, i, 292; i, 643). E. F. A.

**Fermentation and Production of Formic Acid by Yeast. A Correction.** HARTWIG FRANZEN and O. STEPPUHN (*Zeitsch. physiol. Chem.*, 1912, 78, 164. Compare this vol., ii, 475).—A correction of the theoretical considerations involved in the unsymmetric elimination of water from the glycol form of dihydroxyacetone, leading to the formation of  $\alpha$ -lactic acid and of formic acid. E. F. A.

**Formation of Acetaldehyde in the Alcoholic Fermentation of Sugar.** S. KOSTYTSCHIEFF (*Ber.*, 1912, 45, 1289—1293\*).—Zinc chloride was found to have an inhibitory action on the production of carbon dioxide from dextrose or sucrose by hefanol (dried yeast), whilst at the same time a small quantity of acetaldehyde was produced. The resulting mixture was distilled, and the aldehyde identified in the distillate by the blue coloration obtained with sodium nitroprusside and diethylamine, and also by means of its *p*-nitrophenylhydrazone. By fermenting 200 grams of sucrose for four days in presence of 5 grams of zinc chloride, 0.4917 gram of the *p*-nitrophenylhydrazone was obtained.

No aldehyde, or merely a trace, was obtained from the fermentation of sugar in the absence of zinc chloride, or from the autofermentation of the yeast in presence of zinc chloride. No formaldehyde could be detected in the products, but indications of the presence of formic acid were obtained.

In these experiments the aldehyde is probably a primary product of the fermentation of the sugar, and may thus be an intermediate

\* and *Zeitsch. physiol. Chem.*, 1912, 79, 130—145.

compound in alcoholic fermentation, further reacting with formic acid to produce carbon dioxide and alcohol according to the theory of Schade. W. J. Y.

**Chemical Composition and Formation of Enzymes. IV. The Adaptation of a Yeast to Galactose.** HANS VON EULER and DAVID JOHANSSON (*Zeitsch. physiol. Chem.*, 1912, 78, 246—265).—Various researches are quoted to show that micro-organisms habituated to various nutrients develop enzymes capable of splitting them. This is confirmed in the present experiments on yeast in a nutritive medium containing galactose. Details of the rate of formation of galactose are given. W. D. H.

**Paralysis of Enzymes.** L. LICHTWITZ (*Zeitsch. physiol. Chem.*, 1912, 78, 128—149).—Tammann's term paralysis of enzymes (Fermentlähmung) means the harmful effect produced on an enzyme by the action of the products formed. It was found that yeast grown in solutions of invert-sugar possesses a smaller invertase action than yeast grown in solutions of pure sucrose; this weakening depends on the concentration of the invert-sugar. W. D. H.

**Conversion of Amines into Alcohols by Yeasts and Moulds.** FELIX EHRlich and P. PISTSCHIMUKA (*Ber.*, 1912, 45, 1006—1012).—The action of yeasts on amino-compounds has been extended to the primary amines, which are converted thereby into the corresponding alcohols with liberation of ammonia:  $R \cdot CH_2 \cdot NH_2 + H_2O = R \cdot CH_2 \cdot OH + NH_3$ .

In this way tyrosol (*p*-hydroxyphenylethyl alcohol; Abstr., 1911, i, 127) was obtained from *p*-hydroxyphenylethylamine, and isoamyl alcohol from isoamylamine.

Brewers' and distillers' yeasts only bring about the conversion to a very slight extent, either when grown in the medium or when added in quantity in the form of pressed yeast. Wild yeasts and mycoderma yeasts, such as *Willia anomala*, and moulds of the type of *Oidium lactis*, however, convert these amines almost quantitatively into the alcohols when grown in sterile solutions of these substances containing sugar and nutrient salts. Amines are probably intermediate compounds in the formation of alcohols from amino-acids by yeast. W. J. Y.

**Decomposition of Fats by the Higher Fungi. I. Degradation of Glycerol and the Absorption of Fat by the Fungus Cell.** ALB. SPIECKERMANN (*Zeitsch. Nahr. Genussm.*, 1912, 23, 306—331).—Methods are described for growing mould fungi in solid or liquid culture media containing fatty acids or fats. Glycerol is an excellent nutrient for moulds, the growth of which in media containing glycerol depends on the nature of the nitrogenous nutrient. When alkali nitrates are used, there is a selective absorption of nitrate by the fungus and the medium becomes alkaline; when, however, inorganic ammonium salts are used, the ammonia is selectively absorbed and the solution becomes acid. Ammonium salts give better results than nitrates, potassium nitrate gives a larger dry weight of fungus than

the equivalent quantity of sodium nitrate, and ammonium sulphate, gives a larger yield than the equivalent amount of nitrates, including ammonium nitrate.

Glycerol is converted by the fungus into carbon dioxide and water, about two-thirds to three-quarters of the former passing away and the rest of the carbon being incorporated in the new growth.

Experiments are described in detail with illustrations to explain the absorption of fats by the cells. The conclusion is drawn that the fatty acids are absorbed in the main in the form of soap solutions. The glycerides are hydrolysed to glycerol and fatty acid by a lipase outside the cell.

E. F. A.

**Action of Substances Readily Soluble in Water, but not Soluble in Oil, on the Growth of the *Penicillium glaucum*.** JACOB BÖESEKEN and H. WATERMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 14, 1112—1117. Compare this vol., ii, 283, 306).—Retardation phenomena quite different from those observed with substances soluble in oil and probably attributable to the action of hydrogen ions have been observed with oxalic, malonic, tartaric, and lactic acids at definite concentrations. These can be prevented by neutralisation; by the addition of gentisic acid (harmless in itself) to a solution of tartaric acid below the harmful concentration, they can be revived. The harmful concentration of the H-ions for *Penicillium glaucum* has been determined at  $1 \times 10^{-5}$  gram-equivalent; for *Aspergillus niger* at  $4.5 \times 10^{-5}$ .

It is surmised that the coagulation of the colloidal plasmic wall is attended by the neutralisation of the colloids having a negative charge by the hydrogen ions with a positive charge.

H. W.

**Displacement by Water of Nutritive Substances in Seeds.** GUSTAVE ANDRÉ (*Compt. rend.*, 1912, 154, 1103—1105. Compare this vol., ii, 198).—As far as the loss of potassium by exosmosis is concerned, grains of wheat and haricot beans behave in the same way as the potato tubers previously studied. The organs, however, lose nitrogen much more slowly and less completely when steeped in water, experiments showing that about 90% of the nitrogen is present in a non-diffusible form. After two hundred and eighty-one days' steeping, wheat lost 79.57% of its phosphoric acid and haricots 83.4%; most of the loss occurred in the first twenty-seven days.

W. O. W.

**Carbon Nutrition of Phanerogams by means of Certain Organic Acids and their Potassium Salts.** RAVIN (*Compt. rend.*, 1912, 154, 1100—1103).—Experiments on radishes grown in Knop's nutritive medium show that addition of malic, tartaric, citric, succinic, and oxalic acids to the medium causes an increase in the weight of the plants and in the respiratory quotient, the acids being absorbed and assimilated by the organism. The corresponding acid and normal salts of the acids have less effect on development.

W. O. W.

**Phosphorus Compounds Soluble in Water and Alcohol from Plants.** V. HERMANN ULRICH (*Arch. exp. Path. Pharm.*, 1912, 68, 171—185).—The compounds of phosphorus in plants are

divided into (1) those soluble in alcohol; (2) those soluble in water, and (3) proteins. Analytical details are given of the total phosphorus in the alcoholic and acid aqueous extracts of various kinds of oats and bran.

W. D. H.

**Function of Magnesium in Green Plants.** LUIGI BERNARDINI and GIUSEPPE MORELLI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 357—362. Compare Bernardini, *Staz. Agr. Sper. Ital.*, 1909, Nos. 1 and 2).—The authors have estimated the total phosphorus, the phosphatide phosphorus (soluble in ether and alcohol), the phosphorus soluble in 1% hydrochloric acid, the phytin phosphorus, the total magnesium, the magnesium soluble in 1% hydrochloric acid, and the magnesium removed by water in the case of wheat seeds and of etiolated and normal seedlings at various stages of development. In seedlings germinated in the dark, the phosphatide and phytin phosphorus decreases; the proportion of phosphorus soluble in hydrochloric acid to magnesium similarly removable remains constant, whilst the magnesium soluble in water increases until all the phytin has disappeared. When germination occurs in light, the phosphatide phosphorus tends to increase when chlorophyll appears, whilst the phytin phosphorus is not increased; the magnesium soluble in water increases at first, but diminishes again when chlorophyll has been formed. Phytin is to be regarded as a magnesium salt of inositol-hexaphosphoric acid, and the authors consider that the results now obtained indicate that it is hydrolysed by an enzymatic process in germination, magnesium phosphate being formed, and that the transport of the reserve phosphorus is effected in this form. It is suggested that the phosphorus of the salt then serves for the production of nucleoprotein, whilst the magnesium enters into the composition of the chlorophyll.

R. V. S.

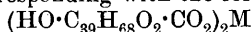
**The Tannin in the Seed Coverings of Barley.** ALBERT REICHARD (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 214—219).—It was recently shown by A. J. Brown (compare Abstr., 1909, ii, 386) that a membrane in the testa of the barley grain exerts a selective action on dissolved substances, inasmuch as only certain of them can pass through it into the seed. The author now shows that there is a kind of tannin in the seed covering of barley, and that there is an undoubted parallelism between the power of a substance to dissolve this material and to penetrate the membrane.

The investigation was made by a variety of methods including direct action of different substances on sections of barley with subsequent examination of the membrane for tannin, and also by adding various substances to ordinary tannin in a test-tube and observing the effects. Further, since there is some evidence that the tannin in barley is associated with a protein, the action of different substances on a compound of protein and tannin was also examined.

The behaviour of a large number of substances as regards their action on the tannin and their capacity of penetrating the membrane is discussed in detail. The results are ascribed mainly to a solvent action on the tannin, thus permitting diffusion, or in certain cases to a

coagulating effect of the reagents on the tannin complex, which prevents diffusion. G. S.

**Chemical Investigation of the Substance of the Birch.** GEORG GRASSER (*Collegium*, 1911, 393—402, 405—412, 413—420, 421—425).—An investigation of the products obtainable from the tissue of birch trees. The following compounds were isolated: an acid,  $\text{HO}\cdot\text{C}_{39}\text{H}_{68}\text{O}_2\cdot\text{CO}_2\text{H}$ ; its *di*- and *mono*-potassium salts; the copper, iron, and zinc salts corresponding with the formula



(M = metal); the mercury salt,  $(\text{HO}\cdot\text{C}_{39}\text{H}_{68}\text{O}_2\cdot\text{CO}_2\text{Hg})_2$ ; the lead salt,  $\text{HO}\cdot\text{C}_{39}\text{H}_{68}\text{O}_2\cdot\text{CO}_2\text{Pb}\cdot\text{OH}$ ; the ethyl ester,  $\text{HO}\cdot\text{C}_{39}\text{H}_{68}\text{O}_2\cdot\text{CO}_2\text{Et}$ ; the acid chloride,  $\text{HO}\cdot\text{C}_{39}\text{H}_{68}\text{O}_2\cdot\text{COCl}$ , and the corresponding amide.

Oxidation with potassium permanganate or nitric acid yielded an odour of butyric acid, and dry distillation furnished a yellow, viscous oil containing a complicated mixture of substances.

Full details of the methods employed with the analytical results are given in the original. F. M. G. M.

**Oil from *Datura stramonium*.** HANS MEYER and ROBERT BEER (*Monatsh.*, 1912, 33, 311—331).—The fatty oil obtained by extraction of the crushed seeds of the thorn apple with benzene is a clear, light green liquid,  $D^{15}$  0.923, acid number 8.1, saponification number 202.2, iodine number 113.2, unsaponifiable matter 1.01. It becomes viscous at  $-12^\circ$ . The unsaponifiable matter showed a very distinct phytosterol reaction, and had m. p.  $128^\circ$ . Neither volatile fatty acids or stearic acid were present, but minute amounts of acids of high molecular weight were found. The composition of the oil is approximately: palmitic acid 10%, daturic acid (*n*-heptadecic acid) 2.5%, oleic acid 62%, linoleic acid 15%, unsaponifiable matter (phytosterol) 1%, glycerol 9.6%.

By oxidation of the unsaturated acids obtained from the oil with potassium permanganate in alkali solution, dihydroxystearic acid was obtained, together with tetrahydroxystearic acid (sativic acid), m. p.  $162$ — $163^\circ$ , and small quantities of an acid, m. p.  $173^\circ$ . These two acids are apparently stereoisomeric, and it is proposed to name them  $\alpha$ - and  $\beta$ -sativic acids respectively. Among the secondary products of the oxidation, azelaic and butyric acids were identified.

Bromination of the unsaturated acids in petroleum solution led to the isolation of tetrabromostearic acid, m. p.  $117^\circ$ . Dibromostearic acid was also formed.

An attempt to determine the relationship between the tetrabromostearic acid and the two sativic acids, by treatment of the former with silver acetate and subsequent hydrolysis of the acetylsativic acid so obtained, was only partly successful. When, however, tetrabromostearic acid was treated with zinc and the product oxidised by cold alkaline permanganate, only  $\alpha$ -sativic acid, m. p.  $163^\circ$ , was obtained.

H. W.

**Nitrogenous Constituents of Fungi.** CAMILLE REUTER (*Zeitsch. physiol. Chem.*, 1912, 78, 167—245).—By artificial digestion of fungi (*Boletus edulis*) a residue is finally obtained which does not give the

protein reactions or yield protein bases when hydrolysed by acids. This consists of chitin and a hemicellulose. It is not certain whether the protein itself contains a glucosamine complex. The protein of fungi is not soluble in 10% sodium chloride solution, and differs, therefore, from the globulins of plant seeds. On hydrolysis, glycine, alanine, valine, leucine, phenylalanine, proline, and aspartic and glutamic acids were obtained. Alanine, leucine, and proline were obtained in greatest quantity. Tyrosine was identified on tryptic digestion. The fungi also contained, present as such, the following bases: guanine, adenine, hypoxanthine, trimethylhistidine, choline, trimethylamine, putrescine, guanidine, phenylalanine, leucine, and *dl*-alanine, the latter constituting the greater part of the free amino-acids present. Small quantities of purine compounds are also present. The viscosine is apparently a mixture of glycogen and a purine compound, probably xanthine united with dextrose to a glucoside similar to vernin.

On further autolysis of the amino-acids and bases listed, physiologically active substances, such as agmatine, etc., are probably formed. In one case, *isoamylamine*, phenylethylamine, and *p*-hydroxyphenyl ethylamine were found, choline and adenine having vanished. Apparently a decarboxylation takes place through the agency of enzymes in the fungi.

Using air-dry *Boletus edulis* about 4% is soluble in ether, consisting of fat and cholesterol, 12% is soluble in alcohol, and 28% is soluble in water, leaving a residue of 46%, consisting of protein 30%, amorphous carbohydrate 10%, and chitin 6%.  
E. F. A.

Presence of Arbutin in the Leaves of "*Grevillea robusta*" (Proteacea). ÉMILE BOURQUELOT and (Mlle.) A. FICHTENHOLZ (*Compt. rend.*, 1912, 154, 1106—1108 \*).—Arbutin was isolated from the leaves of *Grevillea robusta* by extraction with alcohol. The presence of methylarbutin could not be detected.  
W. O. W.

Detection of Arsenic and Lead in Wines, Wine Lees, and Grape Seed from Vines Sprayed with Lead Arsenate. P. CARLES and LÉONCE BARTHE (*Bull. Soc. chim.*, 1912, [iv], 11, 413—417).—Particulars are given of the dates on which lead arsenate was applied and the method of spraying adopted. The arsenic was estimated by the Marsh process, controlled by the Bougault method, and the lead was determined by a process already described by one of the authors (*Bull. Soc. pharm. Bord.*, 1911, p. 441). The following conclusions are drawn: Wines prepared from vines sprayed in a normal manner with lead arsenate contained neither arsenic nor lead, whilst those from vines which had been excessively sprayed yielded negligible traces of both poisons. The wine lees in both cases contained lead and arsenic in quantities too large to be disregarded. Grape seed from vines normally sprayed were free from arsenic and lead (compare Breteau, *Abstr.*, 1908, ii, 887; Moreau and Vinet, *Abstr.*, 1911, ii, 326, 529; Mettelet and Touplain, *Ann. Falsif.*, 1912, p. 9).  
T. A. H.

The Transformations of Nitrogen in Different Soils. HUGO FISCHER (*Landw. Jahrb.* 1911, 41, 755—821).—A detailed

\* and *J. Pharm. Chim.*, 1912, [vii], 5, 425—430.

account of experiments on the changes that nitrogen undergoes in different soils under varying conditions of temperature, moisture, and fertilisation. The processes studied were ammonification, nitrification, denitrification, direct nitrogen assimilation by the bacteria of the soil, and by those of the Leguminosæ; the influence of the presence of fungi and other organisms on the above processes was also considered.

F. M. G. M.

**Movement of Nitric Nitrogen in the Soil and its Relation to Nitrogen Fixation.** ROBERT STEWART and J. E. GREAVES (*Utah Agric. Coll. Exper. Stat. Bull.* 114, 1911, 181–194).—Experiments continued during eight years showed that under very favourable chemical and bacteriological conditions, the amount of nitrogen as nitrates to a depth of ten feet never exceeded 300 lb. per acre.

Referring to the experiments of Headden (*Agric. Exper. Stat. Colorado Agric. Coll. Bull.* 178, 1911), who showed that certain soils sometimes contained more than 2000 lb. of nitrogen as nitrates, which he attributed to abnormal fixation of atmospheric nitrogen under exceptionally favourable conditions, it is pointed out that the amounts of chlorides rise and fall coincidentally with the nitrates, so that it is evident that both are derived from the subsoil.

N. H. J. M.

**Influence of Molasses on Nitrification in Cane Soils.** S. S. PECK (*Exper. Stat. Hawaiian Sugar Planters' Assoc.*, 1912, *Bull.* 39; compare *Bull.* 34).—Application of molasses to land otherwise manured in the usual manner resulted in the production of unavailable forms of nitrogen from the nitrates; it also retarded the ammonification and nitrification of organic manures and the nitrification of ammonium salts. Addition of calcium carbonate along with molasses was without effect.

N. H. J. M.

**Effect of Heat and Oxidation on the Phosphorus of the Soil.** PETER P. PETERSON (*Univ. Wisconsin Agric. Exper. Stat. Research Bull.* 19, 1911).—The solubility of the phosphorus of wavellite is increased from 4 to 50% by heating for five hours at 200°, and to 100% by heating to 240°. In the case of dufrenite the solubility is only slightly increased. The phosphorus in soils does not become more soluble in *N/5*-nitric acid by heating at 100°. At 130° there is a slight increase, whilst at higher temperatures, up to 200°, the solubility of the phosphorus increases rapidly. A still greater increase in the solubility of soil phosphorus was obtained by decomposing most of the organic matter with hydrogen peroxide. After this treatment, heating at 240° has no further action.

The solubility of the mineral phosphates in soils does not seem to be increased by heating to 240°.

As regards the effect of oxidation with hydrogen peroxide on other soil constituents, it was found that the solubility of the iron and aluminium in *N/5*-nitric acid is increased, whilst calcium and manganese are not affected. The conclusion is drawn that the increased solubility of the phosphorus after treatment with hydrogen

peroxide is due to a great extent to the liberation of iron and aluminium phosphates present in insoluble organic matter.

Oxidation has very little effect on the solubility of the phosphorus in subsoils, and heating has more effect on subsoil phosphorus than with surface soils.

N. H. J. M.

**Action of Some Solvents on Soil Nutrients; Phosphoric Acid, Potassium, and Calcium in the Original and Absorptively Combined Condition.** OTTO ENGELS (*Landw. Versuch.-Stat.*, 1912, 77, 269—303).—The solubility of the absorbed phosphoric acid of light, non-calcareous soils in water free from carbon dioxide is considerably greater than that of calcareous and heavy soils. In the case of potassium the differences are less marked. Water saturated with carbon dioxide dissolved twice as much phosphoric acid as water alone, whilst the solubility of the absorbed potassium in a sandy soil was increased from 34·08 to 55·08%.

A 2% solution of citric acid dissolved almost the whole of the absorbed phosphoric acid in a sandy soil, but much less in the case of a heavy soil. The same solution dissolved about 90% of absorbed potassium in sandy soil and about two-thirds in heavy soils.

N. H. J. M.

**Acid Secretion of Roots and the Solubility of Soil Nutrients in Water containing Carbon Dioxide.** THEODOR PFEIFFER and E. BLANCK (*Landw. Versuchs-Stat.*, 1912, 77, 217—268).—Pot experiments in which cereals and leguminous plants were manured with mineral phosphates. In some pots, the soil water was supplied with carbon dioxide.

The results seem to show that the action of roots in dissolving mineral substances cannot be due to respired carbon dioxide alone, but to organic acids secreted by the roots. Carbon dioxide, artificially supplied, was only slightly effective in the case of readily soluble phosphate; phosphorite requires a stronger acid.

N. H. J. M.

**Influence of Rice Bran on the Manurial Value of Phosphoric Acid Contained in Oil Cakes.** Z. KIDA (*J. Coll. Agric. Imp. Univ. Tokyo*, 1911, 1, 367—379).—It was shown by Tsuda (*Bull. Coll. Agric. Tokyo*, 1, 167) that the phosphorus in oil cakes is chiefly in the form of phytin, some being also present as lecithin and as nuclein. Owing to the high temperatures to which oil cakes are exposed, the activity of the phytase present seems to be greatly reduced, and the phosphorus compounds only gradually become available when the cake is applied as manure.

It is found that by mixing rice bran with the cake, the organic phosphorus compounds are rapidly converted into soluble inorganic forms when the conditions are suitable.

N. H. J. M.

**Records of Drainage in India.** JOHN W. LEATHER (*Mem. Dept. Agric. India*, 1912, 2, 63—140).—A summary of the results obtained with the drain-gauges at Cawnpore since 1903 (Hayman, *Abstr.*, 1908, ii, 890), and with similar drain-gauges at Pusa since 1906. At Cawnpore the evaporation was about 18 inches in the 72-inch gauges and

16 inches in the 36-inch gauges, or about half the rainfall; whilst at Pusa the evaporation was about 28 inches, or two-thirds of the rainfall.

The amount of nitrogen as nitrates in the drainage from the Cawn-pore gauges which had no crop varied from 80 to 100 lb. per annum in the 72-inch gauges, and from 50 to 60 lb. in the others. At Pusa the nitrogen as nitrates amounted on the average to 75 lb. and 66 lb. from two gauges. The amounts are much less in the case of the cropped gauges.

Nitrification is vigorous after the first heavy rain, but only continues for a short period.

N. H. J. M.

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## Analytical Chemistry.

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**Apparatus for Gas Measurement.** PAUL NICOLARDOT (*Bull. Soc. chim.*, 1912, [iv], 11, 406—410).—The apparatus is designed for the indirect determination of alumina in aluminium by measurement of the hydrogen evolved in dissolving the metal in acid. Wiborgh's apparatus for carbon dioxide is used as a basis, but the following changes are made : (1) the capacity of the measuring vessel, including the graduated tube, is enlarged to 1.5 litres ; (2) the measuring vessel and its accessories are placed in a vessel with glass windows and filled with running water, so that the temperature remains constant throughout the experiment ; (3) an auxiliary pipette is attached to the measuring vessel by which a known volume of air may be introduced into the measuring vessel to facilitate measurement of the hydrogen when the volume of the latter is small. The apparatus is figured in the original.  
T. A. H.

**Colorimeter for Rapid Work with Widely Varying Standards.** CHARLES H. WHITE (*J. Amer. Chem. Soc.*, 1912, 34, 659—662).—A colorimeter is described which consists essentially of two wedge-shaped hollow glass prisms of exactly the same dimensions and open at the wide end for the admission of the solutions to be tested. The wedges are held side by side in a vertical position in a camera and can be raised or lowered by a rack and pinion. The solutions are viewed through a narrow, horizontal slit across the middle of the camera. The carriers are graduated to correspond with the length of the wedges, the zero of the scale being opposite the index when the sharp edge of the wedge is opposite the slit in the screen. For carrying out a determination, equal quantities of the standard substance and the material to be tested are dissolved and diluted to equal volumes. The solutions are introduced into the wedges, and the wedge containing the unknown solution is set at the graduation representing the percentage, or some multiple of it, of the colouring matter in the standard, and the wedge containing the standard solution adjusted until the two agree in colour. The percentage of

colouring matter in the solution under examination is then found by reading the scale on the carrier containing the standard. The method enables determinations to be made with great rapidity, and the possibility of using any section of the wedge from its thinnest to its thickest part renders the apparatus available for a wide range, and thus permits of much variation in the quantity of the substance used for the test.

E. G.

**Filtering Device for the Collection of Separate Liquids.** KLEEMANN (*Chem. Zeit.*, 1912, 36, 506).—Ammonium phosphomolybdate is frequently washed with ammonium nitrate, followed by alcohol and ether, or acetone. In order to avoid waste of the latter liquids, a device is described for collecting them separately. This is a vacuum dessicator, consisting of a porcelain vessel with glass lid ground on. The vessel is divided into three compartments by vertical partitions, each being provided with a tap. The funnel holding the Gooch crucible has a curved neck, which can be turned until it is over any one of the compartments.

C. H. D.

**A Perforated Silica Plate for Excluding Flame Gases from a Crucible During Ignition.** ALEXANDER C. CUMMING (*Proc. Roy. Soc. Edin.*, 1912, 32, 17—18).—A silica plate, 5 inches square, is bored with a central hole sufficiently large to admit a crucible to one-half its depth. The plate is held in an inclined position during ignition. The hole may be bored on a lathe by means of a copper tube fed with carborundum.

C. H. D.

**The Sensitiveness of Indicators.** HENRY T. TIZARD (*Brit. Assoc. Report*, 1911, 268—276).—A general account of the subject. Indicators which give a sharp end-point usually give an accuracy within 2 parts in 1000. If in any volumetric operation a sharp end-point is not obtained with any indicator, the device must be adopted of selecting an indicator the colour of which is sensibly affected in a pure solution of the salt of the strong and weak electrolytes, and then, using a comparison solution of the salt containing the same proportion of indicator, titrating until the same colour is obtained. A colorimeter may be used for the purpose.

C. H. D.

**Combined Influence of Alcohol and Neutral Salts on the Sensitiveness of Phenolphthalein.** EMIL LENK and JULIUS MONDSCHIEIN (*Chem. Zeit.*, 1912, 36, 534—535).—Results of experiments are recorded showing the increase in acidity of ammonium chloride solutions when these were diluted with water, alcohol, and both water and alcohol respectively. It is already known that an ammonium chloride solution which is neutral to litmus exhibits an acid reaction towards phenolphthalein; this acidity is increased appreciably on the addition of water, and to a very considerable extent by the addition of alcohol; the acidity is also increased to a large extent when both water and alcohol are added. Magnesium sulphate, ammonium sulphate, zinc salts, and aluminium salts behave in a similar way towards phenolphthalein (compare Abstr., 1908, ii, 806).

W. P. S.

**New Method for the Quantitative Analysis of Solutions by Precise Thermometry.** THEODORE W. RICHARDS and JOHN W. SHIPLEY (*J. Amer. Chem. Soc.*, 1912, 34, 599—603).—A method is described for the analysis of solutions which depends on the observation of the precise temperature at which the solution attains exactly the same density as a previously calibrated, solid float. It is shown that this "floating equilibrium temperature" is an almost linear function of the concentration, and hence the reading of the temperature gives a direct determination of the concentration. The method is exceedingly sensitive and is capable of detecting small changes of concentration with great accuracy. When the relations have once been determined for any given substance, the process can be used either to determine concentrations by means of known temperature differences, or to determine temperature differences by means of known concentrations, and can thus be employed, not only for the analysis of solutions but also for calibrating thermometers. It is also of value for the preparation of exact standard solutions for volumetric analysis or other purposes.

E. G.

**System of Qualitative Analysis for the Common Elements.**  
**V. Detection of the Acidic Constituents.** ARTHUR A. NOYES (*J. Amer. Chem. Soc.*, 1912, 34, 609—643. Compare Abstr., 1907, ii, 391; 1908, ii, 538; 1909, ii, 431).—An account is given of the results of an investigation carried out with the object of establishing a systematic and generally applicable method for detecting the acidic constituents of substances, and simultaneously indicating the approximate quantities present. The volatile acids are removed by heating the solid substance with 85% phosphoric acid diluted with two and a-half times its volume of water, and it has been found that by this means they can be separated into two classes according to the readiness with which they distil. Full details are given and numerous supplementary tests are described.

E. G.

**Hydrographical-Chemical Methods.** ERNST RUPPIN (*Zeitsch. anorg. Chem.*, 1912, 75, 69—96. Compare Abstr., 1910, ii, 405, 452; 1911, ii, 123).—An improved apparatus is described for taking samples of sea-water at known depths, and for measuring the temperature of the water at the same time.

It is not possible to estimate the total salinity directly, as sea-water loses carbon dioxide and hydrogen chloride on evaporation. The value is given within 0.01% by estimation of the chlorine,  $S = 0.030 + 1.8050 \text{ Cl}$ , the method used being titration with silver nitrate until a distinct orange tint is perceptible in the solution containing potassium chromate, and comparison with a normal water, containing 3.5% of sodium chloride. The salinity may also be determined by measuring the specific gravity or the refractive index. Sulphates are estimated gravimetrically. The ratio  $\text{SO}_4 : \text{Cl}$  is practically constant for northern seas.

Carbon dioxide cannot be estimated satisfactorily on board ship, but should be estimated in a laboratory on shore, using sealed samples. Oxygen is best estimated by taking 250 c.c. of the water, adding

1 c.c. of a solution containing 48% sodium hydroxide and 15% potassium iodide, followed by 0.5 c.c. of an 80% solution of manganous chloride. After the precipitate has settled, 5 c.c. of hydrochloric acid, D 1.19, are added, and the solution is shaken until all has dissolved. After transferring to another flask, the iodine liberated is titrated with *N*/50-thiosulphate, standardised by means of potassium iodate.

For the determination of the alkalinity, 200 c.c. of sea-water are acidified with 15 c.c. of *N*/20-hydrochloric acid, and boiled to expel carbon dioxide. After cooling, 15 c.c. of *N*/20-potassium iodate are added, followed by 10 c.c. of 10% potassium iodide, and after one and a-quarter hours the liquid is titrated with *N*/50-thiosulphate. The alkalinity is best expressed in c.c. of carbon dioxide per litre.

Measurements of the carbon dioxide pressure are made by shaking a sample of the water in a special tube, and analysing the air in contact with it.

C. H. D.

**The Estimation of Sulphur in Insoluble Sulphides.** THEODOR ST. WARUNIS (*Ber.*, 1912, 45, 869—870).—In a large porcelain crucible, 0.5 gram of the finely powdered sulphide is mixed intimately with a mixture of 4 parts of sodium carbonate and 3 parts of copper oxide. After covering with a thin layer of the sodium carbonate-copper oxide mixture, heat is applied gradually, the full strength of a bunsen burner being finally maintained for two hours. During the heating the contents of the crucible must be stirred from time to time with a stout platinum wire. After cooling, the contents of the crucible are extracted with water, filtered, and the residue boiled with a solution of sodium carbonate and then washed with water until the disappearance of an alkaline reaction. The collected filtrates are made acid with hydrochloric acid, and evaporated down in the usual way to render the silica insoluble. After collecting the silica, the sulphuric acid is precipitated and weighed as barium sulphate.

When the sulphide contains no metal which gives an insoluble sulphate, the contents of the porcelain crucible are best dissolved directly in hydrochloric acid.

T. S. P.

**Estimation of Sulphides in Lime Liquors.** J. R. BLOCKEY and P. V. MEHD (*J. Soc. Chem. Ind.*, 1912, 31, 369—371).—The quantity of sulphides in lime liquors may be estimated by titration with *N*/10-zinc sulphate solution containing 50 grams of ammonium chloride per litre, sodium nitroprusside being used as an external indicator. The presence of ammonium chloride is necessary in order to prevent the zinc being precipitated as hydroxide. The authors also discuss the reactions which take place between calcium hydroxide and sodium sulphide, and give the results of experiments on the absorption of alkali by pelts in lime liquors containing sulphide, and on the amount of hide substance dissolved by the liquors.

W. P. S.

**The Estimation of Sulphates in Solution by the Volumetric Physico-chemical Method.** ALBERT BRUNO and P. TURQUAND D'AUZAY (*Compt. rend.*, 1912, 154, 984—986).—The application of the method of Dutoit and Duboux (*Abstr.*, 1908, ii, 781, 892) to wines

gives results differing from those obtained by the gravimetric method in 75% of the specimens examined. The discordance is shown to be due to the disturbing effect of organic acids and of acid tartrates in the volumetric process.

W. O. W.

**Estimation of Nitrogen in Betaine and in Molasses, etc.** HUGO STOLTZENBERG (*Zeitsch. Ver. deut. Zuckerind.*, 1912, 440—445).—Results of experiments carried out by the author show that the Kjeldahl method of estimating nitrogen yields low results in the case of betaine unless the digestion with sulphuric acid is continued for many hours; the addition of such substances as phosphoric oxide, copper sulphate, and mercuric oxide increases the rate at which the nitrogen is converted into ammonia, but even then it is necessary to heat the mixture for ninety minutes in order to obtain the correct amount of nitrogen. The presence of sugar also accelerates the oxidation, and for the estimation of nitrogen in molasses or other materials containing betaine, it is recommended that 3 grams of the sample be heated with a mixture consisting of 25 c.c. of sulphuric acid containing 10% of phosphoric oxide, 1 gram of copper sulphate, and 1 gram of mercuric oxide, until a colourless solution is obtained. The heating is then continued for one hour, and the ammonia estimated in the usual way.

W. P. S.

**Estimation of Ammonia in Carbonated Waters.** GEORGE D. ELDON and NORMAN EVERS (*Analyst*, 1912, 37, 173—176).—Results of experiments are recorded which show that the presence of carbon dioxide interferes with the coloration obtained when a distillate containing ammonia is treated with Nessler's reagent; should the amount of carbon dioxide exceed 50 parts per 10,000 of water, no coloration is obtained. For the estimation of free ammonia in waters containing much carbon dioxide, it is, therefore, recommended that the portion of the water taken for the estimation should be acidified with sulphuric acid and distilled until 50 c.c. of distillate have been collected; this distillate is rejected. The water is then treated with sodium hydroxide, in quantity equivalent to the acid added, sodium carbonate is added, and the estimation carried out in the usual way.

W. P. S.

**Estimation of Boric Acid in Nickel Plating Baths.** ALFRED WOGGINZ and JOHANN KLITEL (*Chem. Zeit.*, 1912, 36, 433—434).—The nickel is removed from 100 c.c. of the bath by electrolysis, which at the same time destroys any citric acid which may be present. The solution is then evaporated to dryness after the addition of 10 grams of solid sodium hydroxide. The residue is dissolved in 25—30 c.c. of hydrochloric acid, the solution warmed to expel carbon dioxide, cooled, and then neutralised with sodium hydroxide, using methyl-orange as indicator. One hundred c.c. of a 10% solution of mannitol are then added and the free boric acid titrated with alkali, using phenolphthalein as indicator. The quantity of boric acid present in the sample taken should be such that at least 30—50 c.c. of  $N/5$  sodium hydroxide are required in the titration.

The evaporation with sodium hydroxide destroys ammonium salts, since in their presence inaccurate results are obtained in the estimation of boric acid. Glycerol may be used in place of mannitol, but it is then necessary to allow for the acidity of the glycerol in the titrations.

T. S. P.

**Combustion of Volatile Organic Liquids.** LATHAM CLARKE (*J. Amer. Chem. Soc.*, 1912, 34, 746—747).—A method for the combustion of volatile organic liquids is described which obviates the disadvantages attending the usual method in which the liquid is weighed in a small bulb provided with a capillary tube.

The liquid to be analysed is weighed in a small U-tube which is fitted with ground glass stoppers, each perforated on one side with a small hole which, in a certain position of the stopper, coincides with the opening of the side outlet tube. The U-tube, containing a weighed quantity of the liquid, is connected to the combustion tube by the end of one of the side-arms which is ground to fit into a ground glass joint, sealed on to the end of the combustion tube, the latter having previously been drawn out. The other side-arm of the U-tube is attached to the drying apparatus. The combustion tube has meanwhile been heated until it has become red-hot. The stoppers of the U-tube are now turned so as to permit a stream of dry air to pass over the surface of the liquid to be analysed. The vapour of the liquid is carried with the air into the combustion tube and over the hot copper oxide. If the liquid has a low b. p. (such as that of ether), the lower part of the U-tube should be immersed in cold water in order to prevent too rapid volatilisation, whilst for a liquid of b. p. between 100° and 125°, the tube should be heated by placing the lower part in water at 50—60°.

E. G.

**The Electrical Method of Morse and Gray for the Simultaneous Estimation of Carbon, Hydrogen, and Sulphur in Organic Compounds.** E. EMMET REID (*Amer. Chem. J.*, 1912, 47, 416—429).—A modified form of Morse and Gray's apparatus (Abstr., 1906, ii, 399) is described. A quartz combustion tube is considered preferable to one of glass. The small porcelain tube which is placed within the combustion tube (compare Morse and Taylor, Abstr., 1905, ii, 480) is also replaced by a quartz tube, and the end passing through the rubber stopper is bent upwards for convenience at an angle of 45° from the horizontal. It has been found that the asbestos plug in the middle of the combustion tube is liable to retain some of the sulphur, and quartz wool has therefore been substituted for it. Certain other modifications are suggested.

Although carbon, hydrogen, and sulphur can be estimated simultaneously by this method with great accuracy, it has been found, particularly in the case of substances which burn irregularly, that it is more satisfactory and takes less time to make two separate combustions, one for the estimation of the carbon and hydrogen and the other for that of the sulphur.

E. G.

**A New Potash Apparatus.** WLADIMIR SKINDER (*Chem. Zeit.*, 1912, 36, 477).—The inflow tube is sealed into the outer vessel, passes

to the bottom, and is there expanded into a disk with a few central holes. The second vessel is ground into the first, and has a tube sealed in near the top and descending to the bottom. A third vessel, ground into the second, is similar in construction. C. H. D.

**A New Silver Spiral for Use in Organic Elementary Analysis.** AUGUSTUS H. FISKE (*Ber.*, 1912, 45, 870—871).—A carefully cleaned spiral of copper gauze is immersed in a solution of silver nitrate until a uniform deposit of silver has been formed. It is then heated in the blow-pipe flame until the silver just begins to melt, after which it may be used to retain the halogens in the elementary analysis of organic compounds. It gives very good results even with compounds containing as much as 80—86% Br.

If one-half only of the copper spiral is immersed in silver nitrate solution, a combined copper-silver spiral is obtained, which is useful in certain cases. T. S. P.

**Winkler's Method for the Estimation of Carbon Dioxide in Water.** JOSÉ CASARES and S. PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1912, 10, 122—127).—In the authors' experience Winkler's method gives an average error of 2.5% as against 0.4% observed by Winkler. Working with smaller proportions, the error is very much greater and very irregular, amounting in one instance to 48.5%. G. D. L.

**Electro-analysis.** FREDERIC S. KIPPING, FREDERICK M. PERKIN, GEORGE T. BEILBY, THOMAS M. LOWRY, WILLIAM J. POPE, and HENRY J. S. SAND (*Brit. Assoc. Report*, 1911, 98—99).—Hildebrand's apparatus for electrolysis with a mercury cathode is improved by constructing the apparatus of silica. The central cell is kept concentric by having silica rods fused to it and to the inside wall of the outer vessel. C. H. D.

**Estimation of the Mineral Constituents of Foods.** RAGNAR BERG (*Chem. Zeit.*, 1912, 36, 509—511, 523—524).—Methods are given for the estimation of the various mineral constituents which occur in food materials. It is recommended that the substance be heated with nitric and sulphuric acids until all organic matter has been destroyed, and the resulting solution used for the estimation of iron, aluminium, manganese, calcium, magnesium, potassium, sodium, and phosphoric acid. For the estimation of chlorine, a portion of the dry substance is heated with sulphuric acid and chromic acid, and the gases evolved collected in silver nitrate solution containing nitric acid. Sulphur is estimated by mixing the substance with potassium hydroxide, drying it, and fusing the residue with a mixture of potassium sodium carbonate and sodium peroxide. Nitrates may be extracted from the substance by means of alcohol; the alcoholic extract is evaporated, and the residue boiled with potassium hydroxide solution. The solution is then acidified and the nitrate reduced to ammonia by means of iron. W. P. S.

**Cobaltinitrites and their Application to Analytical Chemistry.** LAURIE LORNE BURGESS and OLIVER KAMM (*J. Amer. Chem. Soc.*, 1912, **34**, 652—659).—When a drop of a freshly prepared 25% solution of sodium cobaltinitrite is added to a solution containing 1% of potassium, a yellow precipitate is immediately produced consisting either of potassium cobaltinitrite,  $K_3Co(NO_2)_6$ , or the dipotassium sodium salt,  $K_2NaCo(NO_2)_6$ . As the sodium in sodium cobaltinitrite is replaced by potassium, the products become less soluble, and if the sodium in the potassium sodium salts is replaced by silver, even less soluble salts, the silver potassium cobaltinitrites, are formed, which are of value for the detection of minute quantities of potassium. If a drop of the sodium cobaltinitrite solution is added to a solution containing less than 100 parts of potassium per million, no perceptible precipitate is produced, but if the test is repeated in presence of 0.01*N* silver nitrate, a copious, yellow precipitate immediately appears. This test has the advantage of being more sensitive than the older method (compare Bow-er, *Abstr.*, 1910, ii, 346, 999), and may be carried out by adding a single drop of the reagent to 100 c.c. of the solution. Reference is made to the substances likely to interfere with the test.

Ammonium, rubidium, caesium, and thallium also yield insoluble double silver cobaltinitrites, and the possibility of using some of these in analytical work is indicated. Double cobaltinitrites of lead with ammonium, potassium, rubidium, caesium, and thallium have been prepared. E. G.

**The Separation of Calcium from Magnesium.** O. KALLAUNER and I. PRELLER (*Chem. Zeit.*, 1912, **36**, 449—451, 462—464).—Very discordant results are frequently obtained in the estimation of calcium when present in small quantity relatively to magnesium, as in magnesite. In such cases the oxalate method is only trustworthy if dilute solutions are used and a large quantity of ammonium salts is present, together with an excess of ammonium oxalate, and if the solution is filtered immediately after precipitation, or if precipitation is repeated. The calcium obtained is always 0.15 to 0.2% low, owing partly to incomplete precipitation, and partly to re-solution during washing.

Most methods depending on the separation of the sulphates by means of alcohol are untrustworthy when the magnesium is in large excess. Good results are given by repeated precipitation of the calcium sulphate, or by the use of a solution of lithium sulphate in a mixture of 10% ethyl alcohol and 90% methyl alcohol. The precipitated calcium sulphate is redissolved in hydrochloric acid and precipitated as oxalate. C. H. D.

**Estimation of Copper.** E. C. KENDALL (*Chem. News*, 1912, 104, 184—186).—A modification of the well-known iodometric process. Before titrating, the solution containing about 0.2 gram of the metal in 30—50% nitric acid is neutralised so as to leave about 5 c.c. of free acid, and nitrous compounds are removed by adding a few c.c. of sodium hypochlorite (5 c.c. = 30 c.c. of *N*/10-thiosulphate). When the blue

solution has become greenish, no more need be added, and after a few minutes the chlorine liberated is removed by adding, all at once, 10 c.c. of a 5% solution of phenol and blowing over the surface of the liquid. Aqueous sodium oxide is now added until a precipitate forms, which is then redissolved by a few drops of acetic acid. After adding 10 c.c. of 30% potassium iodide, the iodine liberated, which represents the copper, is titrated with thiosulphate, using starch as indicator. No return of the blue colour, so often experienced in the ordinary process, ever occurs.

L. DE K.

**The Oxalate-Permanganate Process for the Determination of Copper Associated with Cadmium, Arsenic, Iron, or Lead.** H. L. WARD (*Amer. J. Sci.*, 1912, [iv], 33, 423—432).—Copper may be separated from cadmium by precipitation with oxalic acid in the presence of nitric acid, and subsequent evaporation to dryness. After removing the cadmium compound by means of dilute nitric acid, the copper oxalate is titrated as usual with standard permanganate. A better way, however, is to dissolve the mixed nitrates, containing about 0.15 gram of copper, in 100 c.c. of liquid containing half its volume of glacial acetic acid. After adding 5 to 10 c.c. of nitric acid, the whole is heated to boiling, and the copper is precipitated by adding 2 to 4 grams of solid oxalic acid. Copper may be separated from arsenic acid by the process given for cadmium. From small amounts of iron, it may be separated by the desiccation process, but the best plan is to add 6 grams of oxalic acid to the aqueous solution of the salts, and completing the separation of the copper by adding two volumes of acetic acid.

Copper may be separated from lead by removing the latter with sulphuric acid in a solution containing half its volume of acetic acid. The copper is then precipitated with oxalic acid. Unless it is desired to weigh the lead sulphate, this need not be filtered off. L. DE K.

**Estimation of Aluminium in Fæces.** CARL L. A. SCHMIDT and D. R. HOAGLAND (*J. Biol. Chem.*, 1912, 11, 387—392).—The method used briefly consists in incinerating the fæces and sulphuric acid in a silica dish. The soluble aluminium is dissolved out by warm dilute hydrochloric acid. The residue is ignited and fused with sodium carbonate in a platinum dish; the aluminium is then dissolved out from the mass with dilute hydrochloric acid, and added to the main portion. Tin is precipitated by hydrogen sulphide. Diammonium hydrogen phosphate is added to the filtrate, which is heated and while hot a solution of ammonium thiosulphate is added, and then one of ammonium acetate. The precipitate is allowed to settle, redissolved in hydrochloric acid, and the aluminium again precipitated. The precipitate is washed with hot water to remove chlorides, and ignited in a transparent silica crucible until constant weight is reached, to remove excess of phosphoric acid. The results quoted appear to be good.

W. D. H.

**Determination of Ferrous Iron in Chromite.** S. PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1912, 10, 78—81).—The mineral is

dissolved by heating with concentrated hydrochloric acid in a sealed tube filled with carbon dioxide at  $210^{\circ}$ , and the ferrous iron estimated by means of permanganate.

G. D. L.

**Estimation of Ferric Iron in the Presence of Certain Organic Substances.** JOHN T. HEWITT and GLADYS RUBY MANN (*Analyst*, 1912, 37, 179—182).—Ferric iron in the presence of organic substances may be titrated with thiosulphate solution, ammonium thiocyanate being used as the indicator; a small quantity of copper sulphate is added as a catalyst, and the titration is continued until the red colour of the ferric thiocyanate disappears. The end-point of the titration is not, however, sharply defined, and it is better to add a slight excess of thiosulphate and to titrate this with iodine solution, employing starch as the indicator. Mineral acid is added, if required, to break up feebly ionised salts (for example, ferric acetate), but an excess must be avoided. Results of numerous estimations of ferric iron in the presence of different organic substances are given. Acetates do not affect the titration if mineral acid is added, as acetic acid itself has but slight influence; ammonium sulphate is also without effect, unless present in very large quantity. The titration cannot be made in the presence of salicylates and salicylic acid, but it is unaffected by sugars, and not greatly by tartaric acid or citric acid.

W. P. S.

**The Reduction of Ferric Iron (1) by Sulphurous Acid and (2) by Zinc Dust.** ALEXANDER C. CUMMING and E. W. HAMILTON SMITH (*Proc. Roy. Soc. Edin.*, 1912, 32, 12—16).—The reduction of ferric solutions by sulphurous acid takes places rapidly if the solution contains very little free acid, but not at all if alkaline to litmus. In practice, rapid reduction is ensured by adding enough ammonia to precipitate part of the iron, followed by treatment with sulphur dioxide.

Reduction by zinc is little influenced by the amount of acid, but an excess of acid slightly retards reduction. Alloys of zinc with aluminium, silver, and cadmium have not been found to have any advantage over pure zinc. Zinc dust is found to succeed well (compare Carnegie, *Trans.*, 1888, 53, 468). The ferric solution should contain as little free acid as possible. About a gram of zinc dust is added, and, after boiling, the solution is poured through a filter on which a gram of zinc dust is placed. Reduction is complete, but it is necessary to wash with hot dilute sulphuric acid to remove the last of the iron. The solution must be nearly neutralised beforehand. Zinc turnings may also be used, packed to a depth of four inches in a calcium chloride tube, through which the boiling ferric solution is poured. The tube and turnings are then washed with hot, very dilute sulphuric acid.

C. H. D.

**Sensitive Reagent for Acetylene.** F. LAVILLA LLORENS (*Anal. Fis. Quim.*, 1912, 10, 139—141).—A cuprous solution is prepared by saturating copper sulphate solution with sodium chloride, warming, and adding sodium hydrogen sulphite until the solution loses all green

colour. A few drops of ammonia increase the sensitiveness of the reagent, but are not necessary to secure the precipitation by acetylene.

G. D. L.

**Microchemical Investigation of Alcohols.** JAIME FERRER (*Anal. Fis. Quim.*, 1912, 10, 105—113).—Potassium ethyl and methyl xanthates have the same crystalline form, but the cadmium ethyl salt is amorphous, only crystallising after a long time, whereas the cadmium methyl salt, precipitated by adding a solution of the potassium salt to cadmium iodide, is at first amorphous, but rapidly becomes crystalline. When the cadmium methyl salt is prepared by adding the cadmium iodide to the potassium methyl xanthate, the precipitate at first re-dissolves, but on further addition of cadmium solution, separates as glistening, prismatic crystals. Potassium propyl and isobutyl xanthates both form needle-shaped crystals, and differ from the methyl and ethyl compounds in that their crystals group in rectangular patterns. The isoamyl salt forms ill-defined, rhomboidal crystals, grouping in isolated clusters.

The above reaction serves to indicate methyl alcohol in the presence of ethyl alcohol when the proportion of the former is not less than 10 to 15%. The presence of higher alcohols along with ethyl alcohol is shown by the formation of prismatic crystals amongst the acicular forms of the ethyl cadmium salt.

G. D. L.

**Detection of Methyl Alcohol.** FERDINAND WIRTHLE (*Zeitsch. Nahr. Genussm.*, 1912, 23, 345—346).—It is suggested that conversion of the alcohols into their corresponding iodides and fractional distillation of the latter may afford a means of detecting the presence of methyl alcohol in ethyl alcohol. Methyl iodide has b. p. 41—42°, and ethyl iodide 71—72°; after the iodides have been thus separated, a determination of the saponification number will indicate the presence of methyl alcohol, this number being 394.3 for methyl iodide and 358.9 for ethyl iodide.

W. P. S.

**New Method for the Estimation of Glycerol in Wine.** S. ROTHENFUSSE (*Zeitsch. Nahr. Genussm.*, 1912, 23, 332—337).—The wine is first treated with sodium carbonate, and crystallised stannous chloride is then added until the mixture is slightly acid in reaction; the precipitate, which consists of the tin salts of lactic and other organic acids, is removed by filtration, and the filtrate is treated with ammoniacal basic lead acetate solution in order to precipitate sugars (compare Abstr., 1910, ii, 463). Any sucrose present is also precipitated if a somewhat large quantity of the lead solution is added, but the casein solution (*loc. cit.*) must be omitted; should the wine contain more than 1% of sucrose, a preliminary heating after the addition of an acid is necessary. To the filtrate from the lead precipitate are added a small quantity of sodium phosphate and the requisite amount of potassium carbonate, and the solution is evaporated to about one-third of the original volume of the wine. When cold, an excess of potassium permanganate is added, the excess is destroyed, after the lapse of thirty minutes, by the addition of hydrogen peroxide,

and the oxalic acid formed by the oxidation of the glycerol is precipitated as calcium oxalate in the presence of acetic acid. The oxalate is then collected, dissolved in sulphuric acid, and titrated with potassium permanganate solution. W. P. S.

**Estimation of Dextrose in Urine and Blood.** E. FRANK (*Zeitsch. physiol. Chem.*, 1912, 78, 165).—A reply to the criticisms of Oppler (this vol., ii, 100 ; compare Moeckel and Frank, Abstr., 1910, ii, 554, 1116). E. F. A.

**Methods of Estimating Sugar in Blood.** E. HERZFELD (*Zeitsch. physiol. Chem.*, 1912, 77, 420—424).—The various methods at present in use are referred to. Titration methods usually give a higher result than the polarimeter ; although dextrose is the principal sugar present, lævulose, isomaltose, and pentose may also be present, as well as certain complexes, such as compounds of sugar with lipoids and proteins. A new method is proposed, which depends on the fact that alkaline solutions of aldoses, ketoses, and dextrans decolorise methylene-blue on heating. The blood or blood-serum must be fresh to avoid glycolysis ; it is then quantitatively freed from protein by a solution of metaphosphoric acid, and the filtrate, after being rendered alkaline, is titrated and heated with a standard methylene-blue solution. The method is stated to give very correct results, and is specially useful in dealing with dilute sugar solutions. W. D. H.

**The Quantity of Formic Acid in Honey.** HEINRICH FINCKE (*Zeitsch. Nahr. Genussm.*, 1912, 23, 255—267).—Formic acid is not always present in natural honey ; many samples examined by the author were free from this acid, whilst some contained a volatile, reducing acid (as estimated by a method described previously ; Abstr., 1911, ii, 232), possibly formic acid, in quantity generally not exceeding 0·003%. Some of the samples contained up to 0·02% of a reducing acid (calculated as formic acid). The acid was present partly in the free state and partly in the form of salts ; esters of formic acid could not be detected. It was also found that small quantities of formic acid are formed when invert sugar solutions are submitted to steam distillation, provided that the sugar has been inverted by means of an acid ; if the inversion has been made with invertase, the resulting invert sugar does not yield formic acid when distilled. W. P. S.

**The Analysis of Vinegar.** JOHN H. PATERSON (*Proc. Univ. Durham Phil. Soc.*, 1912, 4, 144—146).—A sample of vinegar is boiled in a reflux apparatus with animal charcoal, previously freed from carbonates, and filtered. Twenty grams of the filtrate are diluted to 100 c.c., and portions of 25 c.c. are titrated with *N*/10-potassium hydroxide and phenolphthalein. The solution thus obtained is further diluted to 100 c.c., and titrated with *N*/10-sulphuric acid after adding six drops of methyl-orange. In another vessel, six drops of methyl-orange are added to 100 c.c. of water and titrated with the same acid until the same shade is produced. The quantity of acid taken is, in a normal vinegar, greater than the quantity of alkali, on account of the presence

of sodium acetate and tartrate, but if adulterated with mineral acid these are replaced by free acetic and tartaric acids. The method depends on the fact that sodium acetate and tartrate are alkaline to methyl-orange. C. H. D.

**Tests for Salicylic Acids.** ETIENNE BARRAL (*Bull. Soc. chim.*, 1912, [iv], 11, 417—420).—Four tests are described, which in conjunction with Jorissen's and Denigès' tests are believed to cover all the forms in which salicylic acid is likely to occur.

Two drops of a 5% solution of a salicylate are mixed in a test-tube, with 2 c.c. of sulphuric acid, and sodium nitrite solution (10%) added, drop by drop, with continuous agitation. The liquid becomes in succession orange-yellow, reddish-orange, blood-red with a greenish tinge, gooseberry-red. On adding water, it becomes orange coloured. This reaction is also given by esters of salicylic acid if these do not contain a radicle, which gives an independent colour reaction with the reagents. It is not given by sulphosalicylic acid, probably because the reaction depends on the introduction of a nitroso-group in the para-position. Jorissen's reaction (sodium nitrite in presence of acetic acid and cupric sulphate) is given by sulphosalicylic acid, probably because in this case the  $-NO$  group enters in position five or six.

Two to three c.c. of a 1% salicylic acid solution, warmed with a pea-sized fragment of ammonium persulphate, become yellow, then brown, and finally give a brownish-black precipitate. On long boiling the liquid becomes colourless.

Three or four drops of a dilute salicylic acid solution dissolved in one to two c.c. of sulphuric acid give with two or three drops of Mandelin's reagent a stable indigo-blue colour. This is also afforded by salicylic esters.

Salicylic acid gives with Schlagdenhaufen's reagent in the cold, a yellow coloration, which deepens to orange and orange-brown on warming, with the formation of a red precipitate of selenium and the evolution of hydrogen selenide. This test is given by sulphosalicylic acid, aspirin, and methyl salicylate. T. A. H.

**Reactions of Sulphosalicylic Acid.** ETIENNE BARRAL (*Bull. Soc. chim.*, 1912, [iv], 11, 447—450).—With a view to ascertaining how sulphosalicylic acid is eliminated from the organism, the author has investigated the colour reactions of sulphosalicylic acid, especially those which serve to distinguish it from salicylic acid (compare preceding abstract).

With dilute ferric chloride solution, sulphosalicylic acid gives a Bordeaux-red tint, not destroyed by adding dilute hydrochloric acid (2%), and insoluble in ether, chloroform, or benzene. When both acids are present and the reagent is added drop by drop, the red tint is distinctly visible before the violet-red due to salicylic acid appears. Bromine water gives no precipitate with sulphosalicylic acid. Mandelin's reagent gives an indigo-blue tint with the sulpho-acid, and an olive-green with blue streaks with salicylic acid. Formaldehyde in sulphuric acid gives the same coloration with both acids. Denigès' methylglyoxal test for salicylic acid gives no colour with the sulpho-

acid. Millon's reagent gives a red tint with the sulpho-acid and orange-red with salicylic acid. The above are the most distinctive of the tests described.

T. A. H.

**Souring of Milk.** H. DROOP RICHMOND and HORACE C. HUISE (*Analyst*, 1912, 37, 168—171).—In estimating the acidity of milk the authors recommend that 11 c.c. of the milk should be placed in each of two similar beakers, and to one, which serves as the standard tint, one drop of a 0.01% alcoholic rosaniline solution is added; to the other beaker 1 c.c. of phenolphthalein solution is added, and the contents then titrated with *N*/11-strontium hydroxide solution until its tint is equal to that of the standard. The theoretical considerations relating to the souring of milk are also discussed from a mathematical point of view, and are supplemented by experimental work. As the result of these experiments the authors conclude that: (1) On growing in milk the organisms developing acidity become more active; (2) the organisms are retarded by the acidity they develop, and in the majority of cases this retardation is balanced by the acceleration due to their growing in milk; (3) at an acidity of 45° the retardation becomes very great; this point depends on the nature of the salts present in milk, as in whey it is about 30°, and in lactose solution about 20°. It follows that the organisms which normally cause the souring of milk are not those the normal habitat of which is milk, and it is not improbable that they are of intestinal origin.

W. P. S.

**The Schardinger Reaction of Cow's Milk.** PAUL H. RÖMER (*Biochem. Zeitsch.*, 1912, 40, 5—14).—The author confirms some previous experiments, from which the conclusion was drawn that the first milk drawn from the udder does not decolorise Schardinger's reagent, whereas, as a rule, the milk obtained at the end of the milking does. Purchased milk frequently fails to give the reaction. Furthermore, boiled milk, to which a small quantity of alkali or ferrous sulphate solution has been added, gives a positive reaction. For these reasons, the author draws the conclusion that Schardinger's test is of no value for ascertaining whether a given milk sample has been heated or not.

S. B. S.

**The Behaviour of Milk to Ammonium Sulphate, and a New Method for the Estimation of Lactose.** ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1912, 78, 89—95).—Half saturation of milk with ammonium sulphate leaves in the filtrate a small and variable amount of protein, which would interfere with the estimation of lactose polarimetrically in the filtrate; but if complete saturation is employed, there is no such difficulty.

W. D. H.

**Estimation of Morphine by Extraction with Phenylethyl Alcohol.** A. D. THORBURN (*J. Ind. Eng. Chem.*, 1911, 3, 754—756).—An aqueous solution of the morphine is rendered alkaline, and repeatedly extracted with a mixture of phenylethyl alcohol (3 parts) and benzene (1 part); the extract is carefully evaporated to a convenient volume on a steam-bath, transferred to a separating funnel, and vigorously shaken with 10 c.c. of *N*/10-sulphuric acid; the liquids

separated, the alcoholic portion thoroughly washed, and the excess of sulphuric acid titrated with *N*/10-potassium hydroxide with hæmatoxylin as indicator. The experiment requires about four hours for completion, and is designed for samples representing less than 0.175 gram of anhydrous alkaloid.

F. M. G. M.

**A Biological Method for the Detection of Morphine.** ORTO HERRMANN (*Biochem. Zeitsch.*, 1912, 39, 216—231).—The subcutaneous injection of morphine into mice produces, amongst other symptoms, paresis of the hind limbs and a peculiar characteristic catatonic condition of the tail, which forms an S-shaped curve over the back. Some conception as to the dose injected can be formed by observing the time of onset and duration of this condition. The reaction was tested with other alkaloids, and also with alcoholic extracts (containing tartaric acid) of organs of animals to which morphine had been administered. As a general result, the author draws the conclusion that the reaction can be used for forensic purposes, only as a preliminary reaction, which can be carried out with materials obtained in the preliminary stages of the Stas-Dragendorff process.

S. B. S.

**Refractive Indices of Solutions of Certain Proteins. VI. The Proteins of Ox-serum; a New Optical Method of Determining the Concentrations of the Various Proteins Contained in Blood-sera.** T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1912, 11, 179—200).—The value of  $\alpha$  (change in refractive index of a solvent caused by solution of 1 gram of protein) for the mixed proteins of ox-serum is the same whether they are dissolved in the native serum or precipitated by alcohol and redissolved in centinormal potassium hydroxide. It is also independent of dilution and acidification of the serum. Its value was  $0.00195 \pm 0.00002$ . Reiss' estimates are too high. The value of  $\alpha$  for the mixed proteins is the sum of the refractivities of the separate proteins. For refractometric purposes, the other constituents of the serum may be regarded as *M*/6-sodium chloride solution. The method may be employed for estimating the proteins, and the following values % are given for ox-serum: insoluble globulins 0.76; soluble globulins 2.34; albumins 5.4. Ox-serum does not contain the crystallisable albumin found in horse-serum.

W. D. H.

**Oxydases. V. Behaviour of Proteins and their Derivatives with the *p*-Cresol-tyrosinase Reagent.** ROBERT CHODAT (*Arch. sci. phys. nat.*, 1912, [iv], 33, 225—248. Compare this vol., ii, 399).—The abnormal behaviour of *d*-alanine in giving a red instead of a blue final coloration with *p*-cresol-tyrosinase was attributed to its belonging to the *d*-series. It is now found that both *d*- and *l*-alanine give a red colour, whilst *d*- and *l*-leucine both show a blue colour. *d*-Valine only furnishes a blue colour with the reagent with great slowness. Glutamine gives an intense blue coloration, arginine behaves similarly, whereas tryptophan acts in virtue of the alanine chain, giving only a rose-red coloration. With  $\alpha$ -proline a characteristic magenta reddish-violet is obtained, which did not become blue. Anthranilic acid gives no reaction.

Similar and characteristic shades of red becoming blue and violet are given by the di- and tri-peptides. The reagent has also been applied to peptones and proteins with which a red coloration only is produced; after their hydrolysis by means of ferments, the blue shades are produced in a characteristic manner.

In general, the proteins and their products of decomposition produce with *p*-cresol-tyrosinase a series of soluble pigments, varying from red to blue, yellow to green, or blue to violet.

Indole gives a very characteristic blue coloration with the reagent, and ultimately slender, deep blue needles crystallise. Methylindole gives no coloration under similar conditions. The synthetic pigment has very marked colouring powers. It is considered that pigments are formed naturally by the interaction of an oxydase, a phenol, and protein degradation products.

E. F. A.

**Estimation of Tannin in Solutions and Especially in Wines.** PHILIPPE MALVEZIN (*Bull. Soc. chim.*, 1912, [iv], 11, 300—302).—In using the process already described (*Abstr.*, 1911, ii, 779), it is advantageous to dissolve the zinc-tannin precipitate by pouring the diluted sulphuric acid over the precipitate on the filter. The permanganate solution should be added five drops at a time until the pink coloration persists for three minutes. One c.c. of *N*/10-permanganate solution is equal to 0.120 gram of gallotannin under these conditions. The results are accurate to within 1%. T. A. H.

**The Analysis of Hæmoglobin.** L. LUTZ (*Chem. Zentr.*, 1912, i, 289; from *Bull. sci. pharmacol.*, 18, 132—138).—All liquid hæmoglobin preparations with a violet sheen, and all crystalline preparations which show an alkaline reaction after precipitation with neutral alcohol containing ether, must be rejected. The analysis consists in the following operations. Estimation of water, ash, globulin, albumin, and proteoses, iron and hæmatin; tests for peptones, nuclealbumins, soluble salts, dried blood, and methæmoglobin; spectroscopic examination, and investigation of the action of heat on the solution. Neutral hæmoglobin solutions become turbid on heating, without agglutinating, and become clear again on addition of a drop of hydrochloric or acetic acid.

S. B. S.

**Estimation of Small Quantities of Bilirubin.** E. HERZFELD (*Zeitsch. physiol. Chem.*, 1912, 77, 280—284).—If an alcoholic solution of bilirubin is warmed with a few drops of *p*-dimethylaminobenzaldehyde solution, a green solution is obtained which lends itself to spectrophotometric observations. The reaction is not given by urobilin and certain lipochromes. By this method small quantities of bilirubin can be detected in the blood. Spectrophotometric estimation yields concordant results.

W. D. H.

**The Acetonitrile Test for Thyroid Substance in the Blood.** HERBERT O. LUSKY (*Amer. J. Physiol.*, 1912, 30, 63—73).—Thyroidectomised mice show the same resistance to acetonitrile as do normal mice; there are therefore other substances in the blood of such animals which cause an increased resistance, and the Hunt test is not specific for thyroid.

W. D. H.

## General and Physical Chemistry.

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**The "Constant of Refraction."** II. and III. FREDERICK SCHWERS (*Bull. Acad. roy. Belg.*, 1912, 252—282, 283—291. Compare this vol., ii, 309).—II. A number of "abnormal" cases have been examined, and the results obtained are set out. In determining the value of  $A$  (*loc. cit.*), abnormal results are obtained with a number of non-aqueous as well as some aqueous binary mixtures. In some cases there is observed to be an increase in density and a diminution in the refractive index (or vice versa) for the same mixture, the value of  $A$  being found to vary regularly with the concentration of one member of the mixture. In other cases, although the density and refractive index vary in the same direction, the value of  $A$  is still found to vary very notably in a definite manner. In some cases one of the physical constants varies greatly and the other negligibly, but always in the same direction.

These irregularities are often found when one of the members composing the mixture contains one or more halogen atoms. A particular study has been made of such mixtures, using liquids containing one, two, three, or four halogen atoms in their molecule. The value of  $A$  is found to increase with increase in concentration of the halogen-containing member of the mixture.

III. A theoretical paper in which the author considers the results arrived at in the two previous communications. He puts forward the explanation that the reciprocal action of two liquids, intermixed, consists in a variation of their attractive forces, thus modifying the space occupied by the molecule as well as by the co-volume, without affecting the internal structure of the molecule. W. G.

**The Mass of the Particles Which Emit the Two Spectra of Hydrogen.** CHARLES FABRY and HENRI BUISSON (*Compt. rend.*, 1912, 154, 1500—1502).—The rays of hydrogen of both the first and second spectra are emitted by particles having the mass of an atom of hydrogen. W. G.

**The Zeeman Phenomenon in the Spectra of Hydrogen and Nitrogen.** F. CROZE (*Compt. rend.*, 1912, 154, 1410—1411).—The Zeeman effect has been measured for the three primary lines ( $H_\alpha$ ,  $H_\beta$ ,  $H_\gamma$ ) in the hydrogen spectrum, and for a group of lines (from 4601.54 to 4803.53) in the blue portion of the nitrogen spectrum. For hydrogen,  $\Delta\lambda/H\lambda^2 = 0.95 \times 10^{-4}$ , and for nitrogen,  $1.41 \times 10^{-4}$ . W. G.

**The Band Spectrum of Sulphur.** JOSEF M. EDER and EDUARD VALENTA (*Zeitsch. wiss. Photochem.*, 1912, 11, 168).—In reference to Johansen's paper on the flame spectrum of sulphur (this vol., ii, 402), the authors point out that they have previously measured the wavelengths of the characteristic bands between  $\lambda = 3940$  and  $\lambda = 4700$ . H. M. D.

**Band Spectrum of Strontium Fluoride in the Electric Arc.** PAUL LEOPOLD (*Zeitsch. wiss. Photochem.*, 1912, 11, 105—118 and 137—149).—Wave-length measurements of the bands in the arc spectrum of strontium fluoride are recorded and compared with those of previous observers. In the case of certain groups of bands the wave-length data are in good agreement with Fabry's interpolation formula. This partial agreement is, however, not sufficient to decide the question as to whether the distribution of the bands is in accordance with the requirements of Deslandres's law. H. M. D.

**Spectrum of Arc Light Aureols.** HEINRICH HERTENSTEIN (*Zeitsch. wiss. Photochem.*, 1912, 11, 119—132).—The author has investigated the arc flame spectra of the halogen salts of various metals. In the case of copper, lead, tin, iron, and aluminium, banded spectra are obtained, whereas cadmium and zinc emit only the arc lines. The arrangement and structure of the bands in the spectra of cupric chloride, bromide, and fluoride show clearly the influence of the halogen, and these spectra are, therefore, due in part to the halogen compounds. On the other hand, the chlorides, bromides, and iodides of lead and tin, silver chloride, and potassium dichromate give rise to spectra which are identical with the arc flame spectra of the metals. The arc flame bands are coincident with the bands in the corresponding oxygen coal-gas flame spectra.

In addition to the bands, the arc flame spectra show the more intense arc spectrum lines. The effect of a carbon dioxide atmosphere is to diminish the intensity of the arc flame spectrum according to experiments with copper and tin, whilst a supply of oxygen increases the intensity of the copper and lead spectra and diminishes that of the tin spectrum.

The arc flame spectra do not extend so far into the ultra-violet region as those of the arc, and this is attributed to the lower temperature of the aureol. H. M. D.

**Excitation of the Principal Spectra of Aromatic Compounds by Ultra-violet Light.** EUGEN GOLDSTEIN (*Ber. Deut. physikal. Ges.*, 1912, 14, 493—505.\* Compare Abstr., 1911, ii, 560; this vol., ii, 216).—The supposition that the emission of the principal spectrum by aromatic compounds when acted on by cathode rays is due to the ultra-violet light emitted when the cathode particles impinge on the substance, has been confirmed by a series of experiments in which it is shown that, under favourable conditions, the principal spectrum is by the action of light rays alone.

In the case of cuminic acid and formo- $\beta$ -naphthalide, the principal spectrum appears if the substances are subjected at the temperature of liquid air to the light rays transmitted by Zeiss's UV filter. If shorter-waved rays are employed, such as those transmitted by Uviol glass ( $\lambda = 260\mu$ ), the effect is also observable with a number of other substances. In many cases it has been found that a preliminary exposure to the action of cathode rays, followed by treatment with short-waved light rays, leads to a considerable increase in the number of bands observable in the principal spectrum excited by the cathode rays.

\* and *Physikal. Zeitsch.*, 1912, 13, 577—583.

Although for some substances the spectrum excited by the cathode rays and by short-waved light rays appear to be identical, this is not always the case. Distinct differences in the wave-lengths of the maxima of certain bands have been found, for instance, in the case of  $\beta$ -naphthol and diphenylene oxide.

Substances which do not readily give rise to the principal spectrum when subjected to the cathode ray and subsequent light treatment in the solid condition have been found to respond when dissolved in certain solvents, if the solutions are then cooled to a low temperature so as to produce solid solutions of the aromatic substances. In the case of benzene derivatives, these solution spectra are identical with the ordinary principal spectra of the solid compounds, but a difference is found when the aromatic compounds in question contain two or more benzene rings. When the solid solutions of these are subjected to the action of the short-waved rays, the initial solution spectra are gradually replaced by the corresponding principal spectra. In some cases, however, the transition from the solution spectrum appears to be incomplete, and the final emission differs from that of the solid compound; it varies also to some extent according to the solvent in which the aromatic compound is dissolved.

Other experiments show that the principal spectra are more easily developed when the substances are contained in evacuated tubes. This effect may, however, be due to the resulting difference in thermal conductivity of the contents of the tube, and therefore to a difference in the temperature of the substance exposed to the light treatment under the two conditions.

H. M. D.

**Fluorescence of the Platinum Double Salts.** JOHANNES BEUEL (*Zeitsch. wiss. Photochem.*, 1912, 11, 150—167).—The fluorescence spectra of the alkali and alkaline earth metal platinocyanides have been examined, the ultra-violet rays obtained by means of a Uviol glass filter in combination with an arc lamp being employed as a means of exciting the fluorescence. From the close agreement of the wave-length measurements of the heads of the bands for the different salts, it appears to be established that the fluorescence is not characteristic of the salt molecules, but is determined by a common constituent group. The several bands which form the spectrum, are, therefore, due in all probability to the platinocyanide group of atoms. The substitution of one alkali or alkaline earth metal atom by another merely changes the relative intensities of the bands. Observations with the anhydrous and hydrated salts show that the influence of the water of crystallisation is of the same kind.

Fluorescence spectra exhibiting the same bands are also obtained when the platinocyanides are acted on by cathode rays, but the emission excited in this way is not sufficiently prolonged for photographic records of the spectra to be obtained. The decrease in the emissive power is accompanied by a colour change in the salts.

H. M. D.

**Photochemical Studies. VI. Spectral Distribution of the Light Sensitiveness of Bromine.** JOH. PLOTNIKOFF (*Zeitsch. physikal. Chem.*, 1912, 79, 641—656. Compare this vol., ii, 218).—The

effect of monochromatic light of different colours and of polychromatic light on the reactions between bromine and cinnamic acid and bromine and benzene has been investigated. It is shown that bromine, like iodine, is most sensitive to the blue region of the spectrum, and that it shows two bands of photochemical absorption, which partly overlap, and a long band of thermal absorption. The photochemical temperature-coefficients and the wave length corresponding with the maximum light sensitiveness of a substance are regarded as characteristic photochemical magnitudes.

G. S.

**The Rôle of Wave-Length in Photochemical Reactions. Analogy between the Photochemistry Making Use of High Frequencies and the Chemistry of High Temperatures.** DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1912, 154, 1597—1600).—A consideration of the results previously obtained (compare Abstr., 1910, i, 349, 543; ii, 564, 606, 813, 814; 1911, ii, 86, 170, 240, 242, 835, etc.) shows that photochemical reactions can be divided into two classes, as is also the case with thermochemical reactions, namely, (a) exothermic and irreversible (sometimes called catalytic), (b) endothermic and reversible. In both cases the efficacy of the radiations used increases with their frequency, which consequently plays the part of potential or of photochemical temperature. Endothermic changes which are produced thermally only by very high temperatures are produced photochemically only by the extreme ultra-violet rays (0.15—0.20 $\mu$ ).

T. S. P.

**Acceleration of the Bleaching of Dyes.** GOTTFRIED KÜMMELL (*Zeitsch. wiss. Photochem.*, 1912, 11, 133—136).—The accelerating influence of various comparable substances on the bleaching of cyanine, methylene blue, and erythrosin has been measured. Data are recorded which show the magnitude of the effect in the two series: (a) thiosinamine, phenylallyl thiocarbamide, allyl sulphide, and allylamine; (b) nitrobenzene, *o*-nitrotoluene, and *o*-nitrophenol. In general, the accelerating influence diminishes as the complexity of the molecule of the accelerator increases, provided that similar substances only are compared.

The actual bleaching is preceded by a darkening of the colour of the dye, and it has been found that the dyes which have been transformed in this way can then be bleached by treatment with a dilute (0.02*N*) solution of potassium permanganate. The changes involved in this bleaching process are considered to be closely similar to those involved in the development of the photographic plate. If the collodion films of the dyes are washed with an alcoholic solution of safrole, the accelerating action of the unsaturated compounds is inhibited.

H. M. D.

**Measurements of Radioactivity by means of  $\alpha$ -Rays.** W. R. BARSS (*Amer. J. Sci.*, 1912, [iv], 33, 546—550).—The relationship between the potential gradient required to produce the saturation current and the direction of propagation of the  $\alpha$ -particles with reference to the lines of electric force is discussed. In connexion with this, experiments have been made which show that when the particles

are moving in all directions with respect to the electric field (emission from radium emanation), the ratio of the currents, obtained from two sources of different intensities, is constant for different potential gradients, provided that the source of the  $\alpha$ -particles is not too intense.

H. M. D.

**The Relation between the Ranges of  $\alpha$ -Particles and the Periods of Transformation of Radioactive Substances.** HAROLD A. WILSON (*Phil. Mag.*, 1912, [vi], 23, 981—983).—An attempt is made to find an analogy between the law representing the variation of the velocity of emission of thermions with temperature and that representing the variation of the velocity of  $\alpha$ -particles with the period of the change in which they are expelled. It is supposed that the kinetic energy of the  $\alpha$ -particles expelled is a measure of the "atomic temperature," and that this can be substituted for the absolute temperature in the thermionic equation. On this view curves are drawn, analogous to those of Geiger and Nuttall connecting the logarithms of range or velocity of  $\alpha$ -particles and the logarithms of the periods of the changes in which they are expelled, which exhibit agreement with the theory. It is calculated that the work required to separate 1 gram molecule of  $\alpha$ -particles is  $1.6 \times 10^{13}$  calories, as compared with about  $10^5$  calories for the separation of a gram-molecule of electrons from platinum.

F. S.

**Change in the Velocity of  $\beta$ -Rays in their Passage Through Matter.** OTTO VON BAER ( *Physikal. Zeitsch.*, 1912, 13, 485—489).—The change in the velocity of the  $\beta$ -rays of thorium-A in passing through different metals has been investigated. The results obtained show that the diminution in the velocity of the rays becomes smaller as the speed of the rays increases. If the velocity is plotted as a function of the thickness of the layer of aluminium traversed, a straight line is obtained, but the inclination of the line varies with the initial speed of the rays. From experiments with tin, copper, and platinum, it has been found that the change in velocity for the same thickness of the different metals increases with increase in the density of the metal. The observed diminution is somewhat smaller, however, than that which would be expected from the change in speed observed when the rays are allowed to pass through aluminium.

H. M. D.

**The Retardation Undergone by  $\beta$ -Rays on Traversing Matter.** JEAN DANYSZ (*Compt. rend.*, 1912, 154, 1502—1504).—By means of a radiographic method (compare Abstr., 1911, ii, 840), the author has studied the retardation of  $\beta$ -rays on traversing different substances. The screens employed were metallic, and weighed 0.01 grams per sq. cm. The results show that a screen of given thickness causes a retardation proportional to the density of the metal of which it is made. The results obtained are in accord with those recently obtained by Whiddington for cathode rays (*Proc. Roy. Soc.*, 1912, A, 86, 360).

W. G.

**Mobility of Ions in Gases and Mixtures of Gases.** KARL PRZIBRAM (*Physikal. Zeitsch.*, 1912, 13, 545—547).—Relatively simple formulæ are deduced for the coefficient of diffusion and the mobility of the ions in simple gases and gas mixtures. As in the case of other formulæ, the calculated values of the diffusion coefficient and the mobility are considerably greater than the observed values, and it seems necessary to assume that the radii of the ions are greater than those corresponding with simple gas molecules.

The formula for the ionic mobility in gas mixtures is applied in the calculation of values for the positive and negative ions in mixtures of carbon dioxide and hydrogen, carbon dioxide and air, and hydrogen and methyl iodide, and the results compared with the experimental data.  
H. M. D.

[**Radiant Emission from the Spark.**] WALTER STEUBING (*Physikal. Zeitsch.*, 1912, 13, 520—522).—Polemical against Wood (compare this vol., ii, 114).  
H. M. D.

**Photo-electric Observations on Aluminium and Magnesium** ROBERT POHL and P. PRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1912, 14, 546—554).—When aluminium or magnesium surfaces, prepared by distillation and condensation of the metals in a vacuum on cooled sheets of platinum, are exposed to the action of light rays in an exhausted tube, the metals are found to exhibit photo-electric activity. In the case of the freshly prepared surfaces, the emission of electrons is first observed for light of wave-length between  $\lambda = 365$  and  $\lambda = 405 \mu\mu$ , and the emission increases continuously as the wave-length diminishes beyond this limiting value. As time progresses, however, the photo-electric sensitiveness increases, particularly in the region of the longer waved rays, and at the same time the limiting wave-length of the photo-electrically active rays moves gradually towards the red end of the spectrum. In the condition of maximum sensitiveness the photo-electric effect can be detected in the case of aluminium up to  $\lambda = 700 \mu\mu$ , and for magnesium up to  $1000 \mu\mu$ . This extension of the active wave-lengths is accompanied by the appearance of a maximum sensitiveness corresponding with  $\lambda = 260 \mu\mu$ . No evidence was obtainable of any connexion between this maximum and the phenomenon of resonance associated with the selective photo-electric effect.

After the condition of maximum sensitiveness of the metal surfaces has been reached, which usually requires from six to ten hours, the emissive power remains sensibly constant for several days and then gradually falls. The decay in emissive power is accompanied by a displacement of the position of maximum sensitiveness towards the ultra-violet end of the spectrum, and at the same time the limiting wave-length of the active light moves in the same direction. This effect is attributed to the gradual escape of gas from the various substances contained in the exhausted tube. If air is admitted, whilst the cell is in a sensitive condition and the tube again exhausted after a few minutes, the metals are at first almost inactive, but gradually recover the power of emitting electrons when suitably excited.

H. M. D.

**Absorption of X-Rays and Fluorescent X-Ray Spectra.** CHARLES G. BARKLA and V. COLLIER (*Phil. Mag.*, 1912, [vi], 23, 987—997. Compare Abstr., 1909, ii, 457).—Further experiments have been made on the absorption of X-rays, the penetrating power of which is not far removed from that corresponding with the spectral lines of the absorbing substances. If the absorption in an element *R* is plotted as ordinate and the absorption in aluminium as abscissa, and the scales of the ordinate and abscissa are so arranged that, for each absorbing substance, the absorption of iron radiation in iron, of nickel radiation in nickel, of copper radiation in copper, etc., are all represented by a single point, it is found that one absorption curve is common to all absorbing substances. This is not only true for the spectral lines of series *L*, for according to experiments on the absorption in gold and platinum, it appears to hold equally well in the case of lines belonging to series *K*. The *K* and *L* curves can be combined, and in this way an absorption curve is obtained, which represents the behaviour of all elements which have been examined up to the present. The existence of this curve signifies that there is one fluorescent spectrum characteristic of the different elements, the only difference between these being that the scale of absorbability varies from element to element.  
H. M. D.

**Absorption of Soft Röntgen Rays in Gases.** WILHELM SEITZ (*Physikal. Zeitsch.*, 1912, 13, 476—480).—The absorption of very soft Röntgen rays by various gases and vapours has been examined in order to ascertain whether the absorption phenomena are more closely related to the phenomena of light absorption than is the case with hard Röntgen rays. This does not appear to be the case, and in general the behaviour of the soft rays is less simple than that of hard rays.

When the atomic absorption of the different elements is calculated from the molecular absorption of the various compound gases investigated, it is seen that the absorption is not connected with the atomic weight in any simple manner. The curve showing the relation between the absorption and the atomic weight is, moreover, dependent on the softness of the rays employed in the experiments.

H. M. D.

**Measurements of Induced Activity in the Bolivian Cordilleras.** WALTER KNOCH (*Physikal. Zeitsch.*, 1912, 13, 440—442).—Measurements have been made of the induced activity acquired by positively and negatively charged and by uncharged wires exposed at a height of 5200 metres on the Quimza Cruz Cordilla. The values obtained for the rate of fall of the potential in the case of negatively charged wires are exceptionally large, and exceed any values recorded by previous observers for other localities. The total induced activity increases as the height of the exposed wire above the surrounding surface of the earth is increased. An analysis of the induced activity has shown that it consists of both radium and thorium, the proportion of the former increasing with increase in the

altitude of the insulated wire. Actinium appears to be present also, but its amount could not be estimated.

The induction effects observed on uncharged and positively charged wires were very much smaller, as found by other observers.

H. M. D.

**The Migration and Diffusion of Radium-*A* Atoms.** GERHARD ECKMANN (*Jahrb. Radioaktiv. Elektronik.*, 1912, 9, 157—187).—The effect of altering the potential difference between the metal case of a cylindrical vessel containing radium emanation and a central axial electrode was studied. Calling the activity deposited on the electrode 100 when it was 1000 volts negative to the case, the activity sank according to the well known curve to 15 when no difference of potential was applied and to 3 when the electrode was 1000 volts positive to the case. In other gases the effect of a negative electrode potential was the more marked the lighter the gas. When the ionisation in the vessel was increased by means of an external radium preparation, the negative electrode activity was diminished, especially for small potential differences. The effect of time on the amount of activity deposited on the electrode at +1000 volts was studied, and from the results the diffusion coefficient for radium-*A* atoms was calculated. In other experiments a wire gauze was moved backwards and forwards in an emanation atmosphere, and the variation of the amount of activity collected with the time for which it had remained undisturbed examined. In equilibrium the number of radium-*A* atoms floating in the atmosphere was calculated to be equivalent to the number produced during 45 seconds. The abnormal deposition of activity on both anode and cathode, from an emanation atmosphere which had been left for long to accumulate active deposit without the action of an electric field, was studied, and ascribed to the aggregation of the single radium-*A* atoms together into relatively larger particles. The theory of the phenomena studied is discussed, and the conclusions drawn are (1) that the radium *A* atoms initially positively charged are neutralised by ions, and some 2% are actually charged negatively and migrate to the anode; (2) the diffusion coefficient of unaggregated radium-*A* atoms is 0.06, which is very nearly that found for the emanation; (3) the effect of a field in clearing an emanation atmosphere of aggregated active deposit particles is dependent on the strength of the field and the time it is applied for; (4) equations are given for calculating the number of radium-*A* and -*B* atoms floating in an emanation atmosphere of given concentration after any given time of accumulation.

F. S.

**The Decay Constant of Polonium.** EGON R. VON SCHWEIDLER (*Ber. Deut. physikal. Ges.*, 1912, 14, 536—539).—From a series of galvanometer observations extending over 445 days, the half-decay period of polonium was found to be  $136.3 \pm 0.6$  days. A series of electrometer readings at a later stage extending over 500 days gave  $136.2 \pm 1.4$  days, whilst from the intervening period of about 2200 days the value obtained was  $136.5 \pm 0.3$  days. These values are in good agreement with that found by Regener (*ibid.*, 1911, 13, 1027).

H. M. D.

**Estimation of Radium Emanation in Spring Waters.** HEINRICH GREINACHER (*Physikal. Zeitsch.*, 1912, 13, 435—436).—A method is described by which the spring water can be collected, transported, and examined in the laboratory without loss of any of the contained emanation. The collecting vessel consists of an exhausted glass flask of about 750 c.c. capacity, which is provided with a tap. By opening and closing this when the neck of the flask is immersed in the water to be examined, the sample bottle can be nearly filled without danger of loss. To estimate the amount of emanation, the bottle is connected with a reflux condenser, which at its upper end communicates through a tap with the chamber of an electroscope in which the pressure has been reduced about 20 cm. below that of the atmosphere. The water is boiled, and, after removal of the emanation, the upper tap is opened and the emanation forced over into the chamber. Readings are then taken on the electroscope after suitable time intervals.

If the water contains radium in addition to emanation, the amount of the former can be estimated by repeating the operation after the boiled out water has been kept for one to two days. H. M. D.

**Deductions from a Valence Hypothesis. II. Metallic Conduction of Electricity.** JOHANNES STARK (*Jahrb. Radioaktiv. Elektronik.*, 1912, 9, 188—203. Compare Abstr., 1908, ii, 138; this vol., ii, 403).—The author's valence hypothesis is applied to the interpretation of the conduction of electricity by metals. The essential difference between the metals and the metalloids is supposed to be determined by the relative distances by which the electrons are separated from the corresponding atoms, these distances being much greater for the metals. In a crystalline univalent metal, the valence electrons are symmetrically distributed between the network of positive atomic spheres, and lie on so-called displacement surfaces, in which the electrons move freely under the influence of an applied potential difference. The number of transportable electrons is independent of the temperature, and equal to the number of atoms of the metal. At a given temperature, the resistance is determined by the thermal vibration of the electric yields of valency, and since the thermal vibration vanishes at absolute zero, the metals become perfect conductors at this temperature.

In the case of a metalloid, the electrons which lie on the displacement surfaces and are therefore free to move, form only a small proportion of the total number, and this is the cause of the small electrical conductivity. With rise of temperature and increase in the energy of the vibrating units, the number of the electrons on such surfaces increases, and this increases the conductivity.

The influence of traces of foreign metals on the conductivity of pure metals is also discussed, and the reduction in conductivity referred to the disturbance of the symmetrical arrangement of the electrons on the displacement surfaces, which is brought about by relatively very small numbers of foreign atoms, which are characterised by a different spacial distribution of the component atomic spheres and electrons. H. M. D.

**Difference of Potential at the Contact of Glass with an Electrolyte.** L. RIÉTY (*Compt. rend.*, 1912, 154, 1411—1414. Compare Cameron and Oettinger, *Abstr.*, 1909, ii, 856).—Beginning with dilute solutions, the value of  $\epsilon$ , in Helmholtz's formula for the potential difference at the contact of glass and liquid, is found to diminish with increase in concentration of the solution to a certain point and then to increase again. Solutions of copper sulphate, zinc sulphate, and copper nitrate were examined, and in the case of the last substance the electrolyte was found to have a potential inferior to that of the glass. W. G.

**Electromotive Force Produced by the Flow of Salt Solutions through Capillary Tubes.** L. RIÉTY (*Compt. rend.*, 1912, 154, 1215—1217. Compare *Abstr.*, 1911, ii, 575).—Zinc sulphate solutions and dilute copper nitrate solutions give a greater *E.M.F.* than solutions of copper sulphate under the same conditions; for concentrations below 0.2 gram-molecule per litre, copper nitrate has less effect than the sulphate. When solutions of these salts flow through a capillary tube, the potential rises in the direction of the flow of liquid, whilst the reverse is the case with copper chloride.

Experiments on the *E.M.F.* of filtration are also described. Grumbach (*Thèse*, Paris, 1911) observed a regular fall in *E.M.F.* during filtration of very dilute solutions. For concentrated solutions the phenomena are more complicated, but generally speaking the *E.M.F.* tends towards a limiting value, diminishing in the case of sulphates and increasing in the case of nitrates. The difference in pressure on each side of the filter has no appreciable influence on the results. W. O. W.

**Selenium Cells.** HENRI PELABON (*Compt. rend.*, 1912, 154, 1414—1416).—A study has been made of the alloys of selenium with the metals, silver, lead, copper, and tin. The method employed has been to measure the *E.M.F.* of cells formed by an electrode of the pure metal and an electrode of the alloy in a saturated solution of a salt of the metal, the two electrodes being connected externally by a fine platinum wire. The results obtained confirm those furnished by a study of the fusibility of mixtures of the same elements. W. G.

**A Rotating Cathode.** C. W. BENNETT (*J. Physical Chem.*, 1912, 16, 287—293).—The 1" diameter cathode will rotate at any speed up to 6000 revolutions per minute and carry 300 amperes, giving a density of 3500 amperes per sq. foot when 4" of cathode is receiving a deposit. The cathode consists of an aluminium tube 10" long held in a brass socket by a set screw. The socket is carried by a  $\frac{5}{8}$ " steel spindle provided with a water-cooled roller bearing at the lower end, a ball thrust-washer in the middle to take the weight, a set of pulleys driven direct from a 1 H.P. motor, and a plain white metal bearing at the top end. The whole is mounted on a stiff frame arranged to swing about a vertical axis and adjustable vertically. Current is conveyed to the cathode through brush contacts held against the brass socket.

If the electrical supply is not provided with an earthed return, the whole apparatus is insulated.

The electrolyte is contained in a two-gallon earthenware jar with a closely fitting wooden lid, through which pass the cathode and the connecting strips to the two anodes, which are cast copper bars,  $7'' \times 2\frac{1}{2}'' \times 1''$ . Aluminium was found to be an ideal metal for the cathode, since the copper deposit, having been suitably machined, can be stripped away easily from its slightly oxidised surface without bending or heating. If it is desired to remove the cylindrical copper deposit whole, a thin shell of fusible metal is cast round the aluminium.

R. J. C.

**Electrical Endosmose.** WILDER D. BANCROFT (*J. Physical Chem.*, 1912, 16, 312—317).—According to Perrin (Abstr., 1905, ii, 138), acidic solutions are carried to the anode through a porous diaphragm and alkaline solutions to the cathode, this effect resulting from the electrification of the diaphragm by contact with the solutions. The author explains some exceptions to Perrin's rule on the hypothesis that different ions are adsorbed to very different extents by the diaphragm, so that under certain conditions the diaphragm may acquire a negative charge in an acidic solution and vice versa.

In a slightly acidic solution of copper sulphate, assuming that copper ions are only slightly adsorbed, the negative charge due to the sulphate ions will outweigh the positive charge from the hydrogen and copper ions. The endosmosis of slightly alkaline barium chloride through a porous cup is abnormal in direction for a similar reason.

Colloids travel towards the anode or cathode according to their specific absorptive power for the various ions present. Solutions are known in which gelatin moves to the cathode and starch to the anode. In order that lead deposits may be improved by the presence of gelatin, the solution must be sufficiently acidic to cause the gelatin to travel towards the cathode. Colloidal ferric oxide behaves similarly to gelatin in the electro-deposition of lead.

In slightly acidic copper sulphate solutions, colloidal cupric oxide is deposited at the cathode and improves the quality of the copper obtained, but under certain conditions an excess of colloidal cupric oxide is deposited, yielding a black unsatisfactory cathode. In strongly acidic solutions or in solutions of complex copper salts, this cannot happen, because the amount of free cupric oxide is negligible, whilst in neutral or alkaline solutions the colloid is carried towards the anode and does not affect the cathode deposit.

The author suggests that the contact potential between a metal and an aqueous solution is not a function of the ionic concentrations only, but varies to some extent with the nature of the anion and the other cations present in so far as these are adsorbed by the metal in question.

R. J. C.

**Influence of Pressure and Temperature on the Electrolytic Conductivity of Solutions.** SILVIO LUSSANA (*Zeitsch. physikal. Chem.*, 1912, 79, 677—680. Compare Abstr., 1911, ii, 462).—Polemical against Körber (Abstr., 1911, ii, 863).

G. S.

**Reduction of Solutions of Potassium Permanganate by the Alternate Current.** G. WENGER and HECTOR H. ALVAREZ (*Ann. Chim. anal.*, 1912, 17, 202—204).—A number of experiments as to the reduction of acid solutions of potassium permanganate are communicated, and the results have been tabulated. The authors have arrived at the following conclusions: (1) The reduction is strongest with rotating electrodes whatever may be their nature. (2) Copper electrodes reduce the solution the most rapidly, whilst aluminium in twice the time only effects a partial decomposition. (3) In the experiment with the current, the phenomenon is more pronounced at the beginning than at the end of the experiment. (4) The reduction due to the sole action of the metal is, of course, almost negligible with platinum electrodes (non-oxidisable metal).  
L. DE K.

**The Standard Scale of Temperatures between 200° and 1100°.** L. H. ADAMS and J. JOHNSTON (*Amer. J. Sci.*, 1912, [iv], 33, 534—545).—A calibration curve has been determined for copper-constantan thermo-elements, in which 0°, 100°, and the boiling points of naphthalene (217·95°) and benzophenone (305·9°) have been used as fixed points. By means of this, the following freezing points were measured: tin 231·8°, bismuth 271·0°, cadmium 320·9°, lead 327·3°. The concordance of these values with those obtained by other methods show that the thermo-element is not inferior to the resistance thermometer over the range 0—360°.

A comparison has also been made between the results of resistance and gas thermometer measurements, and it is shown that these are in good agreement over the range 0—1100°. This concordance serves as an efficient check on the trustworthiness of the gas thermometer scale between these limits of temperature.  
H. M. D.

**The Linear Expansion of Solid Elements as a Function of their Absolute Melting Point.** GEORGE RUDOLF (*Zeitsch. anorg. Chem.*, 1912, 75, 160).—The relation observed by Stein (this vol., ii, 128) is well known, having been first stated by Pictet (*Compt. rend.*, 1897, 88, 855).  
C. H. D.

**The Specific Heat of Water According to Regnault's Experiments.** CHARLES ED. GUILLAUME (*Compt. rend.*, 1912, 154, 1483—1487).—The author has recalculated the values for the specific heat of water for temperatures from 60° to 100°, using Regnault's figures, but with a slightly different formula, based on the more recent work of Barnes, Callendar, and Dieterici. The results are set out in a table.  
W. G.

**Theory of the Specific Heats of Binary Liquid Mixtures.** ALFRED SCHULZE (*Physikal. Zeitsch.*, 1912, 13, 425—433).—The experimental results communicated in previous papers (this vol., ii, 327, 428 and 532) are examined, and it is shown that the deviations between the observed specific heats and those calculated from the specific heats of the two components by the simple mixture rule can be accounted for on the assumption that the components combine

to form a compound, or that one of the components is associated in the pure condition. If the dissociation constant of the compound or the association constant of the associating liquid is known, the proportions of the three kinds of molecules in a binary mixture of either class can be calculated. By making use of the numbers obtained in this way, it is shown that the mixture rule can be applied to calculate the specific heats of such binary mixtures if the heat capacities of the three kinds of molecules are taken into consideration, and that the calculated results are in satisfactory agreement with the observed data. The specific or molecular heat of binary mixtures is therefore equal to the sum of the specific or molecular heats of the components, if by this is understood the molecular aggregates which are actually present in the mixture. H. M. D.

**A New Melting-point Apparatus.** D. S. PRATT (*J. Ind. Eng. Chem.*, 1912, 4, 47).—A description with sketch of an accurate melting-point apparatus, the form of which is based on a Thiele tube, with electricity supplanting the Bunsen flame as heating agent. The lower half of the side-arm is wound with resistance wire, such as fine manganin or nichrome, the whole arm is then enclosed with asbestos paste. Using a lamp board, or rheostat, the current sent through the heating coil may be varied at will, and thus the rise of temperature very accurately controlled. By calibrating the instrument in terms of lamps and temperature, it is only necessary to turn on the proper number of lamps, and the rise of temperature will be exactly uniform each time it is used, whilst the rate may be varied from an almost imperceptible rise to a very rapid one, and the range is limited only by the fluid used. F. M. G. M.

**Cryoscopy in Camphor.** JOUNIAUX (*Compt. rend.*, 1912, 154, 1592—1594).—The eutectic temperatures and molecular percentages of camphor in the eutectics of the following mixtures are: camphor—naphthalene, 32.5°, 58%; camphor— $\alpha$ -mononitronaphthalene, 27.3°, 54%; camphor— $\beta$ -naphthylamine, 55°, 64%; camphor—pyrogallol, 21°, 69%; camphor—benzoic acid, 57.2°, 63%. The application of Raoult's law to these mixtures gives the following values for the cryoscopic constant of camphor as a solvent: 494, 499, 505, 500, 492, the mean being 498. Using this value, the molecular weights of the following substances dissolved in camphor were found to be normal, the error being about 1.6%: catechol, tribromophenol, vanillin, benzophenone, methyl oxalate, azobenzene, and silicon tetraphenyl. On the other hand, the mean value for the cryoscopic constant deduced from these results is 495. Using this value the latent heat of fusion of camphor is calculated to be 8.24 Cals., whilst the value deduced from the vapour pressure measurements of Ramsay and Young, etc., is also 8.24 Cals. T. S. P.

**Formation of Metal Mirrors by Distillation in a Vacuum.** ROBERT POHL and P. PRINGSHEIM (*Ber. Deut. physikal. Ges.*, 1912, 14, 506—507).—A method of producing optically plane metallic surfaces by distillation of the metals in a vacuum is described. The metal to

be distilled is placed in a small cylindrical magnesia crucible, which is heated electrically by passing a suitable current through a sheet of iron or platinum foil in close contact with the outer wall of the cylinder. By distillation in this way, satisfactory mirrors of silver, cerium, indium, aluminium, and calcium have been obtained. The method is also recommended for the production of compact sheets of metals, which, like beryllium, cannot be obtained in this form by the usual melting process.

H. M. D.

**Fractional Distillation in the Laboratory and a New Rectifying Apparatus.** A. GOLODETZ (*Chem. Ind.*, 1912, 35, 102—108, 141—145).—A discussion of the theories of the separation of liquids by fractional distillation.

Sketches with descriptions of three forms of apparatus designed by the author are given, and the results of their employment in the case of mixtures, such as benzene with toluene, or amyl formate with amyl acetate, are tabulated and demonstrated by means of curves.

F. M. G. M.

**Heat of Hydration.** WILLEM P. JORISSEN (*Chem. Weekblad*, 1912, 9, 415—420).—A comparison of the heats of hydration calculated by van't Hoff's formula for the hydroxides of magnesium, barium, and strontium with those experimentally determined by various investigators.

A. J. W.

**Thermochemistry of Silicic Acid and the Silicates.** OTTO MULERT (*Zeitsch. anorg. Chem.*, 1912, 75, 198—240).—Calorimetric measurements have been made, 0.5—1 gram of silicate being dissolved in 470 c.c. of 20% hydrofluoric acid in a platinum calorimeter. The specific heat of 20% hydrofluoric acid is 0.84, which is higher than that of other mineral acids.

The heat of solution of crystalline quartz is 29.93 Cal. per gram-molecule, and of vitreous silica, 32.14 Cal., whilst that of hydrated silicic acids varies with the hydration, extrapolation of the curve showing that these acids are derived from the amorphous modification. A maximum heat of hydration is found at 3%  $H_2O$ . Contrary to Thomsen's statement, the reaction ceases with the formation of the acid  $H_2SiF_6$ , and the abnormal results obtained by Thomsen must be attributed to an error in the analysis of the sodium silicate used.

The following heats of formation have been obtained by this method: vitreous zinc orthosilicate, -23.74 Cal.; crystalline zinc metasilicate, +2.49 Cal. The heat of crystallisation of zinc orthosilicate is 9.04 Cal., and of manganous metasilicate, 8.52 Cal. Magnesium silicates dissolve too slowly to allow of an estimation.

Alumina dissolves in hydrofluoric acid, forming a hydrofluoaluminic acid, but in presence of an excess of alumina, insoluble compounds are slowly formed. This reaction has been studied by means of the electrical conductivity. The heat of solution of anhydrous alumina is found to be, with some uncertainty, 93.86 Cal. Using this value, the following heats of formation are obtained: crystalline andularite, 131.2 Cal. (heat of crystallisation, 55.72 Cal.); crystalline leucite,

101.8 Cal.; crystalline microcline, 104.2 Cal.; crystalline sodium metasilicate, 97.85 Cal.; analcite, 85.22 Cal.; natrolite, 95.76 Cal., and heulandite, 59.44 Cal. The heat of solution of glucinum, cadmium, nickel, and ferric hydroxides has also been determined. C. H. D.

**Viscosity of Ethylene and Carbon Monoxide and its Variation at Low Temperatures.** OTTO ZIMMER (*Ber. Deut. physikal. Ges.*, 1912, 14, 471—492).—The viscosity of ethylene has been measured at temperatures between  $+14^{\circ}$  and  $-76^{\circ}$ , and of carbon monoxide between  $+11^{\circ}$  and  $-149^{\circ}$ . The influence of temperature on the viscosity cannot be represented by means of Sutherland's formula in the case of ethylene when the temperature is lower than  $-20^{\circ}$ . A similar deviation is found for carbon monoxide at the lowest temperature at which it was examined. The discrepancy between theory and experiment is attributed to polymerisation of the gases at the lower temperatures, and density determinations have been made which appear to support this hypothesis. H. M. D.

**Dissociation Pressures of Sodium and Potassium Hydrides.** FREDERICK G. KEYES (*J. Amer. Chem. Soc.*, 1912, 34, 779—788).—A study has been made of the dissociation pressures of sodium and potassium hydrides. The following equations express the dissociation pressure between  $250^{\circ}$  and  $400^{\circ}$  in mm. of mercury: for sodium hydride,  $\log_{10} p = -5700/T + 2.5 \log_{10} T + 3.956$ ; and for potassium hydride,  $\log_{10} p = -5850/T + 2.6 \log_{10} T + 3.895$ . The vapour pressure equations for liquid sodium and potassium have been calculated from (1) their b. p.'s; (2) their heats of vaporisation, derived from Trouton's rule (assuming the same constant as for mercury), and (3) the heat capacities of the liquids and the vapour, and have been found to be: for sodium,  $\log p = -6200/T - 1.35 \log T + 12.4$ ; and for potassium,  $\log p = -6000/T - 0.40 \log T - 0.0008T + 10.73$ . The heat of reaction at ordinary temperatures has been calculated from the measurements, and found to be 13,860 cal. per formula-weight of sodium hydride (NaH), and 14,240 cal. per formula-weight of potassium hydride (KH). E. G.

**Surface Tension of Solutions Containing Two Solutes.** W. SREBNITSKY (*J. Russ. Phys. Chem. Soc.*, 1912, 44, *Phys. Part*, 145—150).—The author has measured, by the capillarity method, the surface tensions of mixtures in varying proportions of solutions of: (1) *N*-sodium chloride and *N*-citric acid; (2) 0.5*N*-potassium chloride and 0.5*N*-sodium valerate; (3) 0.5*N*-potassium chloride and 0.5*N*-sodium butyrate; (4) 0.2*N*-potassium chloride and 0.2*N*-butyric acid; (5) 0.5*N*-calcium chloride and 0.5*N*-sodium valerate.

The results show that if the surface tension changes but slightly with change in the concentrations of the two solutes and remains near to the value for water, the surface tension curve is approximately a straight line. Where the concentrations are small, the straight line law holds for wider variations in the relative amounts of the two solutes. T. H. P.

**Capillary Constants of Liquid Esters.** PAUL WALDEN and RICHARD SWINNE (*Zeitsch. physikal. Chem.*, 1912, **79**, 700—758).—By means of the capillary tube method the surface tension of thirty-eight liquids (at the boundary liquid-air) has been measured at four different temperatures between 0° and 100°. For thirty-one of these liquids, the surface tensions of which have not been previously determined, the specific cohesion, free surface tension, and molecular surface energy at different temperatures are given, and the densities of the liquids have also been determined where no trustworthy data are available. The temperature-coefficients of the molecular surface energy  $dE/dt$  are also tabulated, and the conclusions which may be drawn from the data as to the degree of association of the liquids are discussed in detail.

The substitution of a phosphorus or antimony atom for nitrogen increases considerably the value of  $dE/dt$ , which for triphenylstibine at 40° is about 2·87, and for triphenylphosphine at the same temperature about 3·40. On the other hand, the substitution of sulphur for hydrogen in the hydroxyl group gives a higher value for  $dE/dt$ , and therefore diminishes the degree of association. The presence of the CN group, as usual, causes association. With increasing complexity of the substituting groups, for example, in a homologous series, the coefficient  $dE/dt$  gradually increases; the substitution of a chlorine atom for hydrogen, as in diethyl chlorofumarate, also gives a higher value for  $dE/dt$ .

In eighteen out of the thirty-one liquids examined, the temperature-coefficient of the molecular surface energy  $dE/dt$  is approximately constant. It increases as the temperature rises with methylene cyanide, isobutyl phenylpropionate, triphenylphosphine, and triphenylstibine, and diminishes considerably with increasing temperature in the case of phenyl mercaptan and of diethyl and diamyl phthalate.

As regards the magnitude of the temperature-coefficient, it is greater for almost all the esters examined than the normal value of Ramsay and Shields, 2·12, which would appear to indicate dissociation. It is shown, however, that when Walden's formula  $Ma_s^2/T_s = 0·00435 \log T_s$  is used (compare Abstr., 1909, ii, 122), the liquids are either normal or associated, from which it follows that the Ramsay-Shields method of determining the molecular complexity of liquids is not valid for substances of high molecular weight. A liquid which according to Walden's formula is highly associated is ethylene cyanoacetate, whilst ethyl lactate and symmetrical and non-symmetrical diethyl sulphite are slightly associated. A formula connecting molecular cohesion, absolute temperature, and vapour pressure of liquids suggested by Dutoit and Mojoiu (compare Abstr., 1909, ii, 470) gives results in good agreement with those obtained by means of the Walden formula.

G. S.

**Pore Diameters of Osmotic Membranes.** F. E. BARTELL (*J. Physical Chem.*, 1912, **16**, 318—335. Compare Abstr., 1911, ii, 1072).—Osmotic phenomena were first observed by Graham in 1854, using unglazed porcelain as the membrane. Ordinary laboratory porous plates do not exhibit osmotic effects, whereas battery cups and

other fine grades of porcelain do. Examination with the microscope confirmed the view that only porcelains of close texture are capable of acting as semipermeable membranes. The efficiency of the membranes was increased by clogging the pores with barium sulphate and other fine precipitates.

The average diameter of the pores in these semipermeable membranes was estimated by the application of Jurin's formula:  $hr = 14.823$  sq. mm., where  $h$  is the capillary rise of water at  $20^\circ$  in a tube of radius  $r$ . An air pressure greater than the hydrostatic pressure of a column  $h$  mm. high forces the water out of the tube, so that the average pore diameter in a given porcelain can be calculated from the minimum air pressure requisite to force absorbed water out of the pores.

In the author's experiments disks of porcelain were clamped to the end of a stout glass tube 14 mm. in bore, which could be connected at will to a compressed air cylinder or a long, narrow glass tube. The disks were soaked in water and then covered with a layer of water and subjected to an increasing air pressure from below, whilst the surface was observed with a lens. The pressure range from the appearance of the first air bubble to the appearance of innumerable air bubbles was found to be small. Several minutes were required for the maximum number of bubbles to develop at any given pressure.

A typical porcelain plate had five pores only of diameter  $0.388\mu$ , whilst an innumerable number of pores had diameters more than  $0.360\mu$ . The value taken was the diameter corresponding with the appearance of 100 to 125 bubbles on the top of the porcelain—in this case  $0.369$  microns.

After the pore diameters had been estimated, the cell was filled with normal sugar solution and inverted in a beaker of water. A rise of 5 mm. in the glass tube was taken as a definite osmotic effect. In the eighty-one samples of porcelain examined, the smaller the pore diameter the greater the osmotic effect. Where there were 100 to 125 pores in the area measured of diameter greater than  $0.42\mu$ , no osmotic effects were obtained.

A number of microcrystalline and colloidal substances were precipitated in the pores of porous plate porcelain which before treatment had an average pore diameter of  $1.18\mu$ , and gave no osmotic effects. Alternatively, in some experiments the clogging agent was first precipitated and then forced into the pores of the membrane in suspension in water.

The limiting diameter for osmotic effects was higher in coarse porcelain with a clogging precipitate than in fine porcelain alone, and varied with the nature of the clogging precipitate. The limiting diameters were: with sulphur  $0.591\mu$ , barium sulphate  $0.738\mu$ , cupric sulphide  $0.738\mu$ , lead chromate  $0.777\mu$ , lead sulphate  $0.923\mu$ , copper ferrocyanide  $0.923\mu$ . The values are of the same order and are sufficiently alike to indicate that pore diameter is one of the main factors in these osmotic phenomena.

The author admits that there is an alternative view, namely, that osmosis inwards occurs through pores of molecular dimensions, and in imperfect membranes it is more or less neutralised by leak outwards through visible pores. In this case what he has measured is the

limiting pore diameter at which solution leak outwards begins to be smaller than the true osmotic flow inwards. The outer liquid was not tested for sugar after the experiments. R. J. C.

**The Dependence of Crystalline Form on Temperature, and Recrystallisation in Conglomerates.** GUSTAV TAMMANN (*Nachr. k. Ges. Wiss. Göttingen*, 1912; Reprint, 9 pp.).—The existence of a surface tension in a crystal face is not manifest when the cohesive forces,  $f$ , are greater than the surface tension,  $\alpha$ . It is possible, however, for  $f$  to become less than  $\alpha$  at some temperature, and the face then becomes curved. When this is the case for all faces, the crystal becomes spheroidal. If the transition point occurs below the melting-point, the substance will form rounded crystallites. In a binary system, if at some temperature  $f=2\alpha$ , rounded crystallites will be formed above, and polyhedral crystals below, that temperature. The frequency of rounded forms in metallic alloys is taken to indicate that this case actually presents itself.

A thin lamella of an isotropic solid will contract owing to surface tension at the temperature at which  $f=2\alpha$ . It is shown that this temperature rises with increasing thickness of the lamellæ. In anisotropic substances, the thickness of the lamellæ depends on the development of cleavage planes, and in metals this increases with the amount of mechanical work. The recrystallisation of such masses, which is attributed to the contraction of the lamellæ, therefore takes place at a lower temperature, the more highly worked the metal is. The greater solubility of small as against large crystals, which is usually invoked to explain the recrystallisation of conglomerates, is considered to be insufficient, as it depends on oscillations of temperature.

C. H. D.

**Changes in Metallic Foils on Heating, Due to Surface Tension.** HERMANN SCHOTTKY (*Nachr. k. Ges. Wiss. Göttingen*, 1912; Reprint, 9 pp. Compare preceding abstract).—Metal foil may be regarded as a crystalline material, composed of very thin lamellæ. The effect of surface tension when a certain temperature is reached is thus readily studied in it (compare Beilby, *Proc. Roy. Soc.*, 1904, 72, A, 226; Turner, *Abstr.*, 1908, ii, 1034; Chapman and Porter, *Proc. Roy. Soc.*, 1911, 83, A, 65). Experiments on the tensile strength of silver foil at high temperatures show that the strength per unit area of cross-section diminishes with diminishing thickness. A gold leaf under load expands on heating up to  $170^\circ$ ; the length then remains constant up to  $340^\circ$ , at which temperature a rapid contraction takes place. From the evidence the conclusion is drawn that the surface tension forces in metal foil at high temperatures are quite sufficient to bring about recrystallisation.

C. H. D.

**The Internal Movement of Liquid Crystals.** CHARLES MAUGUIN (*Compt. rend.*, 1912, 154, 1359—1361).—If liquid crystals are examined in parallel light between crossed Nicols, black and white spots are observed in which the particles are in rapid motion. The movement persists as long as the substance remains in the

anisotropic liquid phase, and increases in intensity if the temperature is raised. It ceases abruptly when the liquid becomes isotropic, but recommences on again cooling. The agitation appears to be irregular, and generally resembles the brownian movements of colloidal suspensions. Under the ultra-microscope, only a uniform distribution of light is observed. When subjected to a magnetic field acting normally to the glass surfaces within which the crystals are enclosed, this agitation disappears. The case of ethyl *p*-ethoxybenzylidene-amino- $\alpha$ -methylcinnamate (Abstr., 1908, i, 641) is noteworthy. This substance has two crystalline liquid phases. That between 75° and 125° exhibits the phenomena described above; that below 75° does not show these movements.

H. W.

**Magnetic Analysis of Liquid Crystals.** OTTO LEHMANN (*Physikal. Zeitsch.*, 1912, 13, 550—559).—The influence of a magnetic field on the optical properties of liquid crystals has been examined in detail, and photographs are given illustrating the different effects which are observed in the case of small and large drops in both transverse and longitudinal magnetic fields. The observations are discussed in reference to the author's theory of the liquid crystalline condition.

H. M. D.

**India Rubber as a Protective Colloid. Formation of Colloidal Metallic Sulphides in Rubber Solutions.** EDWARD W. LEWIS and H. WAUMSLEY (*J. Soc. Chem. Ind.*, 1912, 31, 518—519).—A dark brown colloidal solution of lead sulphide is obtained when lead is kept immersed for some time in a solution of rubber in benzene containing carbon disulphide. The formation of the coloured solution is most marked in a 2% rubber solution, and practically ceases when the rubber solution reaches a dilution of 0.5%; it is favoured by increasing the proportion of carbon disulphide, also by the addition of alcohol. A coloured solution is not obtained in the complete absence of rubber.

Two other metals are found to behave like lead in this respect, namely, copper and mercury. Further, colloids other than rubber act similarly; for example, a similar darkening of the solution occurs when a strip of lead is immersed in a solution of celluloid in acetone containing a small quantity of carbon disulphide.

W. H. G.

**Necessity for Revising the Law of Mass Action and of Homogeneous Equilibrium.** ALBERT COLSON (*Compt. rend.*, 1912, 154, 1420—1423).—A theoretical paper in which the author criticises a number of the formulæ at present employed in physical chemistry, and in particular the one concerning the law of mass action.

W. G.

**The Law of Mass Action.** HENRY LE CHATELIER (*Compt. rend.*, 1912, 154, 1563—1566).—The author points out that the reasoning employed by Colson (preceding abstract) in his criticism of the law of mass action is false. Moreover, Lemoine's experiments on the dissociation of hydrogen iodide are not sufficiently accurate to draw conclu-

sions from, whereas those of Bodenstein (Abstr., 1897, ii, 252) afford a satisfactory verification of the law of mass action.

The experimental evidence which is at present available supports the law of mass action within the limits of the errors of experiment.

T. S. P.

**Dissociation without Change of Volume, and the Law of Mass Action.** ALBERT COLSON (*Compt. rend.*, 1912, 154, 1589—1590).—An extension of the author's theory (preceding abstracts) to the case of the system  $[H_2 + nI_2]$  changing from the total pressure  $P$  to the total pressure  $P'$ . The application to this case of the reversible cycle considered by the author leads to the expression:  $p_1 p_2^n / P^{(n+1)} = p_1' p_2'^n / P'^{(n+1)}$ , where  $p_1, p_2$ , etc., are the partial pressures of the hydrogen and iodine respectively. This is not identical with the ordinary expression deduced by the law of mass action. T. S. P.

**The Law of Guldberg and Waage in the Case of Gaseous Dissociation.** J. CARVALLO (*Compt. rend.*, 1912, 154, 1590—1592).—In contradiction to Colson (preceding abstracts), the author shows, by the consideration of a thermodynamic cycle, that the law of mass action is applicable to the case of dissociation of a gas. The cycle is carried out in the usual way by making use of semi-permeable membranes, a necessary condition being that the gases must behave as perfect gases. T. S. P.

**The Equilibrium Solid-Liquid-Gas in Binary Systems Containing Mixed Crystals.** I. HUGO R. KRUYT (*Zeitsch. physikal. Chem.*, 1912, 79, 657—776).—A more detailed account of work already published (compare Abstr., 1910, ii, 195, 837). G. S.

**Gaseous Mineralisers in a Magma.** I. PAUL NIGGLI (*Zeitsch. anorg. Chem.*, 1912, 75, 161—188).—Mineralisers in a magma are substances which exert a large effect on the conditions of crystallisation in proportion to the quantity in which they are present. Gaseous mineralisers are the most important.

A theoretical discussion of ternary systems in which one component is gaseous and the other two are miscible in the liquid and solid state is given. The only binary system of the kind that has been completely investigated is ether-anthraquinone (Smits, Abstr., 1904, ii, 15), but on addition of alizarin to this, some decomposition takes place near the melting point. The system  $SO_2$ - $HgBr_2$ - $HgI_2$  has, therefore, been adopted. The two salts form a continuous series of solid solutions, the freezing-point curve having a minimum (Reinders, Abstr., 1900, ii, 70). The experiments are made in sealed glass tubes, in an electrically heated oil-bath, the first measurements being those of the critical temperature. The critical temperature of sulphur dioxide is found to be  $157.6^\circ$ , and is raised by the presence of mercuric bromide. The conclusion that the elevation is proportional to the concentration of the dissolved salt (Centnerzwer, Abstr., 1903, ii, 716) is confirmed. For small concentrations, the elevation due to solid solutions is the sum of the two elevations taken singly. The solubility continues to

increase on heating above the critical temperature, and large crystals are obtained on cooling such a gaseous solution. At  $254^{\circ}$ , 6.2%  $\text{HgI}_2$  or 8.5%  $\text{HgBr}_2$  is present in the liquid phase in the corresponding binary system. The solubility of sulphur dioxide in the fused salts increases only slightly with the pressure. Some sulphur dioxide is absorbed by the solid salts without change of colour. C. H. D.

**Kinetics of the Transformation of Chloralkylamines into Heterocyclic Compounds.** HERBERT FREUNDLICH and MARION B. RICHARDS (*Zeitsch. physikal. Chem.*, 1912, 79, 681—699).—The transformation of  $\epsilon$ -chloroamylamine into the isomeric piperidine hydrochloride  $\text{CH}_2\text{Cl}\cdot[\text{CH}_2]_4\cdot\text{NH}_2 \rightarrow \text{C}_6\text{NH}_{11}\cdot\text{HCl}$ , which was previously investigated in aqueous solution (compare Freundlich and Krestovnikoff, *Abstr.*, 1911, ii, 266) has now been investigated in tetrachloroethane, nitrobenzene, and benzene, the solvents being saturated with moisture, and containing drops of water. The reaction is unimolecular in all the solvents examined; it is less rapid in tetrachloroethane and nitrobenzene than in water, and still less rapid in benzene. The temperature-coefficient for  $10^{\circ}$  in the organic solvents is about 2.5, as compared with 3.9 for water.

The solubility of piperidine hydrochloride in water (5.19 mols. per litre at  $25^{\circ}$ ) and in the other three solvents, as well as the distribution coefficient of  $\epsilon$ -chloroamylamine between water and the organic solvents was determined. There is no apparent connexion between these factors and the velocity constants, from which it appears that the medium exerts a specific influence on the reaction-velocity.  $\epsilon$ -Chloroamylamine is adsorbed from aqueous solution by charcoal to a much greater extent than its isomeride piperidine hydrochloride.

The rate of transformation of  $\epsilon$ -chloro- $\beta$ -hexylamine into the isomeric  $\alpha\alpha$ -dimethylpyrrolidine hydrochloride in the presence of excess of sodium hydroxide has been measured at  $0^{\circ}$  and  $25^{\circ}$ . The results are somewhat uncertain, owing to the fact that the original substance was impure, but the reaction appears to be unimolecular, and is slower than the change of  $\delta$ -chlorobutylamine to pyrrolidine hydrochloride, already investigated (*loc. cit.*). The temperature-coefficient for  $10^{\circ}$  is about 4.4. G. S.

**Velocity of Reaction.** I. G. POMA and B. TANZI (*Gazzetta*, 1912, 42, i, 425—437. Compare *Abstr.*, 1911, ii, 707).—The authors have studied the effect of the presence of water, etc., on the kinetics of the bimolecular reaction:  $\text{NMe}_2\text{Ph} + \text{EtBr} = \text{NMe}_2\text{EtPhBr}$  in absolute alcohol.

The presence of 2% of water in the solvent produces but slight effect, but the value of  $10^6K$  at  $30^{\circ}$  is raised from 1.5 to 3.8 by 5% and to 8.7—11.7 by 10% of water (compare Kremann, *Abstr.*, 1905, ii, 307). In the last case the value of  $K$  increases appreciably with time, probably owing to secondary reactions. The velocity of the reaction in acetone solution is also increased by addition of water.

Acetonitrile, the dielectric constant of which is only about one-half of that of water, but still markedly higher than that of alcohol, causes increase of the velocity of the reaction in absolute alcohol, but the extent of the increase is much less than that produced by water.

Benzene, even when present in the solvent to the extent of 10%, has no sensible influence on the kinetics of the reaction.

These results indicate that Menshutkin's conclusion, that the reaction constant increases with the dielectric constant of the solvent, cannot be extended to the case of mixtures of two solvents (Abstr., 1890, 1366; compare Carrara, Abstr., 1901, ii, 3). T. H. P.

**Is Ionisation, as Indicated by Conductivity, a Necessary Prerequisite for the Combination of Acids with Bases?** OTTO FOLIN and FRED F. FLANDERS (*J. Amer. Chem. Soc.*, 1912, 34, 774—779).—Folin and Wentworth (Abstr., 1910, ii, 757) have described a method for the estimation of fatty acids by titration with sodium ethoxide, organic liquids, such as chloroform, benzene, toluene, and carbon tetrachloride, being used as the solvents. Folin and Flanders (Abstr., 1911, ii, 1039; this vol., ii, 501) have devised similar methods for the estimation of benzoic and hippuric acids, and it is now shown that solutions of acids of all classes in organic solvents may be titrated with sodium ethoxide. It is pointed out that the conditions of these titrations are unusual, and do not seem to harmonise with the usual views based on the electrolytic dissociation theory in accordance with which the reaction between an acid and an alkali is actually a reaction between hydrogen and hydroxyl ions. It has been stated by Ostwald and others that substances do not undergo ionisation in solvents of the character of benzene, and an acid dissolved in benzene would therefore be present in the non-ionised state.

In view of this lack of agreement between experiment and theory, the conductivity has been determined of certain solutions, such as sodium ethoxide in alcohol, benzoic acid in benzene and in a mixture of benzene and alcohol, and sodium benzoate in a mixture of benzene and alcohol. The conductivity of benzoic acid in benzene is too small to be measurable. The results obtained with solutions of sodium amyloxyde and benzoic acid in amyl alcohol, and of sodium amyloxyde and sodium oleate in a mixture of equal parts of amyl alcohol and benzene indicate that the conductivities of these solutions are independent of the solute, since they are of about the same order as that of amyl alcohol itself and are probably due to it in each case.

In general, the experiments prove that the solutions of acids and alkalis used in the titrations have scarcely any conductivity, and that the resulting salt solutions are also almost non-conducting. Emphasis is laid on the facts that the reactions are instantaneous, and that the action of the indicator does not differ materially from that observed in aqueous solutions. E. G.

**The Oxidation Relations of Certain Heavy Metals.** CARLO CERVELLO (*Arch. exp. Path. Pharm.*, 1912, 68, 318—322).—Oxidation of indigotin and pyrogallol occurs in the presence of certain metallic chlorides, that of manganese, of those used, being an exception. The metals arranged in ascending order of activity in influencing the intensity and rapidity of the oxidation are: iron, copper, mercury, zinc. By contact with indigotin or pyrogallol, reduction of the chlorides of iron, copper, and mercury takes place to lower oxidation products.

If air is completely or almost completely excluded, the intensity of oxidation is lessened. W. D. H.

**Importance of Temperature-correction in Weighing.** H. I. WATERMAN (*Chem. Weekblad*, 1912, 9, 385—386).—The author points out that a knowledge of the temperature-coefficient of the balance is a most important factor in accurate analysis. A. J. W.

**An Apparatus for the Absorption of Fumes.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1912, 11, 503—506).—A simple apparatus to absorb fumes evolved from a test-tube, etc., is described and figured. W. D. H.

**A Flame Experiment.** ALFRED C. EGERTON (*Chem. News*, 1912, 105, 232—233).—A glass cylinder is provided with a cork at the lower end, through which two glass tubes pass, one for the admission of hydrogen, whilst the other, longer, tube is provided with a copper nozzle. The upper end of the cylinder is also fitted with a copper foil nozzle. Hydrogen is first admitted, and burns in air at the top, the flame being coloured green by copper. Chlorine is then admitted through the small tube, and burns in the hydrogen with a blue flame. C. H. D.

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## Inorganic Chemistry.

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**Prevention of Hydrogen Explosions by the Interposition of Steel Wool.** O. OHMANN (*Chem. Zentr.*, 1912, i, 1426—1427; from *Zeitsch. physik-chem. Unterr.*, 25, 26—28).—A roll of steel wool, about 2—3 cm. long, is pressed firmly into the jet of a hydrogen apparatus. If an explosive mixture is being evolved from the apparatus, and a light is applied to the jet, the explosion travels back only as far as the steel wool, where the flame is put out owing to the rapid cooling which there takes place.

The wool prevents an explosion even with a mixture of  $\frac{2}{7}$ ths hydrogen and  $\frac{5}{7}$ ths air, that is, with a mixture of maximum explosive power. It can also be used with mixtures of air and coal gas, but is of no effect with a mixture of hydrogen and oxygen in the proportions necessary to form water.

The magnetisability of steel wool is much less than that of iron powder. T. S. P.

**Decomposition of Water at Ordinary Temperatures by Magnesium.** ARTHUR W. KNAPP (*Chem. News*, 1912, 105, 253).—Magnesium powder is added to ten times its weight of water, and followed by a small quantity of palladous chloride. Metallic palladium is formed, and the water boils. The escaping hydrogen ignites spontaneously. C. H. D.

**Weight of a Normal Litre of Atmospheric Air at Geneva.** PHILIPPE A. GUYE, G. KOVACS, and E. WOURTZEL (*Compt. rend.*, 1912, 154, 1424—1426).—The results of thirty determinations of the weight of a normal litre of dry air, freed from carbon dioxide, give, as a mean, the value 1.2930 grams (compare Rayleigh, *Abstr.*, 1893, ii, 514). Evidence is afforded of slight variations in the density of air at the same spot, with variation in barometric pressure, probably caused by influx of air from other regions richer or poorer in oxygen (compare Morley, *Abstr.*, 1882, 278, 1026). W. G.

**Weight of a Normal Litre of Air at Geneva.** PHILIPPE A. GUYE, J. KOVACS, and E. WOURTZEL (*Compt. rend.*, 1912, 154, 1584—1586).—Comparison of the results previously obtained by the authors (preceding abstract) for the weight of a normal litre of dry and carbon dioxide-free air at Geneva, with those obtained by Rayleigh in London and Leduc in Paris, shows that the air at Geneva is 0.2—0.3 mg. per litre heavier than at London and Paris. The analyses of Watson (*Trans.*, 1911, 99, 1460) show that the composition of air collected on the same day at places not very far from each other may vary. From these results the authors draw the conclusion that the weight of a normal litre of dry and carbon dioxide-free air may vary, on the same day, from place to place to the extent of several tenths of a milligram. It follows that the density of air should not be used as a standard of comparison for the density of other gases. T. S. P.

**The Investigation of the Upper Layers of the Atmosphere.** ALFRED WEGENER (*Zeitsch. anorg. Chem.*, 1912, 75, 107—131).—The hypothesis of an upper atmosphere of hydrogen, arrived at from calculations of partial pressure, is confirmed by observations of the total reflection of sound waves, of the appearance and disappearance of twilight, of luminous night-clouds, and of the glowing of meteors. All these observations indicate 70—80 kilometres as the approximate height of the base of the hydrogen stratum. In the spectrum of the aurora, the intensity of the nitrogen lines diminishes, and that of the hydrogen lines increases, with increasing height.

On the basis of a review of the evidence, a table and diagram are given of the probable distribution of the gases of the atmosphere. The hydrogen increases very rapidly between 60 and 80 kilometres. Hydrogen and geocoronium are present in equal volumes at 200 kilometres, above which the latter gas predominates. Geocoronium is probably identical with coronium, in spite of the difference of their spectra. C. H. D.

**Atmospheric Ozone.** HARRY N. HOLMES (*Amer. Chem. J.*, 1912, 47, 497—508).—This investigation was undertaken with the object of ascertaining approximately the variation in the amount of ozone in the air with the different seasons and during sudden atmospheric disturbances. The presence of appreciable quantities of ozone in the air during the winter has been established by the starch-potassium iodide test; the blue colour produced is usually due to ozone alone, but occasionally to a slight extent to nitrogen peroxide. Hydrogen

peroxide does not occur in the air in sufficient quantities to affect the most delicate reagents. Nitrogen peroxide is occasionally present, but the maximum amounts are such as to have little effect on the starch-potassium iodide test. The maximum amount of ozone in the air is only found when "high" barometric areas are so near that the air from great heights flows rapidly down to the earth. The effect of thunderstorms on the formation of ozone is probably very small. Most of the ozone is produced by the action of the sun's ultra-violet rays on the upper air. The quantity of ozone in the air is much greater in winter than in summer. E. G.

**Formation of Hydrogen Sulphide through "Galvanic Action."** WILHEM P. JOBISSEN (*Chem. Weekblad*, 1912, 9, 406—407. Compare Skey, *Chem. News*, 1873, 27, 161; Casamajor, Abstr., 1881, 876).—Iron disulphide,  $\text{FeS}_2$ , and the sulphides of lead and bismuth are practically unattacked by dilute hydrochloric acid. When connected with an amalgamated zinc rod immersed in the acid, a steady stream of hydrogen sulphide is evolved. A. J. W.

**Blue Acid (the Reduction Product of Nitrous-Sulphuric Acid).** III. WILHELM MANCHOT (*Zeitsch. angew. Chem.*, 1912, 25, 1055—1058. Compare Abstr., 1910, ii, 956, 1055; 1911, ii, 107).—When the solution of the "blue acid" is cooled in a mixture of solid carbon dioxide and acetone, it changes to an intense carmine-red colour. The formation of this colour is a very delicate test for the presence of "blue acid," since very dilute solutions which are colourless at ordinary temperatures become red at low temperatures.

"Blue acid" is not produced in the absence of sulphuric acid, as shown by experiments in which concentrated sulphuric acid was replaced by glacial acetic acid or concentrated phosphoric acid the nitrous acid being reduced either by sulphurous acid or by mercury.

The presence of sulphurous acid is not necessary for the formation of "blue acid." When mercury is used as the reducing agent, the temperature is such that no sulphurous acid is produced by the interaction of mercury and sulphuric acid. "Blue acid" is not formed when sulphur dioxide is passed through liquid nitrogen trioxide, or by the interaction of nitric oxide and concentrated sulphuric acid. It is readily produced when formic acid is used as the reducing agent instead of mercury or sulphur dioxide.

The formation of "blue acid" by the use of mercury or formic acid shows that the reducing agent does not attack the sulphuric acid molecule. "Blue acid" must therefore be a compound of sulphuric acid and an oxide of nitrogen. This oxide must be a higher one than nitric oxide and a lower one than nitrogen trioxide, since it is produced by the reduction of nitrous acid. It is probably somewhat complex in constitution, because of the change in colour which takes place with alteration in temperature. Since very concentrated sulphuric acid does not give the formation of "blue acid," it is probable that this compound also contains water in the molecule. In any case, Raschig's formula,  $\text{H}_2\text{SNO}_5$ , cannot be correct.

The remainder of the paper is polemical against Raschig (Abstr., 1911, ii, 200). T. S. P.

**Purification of Sulphuric Acid.** GIUSEPPE BRESSANIN (*Gazzetta*, 1912, 42, i, 456—458. Compare Abstr., 1911, ii, 1133, 1134).—In sulphuric acid solution, not only arsenic, but also tin, copper, cadmium, and lead are precipitated as iodides on addition of potassium iodide, selenium being precipitated as such at the same time; also nitric and nitrous acids are reduced to nitric oxide. With mercury and bismuth, the precipitate first formed redissolves in excess of the iodide. The elements of the third and successive groups are not precipitated. A sulphuric acid solution of arsenic containing 0.001 mg. As per c.c. gives an immediate precipitate with potassium iodide, whilst with 0.0005 mg. per c.c., a precipitate forms after some time.

The following method is suggested for the purification of sulphuric acid. To each litre of the cold acid having  $D_{20}^{20}$  1.53 are added 10 c.c. of a 30% hydriodic acid solution. After twelve hours, the acid is passed through a filter consisting of a lower layer of glass wool, and an upper one of fine asbestos pulp washed with hydrochloric acid; before being used, the whole filter is washed with the acid to be filtered, the first portions passing through being rejected. The filtered acid is coloured with iodine, which is eliminated by heating in a vessel of non-arsenical material, such as Jena glass. If a delivery tube dipping into potassium hydroxide solution is fitted to the vessel, it can be seen when all the iodine not used in the precipitation is evolved.

T. H. P.

**Electrolytic Preparation of Persulphates.** CARL SCHALL and K. ANDRICH (*Chem. Zeit.*, 1912, 36, 645).—In the electrolytic preparation of persulphates according to the method described by Blumer (this vol., ii, 41), the yields obtained were determined by titration of the electrolyte. The authors have endeavoured to determine the yields by collecting and weighing the solid persulphate, but were unsuccessful in the case of ammonium persulphate. With potassium persulphate, however, a current-yield of the solid salt amounting to 71.1% was obtained.

The electrolyte used consisted of 1250 c.c. of a saturated (at 18.5°) solution of potassium persulphate, to which were added 600 grams of potassium hydrogen sulphate, 2 grams of potassium ferricyanide, and 10 c.c. of concentrated sulphuric acid. It was kept saturated with potassium hydrogen sulphate by immersing a glass vessel, pierced with holes and containing the salt, in the electrolyte. The anode was of platinum wire and the cathode of nickel foil, the current densities being 0.12 and 2.11 amperes per sq. cm. at the anode and cathode respectively, using 16 amperes. The temperature was maintained in the neighbourhood of 20°. The details of the apparatus were similar to those given by Blumer (*loc. cit.*).

T. S. P.

**Sulphide of Tellurium.** WALTER O. SNELLING (*J. Amer. Chem. Soc.*, 1912, 34, 802—811).—When a slightly acid solution of tellurous acid or a tellurous salt is treated with hydrogen sulphide, a dark red precipitate is produced, which gradually becomes black. When dried and heated, the substance softens and forms a grey, somewhat lustrous mass. Berzelius regarded this product as tellurium sulphide,

$\text{TeS}_2$ , but subsequent workers have shown that it consists of a mixture of sulphur and tellurium in the proportions required by this formula.

Experiments are now described which show that if the mixture is warmed after precipitation or left for several hours, the whole of the sulphur in the precipitate can be extracted by carbon disulphide. It has been found, however, that at the moment of precipitation only one-half of the sulphur is soluble in carbon disulphide, and that the insoluble residue consists of *tellurium sulphide*,  $\text{TeS}$ . This compound is very unstable and decomposes completely in about four hours at  $0^\circ$ , and much more rapidly at higher temperatures. The reaction between tellurous acid and hydrogen sulphide is expressed by the equation:  $2\text{H}_2\text{S} + \text{H}_2\text{TeO}_3 = \text{TeS} + \text{S} + 3\text{H}_2\text{O}$ . E. G.

**Red Phosphorus.** ALFRED STOCK, HANS SCHRADER, and ERICH STAMM (*Ber.*, 1912, 45, 1514—1528).—The transformation of yellow into red phosphorus was carried out in an exhausted flask provided with a side-tube which contained ordinary phosphorus. By local cooling of the flask, a thin film of phosphorus was deposited, which was subjected to the light from a mercury lamp, so arranged that the film was illuminated on the inner side. Residual yellow phosphorus was removed by cooling the side-tube of the flask during several days in liquid air. The violet portion of the visible spectrum was found to be the active agent in bringing about the change on which temperature has comparatively little influence.

The density of the phosphorus so obtained varied from 1.95 for the yellow and light red specimens to 2.25 for the darker specimens. Under the microscope, the more voluminous preparations appeared to be composed of minute particles (diameter  $1/100$  mm. and less). Other specimens contained larger aggregates which showed distinct brightening when brought between crossed Nicols in the polarisation microscope, a phenomenon which possibly, but not necessarily, points to the presence of crystalline particles.

When phosphorus vapour was rapidly cooled, a portion of it condensed in the form of red phosphorus, the proportion of the latter increasing with increasing temperature of the phosphorus vapour. The duration of heating was found to be of little importance, but cooling must be effected as rapidly as possible. Somewhat similar observations have been made by Hittorf (*Ann. Phys. Chem.*, 1865, [ii], 126, 222). The authors draw the conclusion that red and yellow phosphorus are chemically different, and that the former is probably formed by the union of the dissociated particles of the phosphorus vapour among themselves, or with undissociated phosphorus molecules.

Red phosphorus, prepared in this manner, is yellowish-red to blood-red in thin layers, black with violet glance in compact pieces. When finely ground, it resembles commercial red phosphorus. The highest value observed for its density was 2.115. It appears to be crystalline, is stable towards air, only slowly attacked by boiling sodium hydroxide, and does not form a red solution in aqueous alcoholic potassium hydroxide.

Condensation of red phosphorus is shown to take place independently of the presence of liquid yellow phosphorus. H. W.

**The Iodides of Elements of the Nitrogen Group.** FRANS M. JAEGER and H. J. DOORNBOSCH (*Zeitsch. anorg. Chem.*, 1912, 75, 261—271).—The existence of a compound  $\text{SbI}_5$  was disputed by MacIvor (this Journ., 1876, 29, 328). The freezing-point curve of mixtures of antimony tri-iodide with antimony or iodine shows that only the one compound  $\text{SbI}_3$  exists, melting sharply at  $170.8^\circ$ . It is not appreciably miscible with antimony, but forms two liquid layers, the horizontal branch occurring at  $169^\circ$ . The eutectic point lies at  $80^\circ$  and 88.2 atomic % of iodine. The form of the iodine end of the curve is in agreement with the depression found by Timmermans (*Abstr.*, 1906, ii, 429);  $\text{Sb}_2\text{I}_4$  does not exist.

The freezing-point curve of mixtures of arsenic and iodine indicates the existence of one compound,  $\text{AsI}_3$ , which melts without decomposition at  $140.7^\circ$ , and of another,  $\text{As}_2\text{I}_4$ , which appears as a liquid layer at  $135$ — $136^\circ$ , the eutectic point between the two compounds being at  $120.5^\circ$ . It has not been found possible to isolate this second compound in a pure state, even by extraction with solvents, or by formation of solid solutions with  $\text{P}_2\text{I}_4$ .

Antimony and arsenic tri-iodides form a complete series of solid solutions, the curve passing through a minimum freezing point at  $136^\circ$ . Antimony and phosphorus tri-iodides form a simple eutectiferous series, without solid solutions, the eutectic point lying at  $52^\circ$  and about 86 mol. %  $\text{PI}_3$ . Arsenic and phosphorus tri-iodides form two series of solid solutions, with a transformation point at  $73.5^\circ$ , the saturated solid solutions at that temperature containing respectively 18 and 75 mol. %  $\text{PI}_3$ . C. H. D.

**The Constitution of the Perborates.** E. BOSSHARD and K. ZWICKY (*Zeitsch. angew. Chem.*, 1912, 25, 993—995).—Twenty different perborates have been heated gently at  $55$ — $65^\circ$ , either under diminished pressure or in a current of air free from carbon dioxide, in order to ascertain if hydrogen peroxide is eliminated. In one case only was a trace of hydrogen peroxide found in the distillate; the general result was that the water of crystallisation distilled over, and the percentage of active oxygen in the residue increased.

A potassium peroxide perborate,  $\text{KBO}_4 \cdot \text{H}_2\text{O}$ , is described, which is stable and evolves only traces of oxygen on solution in water (compare the corresponding unstable sodium compound, Melikoff and Pissarjewsky, *Abstr.*, 1898, ii, 332, 374). When dried in a vacuum over phosphoric oxide, four molecules of this salt lose  $1\text{H}_2\text{O}$ , so that it is improbable that it contains hydrogen peroxide of crystallisation.

The velocity of decomposition of an aqueous solution of sodium perborate under the catalytic influence of colloidal platinum is less than that of a solution of hydrogen peroxide under corresponding conditions.

From the above results the authors draw the conclusion that the perborates do not contain hydrogen peroxide of crystallisation, and

have the constitution  $\text{MO} \cdot \text{B} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}$ , and not  $\text{MO} \cdot \text{O} \cdot \text{BO}$ . The above potassium salt would then be formulated as  $\text{KO} \cdot \text{O} \cdot \text{B} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \\ \text{O} \end{smallmatrix}$ , which is in accordance with its stability, since a compound of the alternative formula  $\text{KO} \cdot \text{O} \cdot \text{O} \cdot \text{BO}$  would probably be very unstable, owing to the chain of three oxygen atoms.

Riesenfeld's test (this vol., ii, 156) for distinguishing true per-salts from salts with hydrogen peroxide of crystallisation fails in the case of the perborates. T. S. P.

**Observations on the Silicon Hydrides.** ADOLPHE BESSON (*Compt. rend.*, 1912, 154, 1603—1606).—The silicon hydride obtained from the magnesium silicide prepared by the action of magnesium on silica (quartz) generally contains hydrogen phosphide and hydrogen sulphide as impurities. These are best removed by passing the gas through a dilute aqueous solution of iodine in potassium iodide or hydrogen iodide; the purified gas is then dried by means of phosphoric oxide.

The gas so obtained (designated hereafter as "the mixed gas") generally contains only about 5% of silicon hydride ( $\text{SiH}_4$ ), and is admixed with hydrogen. During the preparation a white solid forms in the reaction mixture, which, on analysis, proves to be silico-oxalic acid,  $\text{Si}_2\text{O}_4\text{H}_2$ ; the yield of this substance generally amounts to 25—30% of the magnesium silicide used.

The dry mixed gas is not acted on by exposure to light. It is decomposed by the electric discharge, a yellow to brown deposit forming on the electrodes and on the sides of the tubes. The deposit readily takes fire on exposure to the air, and contains 2—5% of silicon, but no compound of definite composition could be isolated.

The mixed gas has no action on a concentrated solution of ammonia, or on dry liquid ammonia. In the presence of moisture, however, the liquid ammonia gives a white solid, which, when dried at  $100^\circ$ , has a composition corresponding with the formula  $\text{H}_4\text{Si}_3\text{O}_7$ .

The author has further investigated the white solid produced by the action of air or oxygen on the mixed gas (compare this vol., ii, 255). When dried for several hours in a vacuum at  $100^\circ$ , it has a composition corresponding with the formula  $\text{H}_3\text{Si}_3\text{O}_5$ . The action of heat on this substance did not lead to any very definite results, although when carefully heated in a vacuum it loses hydrogen, and the composition of the residue approaches the formula  $\text{Si}_3\text{O}_5$ . T. S. P.

**Apparatus for Determining the Vapour-pressure Isothermals of the Gel of Silicic Acid.** RICHARD ZSIGMONDY, WILHELM BACHMANN, and ELIZABETH FINDLAY STEVENSON (*Zeitsch. anorg. Chem.*, 1912, 75, 189—197).—A vacuum vessel, provided with a manometer, is connected by means of high vacuum taps with a vacuum pump and a weighing vessel. When alcohol or benzene is used, taps with mercury seal are substituted. A gel being introduced into the weighing vessel in small fragments, water is placed in the vacuum vessel, and, the whole apparatus being kept at  $15^\circ$ , weighings are taken daily until

the weight is constant. The water is then replaced by sulphuric acid of known concentration, and the operation is repeated, the last experiment being made with concentrated sulphuric acid. The series of operations may then be reversed.

The dehydration curve thus obtained for silicic acid gel is similar to that found by van Bemmelen, but the middle portion is less nearly horizontal. Gels containing alcohol are examined in similar manner, using mixtures of alcohol and glycerol in the vacuum vessel. A sharp change in the direction of the curve is observed at the point at which the gel becomes opaque (compare Zsigmondy, *Abstr.*, 1911, ii, 880).

C. H. D.

**Preparation of a Readily Soluble Acid Sodium Borate.** SACCCHARIN-FABRIK AKTIEN-GESELLSCHAFT VORM. FAHLBERG, LIST & Co. (D.R.-P. 244778).—The salt obtained by the interaction of one equivalent of borax with three of boric acid is known; it is now found that by employing four equivalents of boric acid in concentrated aqueous solution that a *sodium hydrogen pyroborate*,  $\text{NaHB}_4\text{O}_7 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ , of constant composition is obtained.

It forms a crystalline, colourless powder with a faintly acid taste, and is sharply differentiated from borax by not giving a pink colour with phenolphthalein, and in that the precipitate obtained with silver nitrate does not darken when boiled.

F. M. G. M.

**Action of Lithium Hydroxide on Calcium Carbonate.** WILLIAM OECHSNER DE CONINCK (*Bull. Acad. roy. Belg.*, 1912, 201—202).—When freshly precipitated calcium carbonate is kept for thirty-four hours in a solution of lithium hydroxide at 97—98°, the calcium is replaced by lithium to the extent of 2.9%. The concentration of the lithium solution does not affect the result. The reaction is entirely reversible, and the reversibility is simply a function of the time.

W. G.

**Systematic Errors in the Determination of Atomic Weights.** GUSTAV D. HINRICHS (*Compt. rend.*, 1912, 154, 1227—1229).—A more detailed mathematical investigation than that already given (this vol., ii, 253) of the work of Richards and Wells on the atomic weight of silver and that of Wourtsel (this vol., ii, 248) on the atomic weight of nitrogen confirms the previous conclusion that the true atomic weight of silver is 108 and that of nitrogen 14.

T. A. H.

**Properties and Chemical Composition of Electrically Prepared Colloidal Silver Precipitated from its Solutions by Electrolytes.** G. REBIÈRE (*Compt. rend.*, 1912, 154, 1540—1543. Compare *Abstr.*, 1909, ii, 312).—A solution of colloidal silver prepared by Bredig's method is added to a 5% solution of barium or calcium nitrate, the mixture centrifuged, and the clear liquid decanted. The residue is washed with water until free from barium or calcium, then with alcohol and ether, and dried over sulphuric acid. The silver precipitate thus obtained is a black powder with a brown tinge, which does not become lustrous on rubbing. With hydrochloric acid it gives silver chloride and silver. It slowly absorbs carbon

dioxide from the air. When warmed in an atmosphere of nitrogen it is decomposed into silver and oxygen. Analyses point to the colloidal silver, precipitated as above, being a mixture of silver and silver oxide in proportions varying according to the conditions of preparation of the colloidal solution. W. G.

**Solubility of Silver Chloride in Water.** C. VAN ROSSEM (*Chem. Weekblad*, 1912, 9, 396—403. Compare this vol., ii, 348).—A continuation of the investigation of the solubility of silver chloride in water by the electro-conductivity method, the experiments being made in presence and in absence of light at 18° and 25°. The problem of the influence of potassium nitrate on the solubility still awaits solution. A. J. W.

**Solubility of Calcium Carbonate in Water.** JAMES KENDALL (*Phil. Mag.*, 1912, [vi], 23, 958—976).—The solubility of calcite and aragonite in water has been determined at 25°, 50°, and 100° by the direct method in which large silica flasks were employed for the preparation and analysis of the saturated solutions. At these three temperatures, the solubility of calcite, expressed in grams per litre, was found to be 0·01433, 0·01504, 0·01779, and that of aragonite 0·01528, 0·01617, 0·01902. The ratio of the solubilities at the three temperatures is constant within the limits of the experimental error.

Experiments were also made in which it was sought to determine the solubility by removal of the carbon dioxide from solutions of calcium hydrogen carbonate. The results for 25° are practically the same as those for calcite at this temperature; those for 50° lie between the values for calcite and aragonite, whilst those for 100° are identical with the value for aragonite. This series of numbers is in agreement with the observations relating to the influence of temperature on the nature of the crystalline product which separates out from hydrogen carbonate solutions.

The solubility of amorphous calcium carbonate could not be determined on account of its instability.

In contact with air containing 3·7 parts of carbon dioxide per 10,000, the solubility of calcite was found to be 0·04608 gram per litre at 25° and 0·02925 at 50°.

Measurements of the electrical conductivity of solutions of sodium and calcium hydrogen carbonates and of calcium sulphate are also recorded. H. M. D.

**Density of Silicate Mixtures.** EDWIN WARD TILLOTSON, jun. (*J. Ind. Eng. Chem.*, 1911, 3, 897—900).—It has been shown by Winkelmann and Schott that the density of a glass may be calculated with a rough degree of accuracy from its chemical composition.

The densities of some pure and mixed silicates have therefore been calculated, using the method and factors suggested by these authors (*Ann. Phys. Chem.*, 1894, [iii], 51, 697) with unsatisfactory results; new factors have therefore been devised; these are:  $\text{CaO} = 4\cdot1$ ,

$\text{MgO} = 4.0$ ,  $\text{Al}_2\text{O}_3 = 2.75$ ,  $\text{Li}_2\text{O} = 3.7$ , and it is stated that, although the method is not theoretically correct, it is capable of giving results (for a large variety of glass) which are only 1 to 1.5% in error.

F. M. G. M.

**Glucinum Arsenates.** BENNO BLEYER and BR. MÜLLER (*Zeitsch. anorg. Chem.*, 1912, 75, 285—292).—Whilst aluminium arsenates can only be obtained from aqueous solutions in a highly basic form, magnesium arsenates are stable. Glucinum, in accordance with expectation, lies between the two.

*Monoglucinum arsenate*,  $\text{GlH}_4(\text{AsO}_4)_2$ , prepared in concentrated solution and evaporated in a vacuum, forms colourless, hygroscopic leaflets. The *diglucinum* salt,  $\text{GlHAsO}_4$ , has only been obtained in an impure state by heating arsenic oxide with glucinum hydroxide in a sealed tube at  $220^\circ$ . When an attempt is made to prepare it in solution, *triglucinum arsenate*,  $\text{Gl}_3(\text{AsO}_4)_2 \cdot 15\text{H}_2\text{O}$ , is obtained as an amorphous powder, whilst solutions in the proportions to yield the latter compound yield instead a *basic* salt,  $\text{Gl}_3(\text{AsO}_4)_2 \cdot \text{GlO} \cdot 8\text{H}_2\text{O}$ .

*Potassium glucinum arsenate*,  $\text{KGlAsO}_4 \cdot \frac{1}{2}\text{GlO} \cdot 5\text{H}_2\text{O}$ , from potassium arsenate and glucinum sulphate, is unstable and amorphous, and yields more highly basic salts on hydrolysis. The corresponding *sodium* salt,  $\text{NaGlAsO}_4 \cdot \frac{1}{2}\text{GlO} \cdot 6\text{H}_2\text{O}$ , behaves similarly, whilst *ammonium glucinum arsenate*,  $\text{NH}_4\text{GlAsO}_4 \cdot 4\frac{1}{2}\text{H}_2\text{O}$ , is more stable, although it also undergoes further hydrolysis.

For analysis, the salts are dissolved in cold concentrated hydrochloric acid and saturated at  $0^\circ$  under pressure with hydrogen sulphide. The  $\text{As}_2\text{S}_5$  is collected, washed with alcohol, and dried at  $105^\circ$ . The glucinum is precipitated from the filtrate by ammonia.

C. H. D.

**Preparation and Heat of Formation of Magnesium Nitride.** CAMILLE MATIGNON (*Compt. rend.*, 1912, 154, 1351—1353. Compare Matignon and Lassieur, this vol., ii, 255).—Magnesium nitride is most conveniently obtained by the interaction of finely divided magnesium and ammonia. From the heat developed when the nitride is decomposed by dilute sulphuric acid, the heat of formation of the former is calculated to be  $+119.7$  cal.

H. W.

**Alkaline Solutions of Zinc Hydroxide.** ARTHUR HANTZSCH (*Zeitsch. anorg. Chem.*, 1912, 75, 371—372. Compare Klein, this vol., ii, 351).—The author's description of alkaline solutions of zinc hydroxide as pseudo-solutions (Abstr., 1902, ii, 395) was not intended to exclude the existence of zinc oxides, and the existence of modifications of zinc hydroxide was held to be probable. Moreover, the work of Mecklenburgh on stannic acids (this vol., ii, 355) has shown that such differences of solubility may be partly chemical and partly physical.

C. H. D.

**Attempt to Determine Certain Atomic Weights.** HECTOR PÉCHEUX (*Compt. rend.*, 1912, 154, 1419—1420).—The weights of metal deposited on the cathode in a number of electrolytic cells,

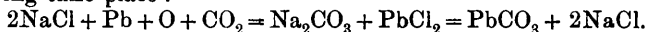
arranged in series and containing solutions of pure, neutral metallic salts, submitted to the influence of the same current for the same time were determined. Silver (A.W. 107·88) being taken as the standard, the atomic weights of the other metals were calculated from the results obtained, giving the values  $\text{Pb}=206\cdot86$ ;  $\text{Cu}=63\cdot43$ ;  $\text{Zn}=65\cdot44$ .  
W. G.

**Porous Metals.** HANNOVER (*Compt. rend.*, 1912, 154, 1594—1597).—When a binary alloy containing a greater percentage of the one component than corresponds with the eutectic composition is centrifugalised whilst in the liquid (somewhat pasty) condition, the eutectic can be expelled, leaving the component in excess in a porous condition. Using an alloy of lead and antimony containing 90% of lead, and one of tin and lead containing 80% of tin, the author has obtained both porous lead and porous tin. Similarly, from an alloy of lead with an excess of antimony, porous antimony was obtained.

The porous lead so obtained may be used in making accumulator plates of very large capacity. Other uses for these porous metals are suggested.  
T. S. P.

**Spontaneous and Progressive Destruction of Certain Objects Made of Lead.** CAMILLE MATIGNON (*Compt. rend.*, 1912, 154, 1609—1611).—Ancient lead objects preserved in museums often gradually crumble to a fine powder consisting essentially of lead carbonate. When such destruction has taken place, chlorides are always present in the powder. Experiments with lead which had been immersed in a 30% solution of sea-salt and then dried so that crystals of salt clung to it, proved that progressive destruction took place over a period of three years of testing. A blank experiment with lead which had not been dipped into such a solution showed no destruction over the same period of time.

The author supposes that some such cycle of reactions as the following take place:



Coating lead objects which are in the process of destruction with a collodion varnish retards, but does not do away with, the destruction. Washing them with boiling water until the wash-water does not give the test for chlorides, is of no effect.  
T. S. P.

**Optical Characters of Some Lead Silicates.** EDWARD H. KRAUS, HERMON C. COOPER, and A. A. KLEIN (*Centr. Min.*, 1912, 289—297. Compare *Abstr.*, 1909, ii, 890, 1009).—The materials examined consisted of the natural minerals alamosite ( $\text{PbSiO}_3$ , *Abstr.*, 1909, ii, 676) and barysilite ( $3\text{PbO}\cdot 2\text{SiO}_2$ ); numerous crucible fusions of lead oxide and silica in various proportions; and crystals from a lead furnace in Missouri. The microscopical characters indicate the existence of three definite compounds:

(1) Lead metasilicate ( $\text{PbSiO}_3$ ), which shows a good cleavage in one direction, oblique extinction, and a positive biaxial interference-figure with high refraction and birefringence.

(2) Lead pyrosilicate ( $3\text{PbO}\cdot 2\text{SiO}_2$ ), with a columnar structure and transverse cleavage; it is optically uniaxial and negative with high

refraction and low birefringence. The crystals from a lead furnace, with approximately the composition  $7\text{PbO}, 4\text{SiO}_2$ , are hexagonal with  $a:c = 1:1.0246$  and strong positive birefringence; this material is a complex solid solution of lead and other silicates, and is not an artificial barysilite.

(3) Lead orthosilicate ( $\text{Pb}_2\text{SiO}_4$ ), with fibrous to columnar structure and a transverse cleavage, straight extinction and optically biaxial, and negative with high refraction and birefringence.

A eutectic with 58% molecules  $\text{PbO}$  is formed in some of the fusions.

L. J. S.

**The Thallic Salts of Halogen Oxy-acids.** JULIUS GEWECKE (*Zeitsch. anorg. Chem.*, 1912, 75, 272—276).—Thallous chlorate, prepared from thallous nitrate and potassium chlorate, explodes at  $186^\circ$ . *Thallic chlorate*,  $\text{Tl}(\text{ClO}_3)_3 \cdot 4\text{H}_2\text{O}$ , obtained by dissolving freshly prepared, moist thallic oxide in chloric acid and evaporating in a vacuum at  $25^\circ$ , forms colourless, deliquescent, rhombic crystals after recrystallisation from a small quantity of water. *Thallic perchlorate*,  $\text{Tl}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ , from thallic chloride and silver perchlorate, with an excess of perchloric acid, separates in a vacuum in small, white, hygroscopic crystals. *Thallic bromate*,  $\text{Tl}(\text{BrO}_3)_3 \cdot 3\text{H}_2\text{O}$ , is white and hygroscopic. *Thallic iodate*,  $\text{Tl}(\text{IO}_3)_3 \cdot 12\text{H}_2\text{O}$  and  $2\text{H}_2\text{O}$ , is white, becoming brown through hydrolysis. The salt with  $12\text{H}_2\text{O}$  is prepared by means of iodic acid, and that with  $2\text{H}_2\text{O}$  from silver iodate and thallic chloride, or by the action of chlorine on thallous iodate.

C. H. D.

**Tensile Strength of Electrolytic Copper on a Rotating Cathode.** C. W. BENNETT (*J. Physical Chem.*, 1912, 16, 294—311).—Copper was electro-deposited on a 1" aluminium tube which was rotated at varying speeds up to 5500 revolutions per minute, current densities up to 4.3 amperes per sq. cm. being used. A high speed and moderately high current density lead to a cathode in which the crystals are small and the tensile strength correspondingly high. If, however, the current density is so high that the temperature of the cell rises notably, the strength of the deposited copper falls off, since a high temperature of deposition gives rise to a coarser, crystalline structure. With very high current densities the tensile strength is low, possibly because cuprous oxide is deposited.

In the author's apparatus (this vol., ii, 622), the electrolyte not being cooled, there is an optimum current density for each speed of rotation at which the deposit has its maximum tensile strength. The highest tensile strengths attained were 68,000 lbs. per sq. in. at 2500 revolutions per minute and 400 amperes per sq. ft., and 50,000 lbs. per sq. in. at 5500 revolutions per minute and 500 amperes per sq. ft.

When the cell starts working at  $75^\circ$ , or when the cell heats up to this temperature with the current, the deposit has the ductility and tensile strength of annealed copper (30,000 lbs.). Copper of "hard drawn" quality can be deposited at almost any current density if the stirring is efficient and the temperature is kept down.

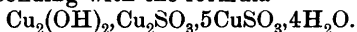
The current efficiency was high. Even at 1000 amperes per sq. ft. the efficiency was 99·6% at 5500 revolutions per minute. As the speed of rotation was increased, the pressure across the cell increased from 3·2 to 4·7 volts. It is not certain whether this was due to increased resistance, as by an air film on the cathode, or to a back *E.M.F.*, due to some frictional effect or centrifugal concentration effect.

There was no evidence in the deposits of a fibrous structure due to the high speed of the cathode. The microcrystalline appearance and the tensile strength were the same in the direction of rotation as at right angles to it. The electrolyte generally used contained 20% of crystallised copper sulphate and 12% of sulphuric acid, but considerable variations in the concentrations were without influence on the tensile strength of the deposit. Nitrate solutions were found to give unsatisfactory deposits.

Attempts were made to deposit bronze and brass electrolytically. The deposits of bronze were unsatisfactory, as the tin came down in a colloidal condition whether oxalate or tartrate electrolytes were employed. Brass deposited from a cyanide electrolyte was good at first, but rapidly deteriorated, owing to some decomposition product of the electrolyte being deposited in the metal, making it very brittle. A similar effect was observed when copper was deposited in presence of gelatin—the deposited copper could be crushed between the fingers.

R. J. C.

**The Method of Decomposition of Copper Sulphite.** HENRI BAUBIGNY (*Compt. rend.*, 1912, 154, 1606—1609).—When a solution of copper sulphate is mixed with the equivalent quantity of a solution of sodium sulphite and the mixture preserved for several days at room temperature in the absence of air, the yellowish-green precipitate first produced changes gradually (after five days) to a red colour; at the same time sulphur dioxide is produced. The red precipitate has a composition corresponding with the formula



The amount of dithionic acid formed (compare this vol., ii, 357, 447) is relatively small, being only about 5·4%. If the copper sulphate is replaced by copper chloride, the precipitate formed consists of cuprous chloride; the yield of dithionic acid is about the same.

At 72—75° the above reactions with copper sulphate are complete in about an hour and a-half, but the yield of dithionic acid is not greater than 8·71%.

T. S. P.

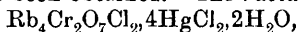
**An Apparatus for the Rapid Distillation of Mercury in a Vacuum.** LOUIS DUNOYER (*Compt. rend.*, 1912, 154, 1344—1346 \*)—The distillation chamber consists essentially of an inverted U-tube; one limb, which can be heated by an electric current and is coated with insulating material, is sealed into a narrow glass tube dipping into a trough containing the mercury to be distilled. The other limb is also sealed into a much longer tube which dips into a reservoir, which can be exhausted by a pump, residual air being expelled by the distilled mercury in its passage down the tube. An automatic cut-off at any required point is provided.

H. W.

\* and *Ann. Chim. Phys.*, 1912, [viii], 26, 419—432.

**Chromates and Mercuric Chloride.** DANIEL STRÖMHOLM (*Zeitsch. anorg. Chem.*, 1912, 75, 277—284).—Mercuric chloride forms two types of compounds with metallic chromates,  $M_2Cr_2O_7 \cdot HgCl_2$ , the ammonium and potassium salts of which are already known, and  $M_4Cr_2O_7Cl_2 \cdot (HgCl_2)_4 \cdot 2H_2O$ , none of which have previously been correctly described.

The salt,  $K_4Cr_2O_7Cl_2 \cdot 4HgCl_2 \cdot 2H_2O$ , is obtained over a wide range of concentration from solutions containing potassium chloride, and usually forms long, thin, yellowish-red tablets. The corresponding ammonium salt,  $(NH_4)_4Cr_2O_7Cl_2 \cdot 4HgCl_2 \cdot 2H_2O$ , resembles the potassium salt. Salts of different composition have not been obtained, even when the proportions of the component salts are varied considerably. Sodium salts have not been obtained. The rubidium salt,



resembles those described above.

In the analysis of these salts, the solution in dilute hydrochloric acid is reduced with alcohol on the water-bath, and after removal of aldehyde the mercury is precipitated with hydrogen sulphide.

C. H. D.

**Influence of Various Impurities on the Activity of Aluminium.** ÉMILE KOHN-ABREST and RIVERA-MALTES (*Compt. rend.*, 1912, 154, 1600—1602).—The activity of aluminium referred to is the reducing power it possesses when amalgamated. It is not affected by the traces of iron and silicon which are present in ordinary commercially-pure aluminium. The presence, however, of about 0.1% of copper so affects the activity that the aluminium is scarcely acted on by water. The results are slightly different when the action towards air, instead of water, is investigated.

The experiments, from the results of which the above conclusions were drawn, were made by dipping a piece of aluminium into solutions of mercuric chloride of varying strengths, and then, after rinsing, exposing it to the action of distilled water or of air.

T. S. P.

**Investigation of Iron-Zinc Alloys by means of Electromotive Force.** ÉMILE VIGOUROUX, F. DUCELLIEZ, and A. BOURBON (*Bull. Soc. chim.*, 1912, [iv], 11, 480—485).—A series of iron-zinc alloys was prepared by melting the two metals together in a current of hydrogen. The *E.M.F.*'s developed when the various alloys so prepared were opposed to poles of zinc in a *N*/20-solution of zinc sulphate were measured.

The results showed that alloys containing from 10.9 to 21% of iron gave an *E.M.F.* of 0.115 volt, those with 22.9 to 71% gave 0.144 to 0.195 volt, those having 72.1 to 80.0% developed an *E.M.F.* of 0.35 volt and those containing from 82.5 to 87.8% of iron gave 0.39 volt. The conclusion is drawn, therefore, that the following definite compounds of the two metals exist:  $FeZn_7$  (10.8% Fe),  $FeZn_3$  (22.19% Fe),  $Fe_3Zn$  (71.9% Fe), and  $Fe_2Zn$  (81.1% Fe). The first two of these have been found already by Vegesack (*Abstr.*, 1907, ii, 170).

T. A. H.

**Methods of Increasing the Resistance of Technical Alloys to Chemical Action.** OTTO BARTH (*Metallurgie*, 1912, 9, 261—276).—Of the alloys of cobalt and tin, those containing only small quantities of one or other of the metals are more readily attacked by acids than the pure metals. An alloy containing 40% of cobalt and 60% of tin is highly resistant to acids, but is brittle and unworkable. If alloyed with four times its weight of copper, a yellow, malleable alloy is obtained, which is resistant to dilute nitric acid.

The addition of 2% of cerium to aluminium, by the addition of cerium fluoride to the electrolytic bath, greatly increases the malleability of the aluminium. The solubility in alkalis or hydrochloric acid is not affected, but the solubility in dilute nitric acid is increased.

C. H. D.

**Hydrates and Ammonia Compounds of Cobalt, Nickel, Manganese, Cadmium, Zinc, and Copper Perchlorates.** ROBERTO SALVADORI (*Gazzetta*, 1912, 42, i, 458—494. Compare Abstr., 1910, ii, 959, 1002).—Cobalt perchlorate,  $\text{Co}(\text{ClO}_4)_2$ , forms compounds with  $6\text{H}_2\text{O}$ ,  $6\text{NH}_3$ ,  $5\text{NH}_3$ ,  $4\text{NH}_3$ ,  $3\text{NH}_3$ ,  $4\text{NH}_3 + 2\text{H}_2\text{O}$ ,  $3\text{NH}_3 + 3\text{H}_2\text{O}$ , and  $2\text{NH}_3 + 2\text{H}_2\text{O}$ . Nickel perchlorate with  $6\text{H}_2\text{O}$ ,  $4\text{H}_2\text{O}$ , and  $6\text{NH}_3$ . Manganese perchlorate with  $6\text{H}_2\text{O}$ ,  $4\text{H}_2\text{O}$ ,  $12\text{NH}_3$ , and  $5\text{NH}_3 + \text{H}_2\text{O}$ . Cadmium perchlorate with  $7\text{H}_2\text{O}$ ,  $4\text{H}_2\text{O}$ ,  $6\text{NH}_3$ , and  $4\text{NH}_3$ . Zinc perchlorate with  $6\text{H}_2\text{O}$ ,  $4\text{H}_2\text{O}$ , and  $4\text{NH}_3$ . Copper perchlorate with  $8\text{H}_2\text{O}$  (?),  $4\text{H}_2\text{O}$ ,  $2\text{Cu}(\text{OH})_2$ ,  $8\text{NH}_3$ ,  $4\text{NH}_3$ ,  $3\text{NH}_3 + \text{H}_2\text{O}$ ,  $\text{Cu}(\text{OH})_2 + 6\text{NH}_3 + 2\text{H}_2\text{O}$ , and  $\text{Cu}(\text{OH})_2 + 4\text{NH}_3 + 2\text{H}_2\text{O}$ .

The hydrated perchlorates of these metals are strongly hygroscopic, and, when heated, decompose before all the water is eliminated, so that the anhydrous perchlorates cannot exist. The solubility of the hexahydrated salts corresponds with about a gram-mol. per 100 grams of water. The molecules of water in the hexahydrates may be replaced, partly or wholly, by ammonia, the ammonia compounds being non-hygroscopic, although in the air they undergo more or less rapid transformation into mixtures of hydroxides of the metals and ammonium perchlorate; the values of the pressure of the ammonia liberated on heating indicate gradual and continuous dissociation of the ammonia compounds.

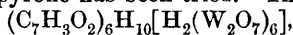
The decomposition of the hydrated and ammoniated perchlorates by heat is preceded by the formation of endothermic compounds, which are most probably oxides of chlorine in the case of the hydrated compounds, and nitrogen chloride in that of the ammoniated compounds. Cadmium and zinc perchlorates are the most resistant to heat, but they surpass the others in explosivity.

With an excess of ammoniated perchlorate in presence of its solution, equilibrium is established between the ammonia and water, which strive to replace each other in the perchlorate. If the excess of the ammoniated perchlorate is removed, a certain quantity of metallic hydroxide is precipitated and ammonia eliminated, whilst the ammoniated perchlorate passes into solution.

T. H. P.

**The Constitution of the Metatungstates.** ARTHUR ROSENHEIM (*Zeitsch. anorg. Chem.*, 1912, 75, 141—144).—Polemical in reply

to Copaux (this vol., ii, 454). The formulæ now proposed by Copaux for the metatungstates are in agreement with those previously proposed by the author, and metatungstic acid is thus a heteropoly-acid. The acid should, however, be decabasic, whilst only hexabasic salts, including the guanidinium salt, have been obtained. In order to obtain a decabasic salt, a weak base yielding insoluble salts must be used, and dimethylpyrone has been tried. The salt,



is, however, only hexabasic. The result must be attributed to the instability of the anion. There is no reason to distinguish between "normal" and "secondary" basicity. C. H. D.

**The Decomposition by Heat of Uranyl Nitrate.** PAUL LEBEAU (*Compt. rend.*, 1912, 154, 1612—1614).—The decomposition by heat of uranyl nitrate dihydrate commences in the neighbourhood of  $100^\circ$ , the first products formed being nitric acid and the uranic hydroxide,  $\text{UO}_3 \cdot \text{H}_2\text{O}$ . Immediately the melting point is reached there also occurs a partial dehydration of the mass, resulting in the formation of some anhydrous nitrate, which then further decomposes with the formation of uranium trioxide,  $\text{UO}_3$ .

These observations explain the formation of a mixture of uranium trioxide and its hydrate by the decomposition of fused uranyl nitrate. T. S. P.

**The Tin-Cadmium Alloys.** W. GUERTLER (*Intern. Zeitsch. Metallographie*, 1912, 2, 90—102, 172—177).—The results of Schleicher (this vol., ii, 256) are discussed, and it is shown that the irregularities observed at the tin end of the diagram are to be attributed to imperfect attainment of equilibrium. The breaking up of the  $\gamma$ -crystals into  $\beta$ -tin and cadmium takes place at too low a temperature to permit of segregation of the components, with the result that an ultramicroscopic mixture is obtained, completely resembling the troostite of hardened steels.

A geometrical method is also described for the measurement of the magnitude of thermal effects from cooling curves. C. H. D.

**Zirconium Oxychlorides.** ÉDOUARD CHAUVENET (*Compt. rend.*, 1912, 154, 1234—1237).—It is shown that zirconium forms two series of oxychlorides, namely,  $\text{ZrOCl}_2$ , which is only known in the form of hydrates containing 2, 3.5, 6, or 8  $\text{H}_2\text{O}$ , and  $\text{ZrOCl}_2 \cdot \text{ZrO}_2$ , which is known in the anhydrous condition and in the mono- and tri-hydrated forms.

The oxychlorides described by Troost and Hautefeuille (Abstr., 1871, 998) and by Hermann (*Jahresb.*, 1886, 189) could not be obtained, but that mentioned by Endemann (Abstr., 1875, 1162) was prepared and shown to have the formula  $\text{ZrOCl}_2 \cdot \text{ZrO}_2$ . It is formed by heating the compound  $\text{ZrOCl}_2 \cdot 2\text{H}_2\text{O}$  first at  $150^\circ$  in hydrogen chloride and then at  $230^\circ$ . It is stable up to  $600^\circ$ , but then begins to decompose into  $\text{ZrCl}_4$  and  $\text{ZrO}_2$ . Water has no effect on the anhydrous salt, but decomposes the trihydrate, probably into  $\text{ZrOCl}_2$  and  $\text{ZrO}_2$ . This fact and comparison of the electrical conductivities of

this salt and those of zirconium chloride and the hydrated oxychloride,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ , support the formula now assigned to the salt.

T. A. H.

**Tetrasulphaminoplato-salts.** LUDWIG RAMBERG and STEN KALLENBERG (*Ber.*, 1912, 45, 1512—1514. Compare Kirmreuther, *Abstr.*, 1911, ii, 1908).—By the action of platinous hydroxide on an aqueous solution of sulphamic acid, *ammonium tetrasulphaminoplatinite*,  $[\text{Pt}(\text{SO}_3\text{NH}_2)_4](\text{NH}_4)_2 \cdot 6\text{H}_2\text{O}$ , has been obtained. From this the corresponding *sodium* salt was prepared by means of sodium platinochloride, whilst from the sodium salt and potassium nitrate the *potassium* salt,  $[\text{Pt}(\text{SO}_3\text{NH}_2)_4]\text{K}_2 \cdot 2\text{H}_2\text{O}$ , was prepared. The same substance was also obtained by the reaction of potassium *cis*-dichlorodisulphaminoplatinite (Kirmreuther, *loc. cit.*) on silver sulphamate. H. W.

**The Alloys of Palladium and Antimony.** W. SANDER (*Zeitsch. anorg. Chem.*, 1912, 75, 97—106).—Alloys of palladium and antimony may be melted in nitrogen in porcelain tubes. Undercooling to the extent of  $40\text{--}50^\circ$  is sometimes observed. The freezing-point curve has two maxima, at  $805^\circ$  and  $1220^\circ$ , corresponding with the compounds  $\text{SbPd}$  and  $\text{SbPd}_3$  respectively. There are also breaks in the curve at  $680^\circ$  and  $839^\circ$ , due to the compounds  $\text{Sb}_2\text{Pd}$  and  $\text{Sb}_3\text{Pd}_5$  respectively. Palladium retains antimony in solid solution up to 15%, and the compound  $\text{SbPd}_3$  also forms solid solutions between 68.5 and 72.5% Pd, and  $\text{Sb}_3\text{Pd}_5$  forms solid solutions between 57.5 and 61.5% Pd. Between 57.5 and 65% a thermal arrest occurs at  $524\text{--}532^\circ$ , and is accompanied by a change from a polyhedral to a lamellar structure. The change is attributed to a transformation of the compound  $\text{Sb}_3\text{Pd}_5$ . The compound  $\text{SbPd}_3$ , which also undergoes a transformation at  $1070^\circ$ , is less readily attacked by aqua regia than the palladium solid solution.

The alloys are brittle up to 85% Pd, the maximum brittleness occurring at the composition of the compound  $\text{SbPd}_3$ . C. H. D.

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### Mineralogical Chemistry.

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**Spitzbergen Coal.** W. HAMILTON PATTERSON (*Chem. News*, 1912, 105, 277).—A specimen of this coal yielded on analysis: moisture (total) 1·99, ash 2·52, carbon 79·79, hydrogen 5·45, sulphur 0·76, nitrogen 1·08, oxygen 8·4%.

A coking experiment gave 65·2% of coke, which was firm and blown out; the gas burnt with a large but not very smoky flame. The calorific value, as calculated from the analysis, was identical with the result obtained in the bomb calorimeter (7705 and 7703 calories).

L. DE K.

**Isomorphous Relations and Constitution of the Marcasite-Mispickel-Glaucodote Group.** ALBERT BEUTELL (*Centr. Min.*, 1912, 225—237, 271—282, 299—310. Compare Abstr., 1911, ii, 485, 728, 1094).—A résumé of the literature and tabulations of published analyses. Normal mispickel is a definite compound,  $S_2As_2Fe_2$ , and intermediate members consist of mixtures of this with marcasite ( $S_4Fe_2$ ) and  $As_4Fe_2$ . L. J. S.

**A Flourey Silicon Dioxide.** FR. TUČAN (*Centr. Min.*, 1912, 296—299).—A cavern in limestone on the island of Brač on the Dalmatian coast is lined with a soft chalky material and fibres of rock-salt. The chalky material (anal. I.) leaves a residue (anal. II.) in dilute hydrochloric acid, which is so very finely divided that it passes through the filter and does not settle in water. It is not attacked by sodium hydroxide solution, and it has a slight action on polarised light, being therefore a crystalline modification of silica, perhaps distinct from quartz.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	Na.	K.	Cl.	H <sub>2</sub> O.	CO <sub>2</sub> .	Total.
I.	20·27	0·03	0·20	40·38	0·89	1·78	trace	3·15	0·42	33·18	100·30
II.	97·92	0·26	0·41	0·72	—	—	—	—	0·18	0·60	100·09

L. J. S.

**Identity of Baeumlerite with Chlorocalcite.** FERRUCCIO ZAMBONINI (*Centr. Min.*, 1912, 270—271).—The double salt,  $KCl, CaCl_2$ , recently discovered in the Prussian salt deposits and named baeumlerite (O. Renner, this vol., ii, 357) is asserted to be identical with the chlorocalcite from Vesuvius described by A. Scacchi in 1872. The Vesuvian mineral was stated by Scacchi to contain chlorides of potassium and sodium, in addition to calcium chloride, and Zambonini (*Mineralogia Vesuviana*, 1910, p. 50) has recently suggested for it the formula  $KCl, CaCl_2$ . This was described as cubic with perfect cubic cleavages, whilst baeumlerite, also with three perfect rectangular cleavages, was described as optically biaxial with complex twinning: the latter feature is now ascribed to "optical anomalies." L. J. S.

**The Natural and Artificial "Burnt Zone" of Meteoric Iron and the Behaviour of Neumann's Lines in Heated Kamacite.** FRIEDRICH BERWERTH and GUSTAV TAMMANN (*Zeitsch. anorg. Chem.*, 1912, 75, 145—159).—Neumann's lines in kamacite are attributed to the presence of twinning lamellæ, which are revealed on etching, owing to the state of strain producing an electrolytic difference. The lines should therefore tend to disappear on annealing. Portions of the Mount Joy meteorite, showing numerous Neumann's lines, are heated at about 870° for varying periods. In less than a minute the lines are much weakened, but some persist even after the kamacite has become granular. The original needles of rhabdite disappear during heating, and the rhabdite finally forms a border to the grains. At 1050° the transformation is complete in a second, whilst at 700° it is not complete in four hours.

The natural burnt zone is conveniently examined in the Avče meteoric iron. In the outer layer of granular kamacite, the lines have completely disappeared. Within this is a layer of irregular structure, containing fragments of the lines, and this passes into the normal internal structure. The structure is in accordance with the diminution of temperature from the surface inwards. Systems of lines perpendicular to the surface undergo alteration more rapidly than those which are inclined or parallel. The effect is similar, but is less clearly seen, in octahedral irons. The net-like structure of the kamacite in the latter is of different origin from the Neumann's lines, as it is entirely undisturbed in the burnt zone. It is due to the presence of intercrystalline films of troilite or taenite.

The thickness of the natural burnt zone is very variable, being greatest at the prominences and least in the hollows of the surface. In the Avče meteorite the limits are 4·8 and 1 mm. An artificial burnt zone is produced by heating sections of kamacite, wrapped in asbestos paper, to incipient fusion in the oxy-hydrogen blowpipe. Three layers are then observed. In the outermost, granules of nickel-iron, separated by oxide, are observed. The middle layer shows granulation, but the rhabdite needles are still present, and this passes into the inner layer, in which Neumann's lines are still visible.

C. H. D.

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## Physiological Chemistry.

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**Absorption of Oxygen by the Lungs.** C. G. DOUGLAS and JOHN S. HALDANE (*J. Physiol.*, 1912, 44, 305—354).—Improved methods are described for using carbon monoxide to determine the arterial oxygen pressure in animals and men. Under normal conditions the passage of oxygen into the blood is due to diffusion. When the oxygen in the air is lessened, during muscular work, and in carbon monoxide poisoning, the oxygen tension in the blood rises higher than the pressure of oxygen in the alveoli. This is due to active secretion of oxygen inwards, which is excited by products of metabolism acting on the alveolar epithelium. W. D. H.

**Gaseous Metabolism of Striated Muscle in Warm-blooded Animals.** I. FRITZ VERZAR (*J. Physiol.*, 1912, 44, 243—258).—On examination of the blood leaving the cat's gastrocnemius, it was found that the oxygen used per gram of muscle at rest is 0.00448 c.c. During and for a long time following contraction this amount is increased; this probably means that oxygen is used in the process of recovery. Carbon dioxide and other acids (probably lactic) are produced in large amount after a tetanus. These acids assist the dissociation of oxy-hæmoglobin. The quantity of blood in muscle is about 2.5%; the rate of blood flow is decreased during muscular

activity, but increased afterwards. Cutting the sciatic nerve accelerates the rate of blood-flow.

W. D. H.

**The Influence on the Respiratory Exchange of Varying Amounts of Carbohydrates in the Diet.** FRANCIS G. BENEDICT and HAROLD L. HIGGINS (*Amer. J. Physiol.*, 1912, 30, 217—232).—With the same individual and the same diet on the preceding day, the respiratory exchange on the morning without food will be the same. It may be necessary to continue the diet two or three days before this agreement is reached, if the diet contains much carbohydrate, or the supply of body carbohydrate at the beginning of the experiment is small. With different individuals the same diet will lead to the same respiratory quotient the next day without food. The supply of body carbohydrate as shown by the respiratory quotient after digestion has ceased, bears a distinct relation to the quantity of carbohydrate in the preceding diet. A diet of 600 grams of carbohydrate and 3100 calories a day does not produce glycosuria in men with sedentary habit.

W. D. H.

**Action of Adrenaline on Respiratory Metabolism.** DIONYS FUCHS and NIKOLAUS RÓTH (*Chem. Zentr.*, 1912, i, 1480; from *Zeitsch. exp. Path. Ther.*, 1912, 10, 187—190).—Subcutaneous injections of 1 to 2.5 mg. of adrenaline produce in normal people, and in those suffering from Addison's disease, an elevation of the respiratory quotient; the rate of breathing, the volume of air breathed, the oxygen intake, and carbon dioxide output are all increased. The changes are attributed to an increase in combustion of sugar brought about by the drug.

W. D. H.

**The Blood of Ascidians.** II. MARTIN HENZE (*Zeitsch. physiol. Chem.*, 1912, 79, 215—228. Compare Abstr., 1911, ii, 740).—The corpuscles in the blood of *Phallusia* are acid, whereas the plasma is neutral or almost so. The acid reaction is due to free sulphuric acid in a concentration of about 3%, and the proportion  $\text{SO}_3 : \text{Cl}$  is about twenty times greater than in sea-water. Full details of the inorganic constituents of plasma and sea-water are given. The vanadium chromogen of the corpuscles is a complex substance containing protein, and vanadium in the form of trioxide; further details of its properties are given. It does not act as an oxygen carrier in the same way as does hæmoglobin, although it may be a pseudo-auto-oxidiser in Engler's sense.

W. D. H.

**The Action of Colloid Solutions which Act as Protein Precipitants on Warm-blooded Animals, and their Relationship to Anaphylactic Processes.** R. DOERR and J. MOLDOVAN (*Biochem. Zeitsch.*, 1912, 41, 27—50).—The action of certain colloids, such as nucleic acid, colloidal ferric hydroxide, silicic acid hydrosol, which precipitate proteins when injected into animals, was investigated. The toxic symptoms which intervene may be ascribed to changes in the blood-plasma proteins, which are manifested in the changes in the coagulability of the blood. Experiments are quoted on the action of

certain antisera (precipitins, etc.) when intravenously injected, and attention is called to the similarity of the toxic symptoms to those produced after injection of colloids. Both kinds of toxins appear to produce similar changes (chiefly apparently in the solution equilibrium of the proteins), and there appears to be some intimate relationship between anaphylaxis (which is thought by the authors to be the same phenomenon as that produced by the injection of anti-sera) and the shock produced by colloid injection. S. B. S.

**A Precipitin for Differentiating between Boiled (Coagulated) Proteins.** W. A. SCHMIDT (*Zeitsch. Immunitätsforsch. exp. Therapie*, 1912, 13, 166—185).—If blood serum is heated to 70° or boiled for three hours and then dissolved by heating in dilute alkali, it no longer reacts with ordinary precipitin, but when injected into the circulation stimulates the production there of a "heat-alkali precipitin" to which it reacts. A similar precipitin can be prepared for coagulated muscle protein. Intense action of alkali destroys ultimately the power of coagulated protein to give rise to a precipitin. W. D. H.

**The Relation of Proteins to Crystalloids. III. Hæmolysis by Alkali. IV. Hæmolysis by Hypotonic Sodium Chloride Solutions. V. Hæmolysis by Rise of Temperature.** HERBERT E. ROAF (*Quart. J. exp. Physiol.*, 1912, 5, 131—148).—Addition of alkali to sodium chloride solution causes an increase in osmotic pressure of a hæmoglobin solution in equilibrium with it, which runs parallel to the hæmolytic action of the alkali. Therefore hæmolysis by alkali may be due to an increase in the osmotic pressure of the hæmoglobin in the corpuscles. In hæmolysis by acid, no such increase in pressure is found. Hæmolysis by dilution is probably the result of a temporary difference in osmotic pressure; if the corpuscle wall is impermeable to sodium and chlorine, a difference of pressure of over 1000 mm. of mercury exists before hæmolysis occurs; the osmotic pressure of hæmoglobin does not show an increase corresponding with hæmolysis by dilution. Hæmolysis by rise of temperature may be due to increase in the osmotic pressure of hæmoglobin. The relation of cells to inorganic substances can be explained without the assumption that the cell-membrane will not allow these substances to pass through it. W. D. H.

**Hæmolysis by Lecithins.** J. C. SCHIPPERS (*Biochem. Zeitsch.*, 1912, 41, 158—159).—Lecithins of different origins do not possess quantitatively the same hæmolytic power. S. B. S.

**Lipolysis.** GUIDO IZAR (*Biochem. Zeitsch.*, 1912, 40, 390—419).—The lipolytic action was investigated by means of the stalagmometer. Blood and most organs contain a ferment capable of hydrolysing triolein. The lipolytic action of the extract of the pancreas is stronger than that of other organs. The lipolytic power of the same organs of different animals is about the same. The curves representing the scission of triolein are nearly the same for Grüber's lipase preparation as for the fresh pancreas extract. The optimal temperature is 40—42°, but lipolysis takes place even at 0°. The reaction takes place best in

slightly alkaline solutions (*N*/150-sodium hydroxide). The action of serum and organ extracts was also investigated on the compounds obtained by the condensation of palmityl, stearyl, lauryl, and myristyl chlorides with glycine and *D*-alanine. It was found that blood-serum has only a small capacity for hydrolysing such products into the amino- and fatty acids. A greater capacity is possessed by the aqueous extracts of lungs, muscles, mucous membrane of the small intestine, brain, ovary, and thymus, and still greater capacity by extracts of testicles, spleen, and suprarenals. A still greater capacity is shown by the extracts of liver, kidneys, and thyroids, whereas aqueous pancreatic extracts are inactive. The extracts of organs from different animals act in a similar manner. The minimum temperature of this reaction is 15°, and the optimal temperature 38–40°. The ferment is destroyed by heating for half an hour at 56–57°. Experiments on these substances carried out by the polarimetric method give the same results as those got by the stalagmometric method. S. B. S.

**Influence of the Diet on the Amount of Sodium and Potassium in the Dog.** P. GÉRARD (*Compt. rend.*, 1912, 154, 1305–1307).—Dogs were fed under parallel conditions, in the one case with a vegetable diet containing twenty-two times as much potassium as sodium, and in the other with a meat diet containing twice as much potassium as sodium. In the first case, potassium was retained, but more sodium was excreted than was received in the food. The proportion of the mineral constituents of the blood remained constant. The relation between the amounts of potassium and sodium was 1.58 in the liver of the vegetarian dog, and 1.28 in the dog fed on flesh. In the kidney the corresponding values were 1.53 and 1.25. The results were confirmed by experiments with mice. The ratio of potassium to sodium was 2.41 with a diet rich in potassium, 1.54 with a diet rich in sodium, and 1.47 with a normal diet.

The results are in agreement with Bunge's theory, that the action of potassium is to displace sodium from the body. E. F. A.

**The Influence on Metabolism of Non-oxidisable Material in the Intestinal Tract.** FRANCIS G. BENEDICT and LOUIS E. EMMES (*Amer. J. Physiol.*, 1912, 30, 197–216).—Notwithstanding the intense peristalsis produced by 15 grams of sodium sulphate, the gaseous metabolism of the body is not materially increased, provided precautions are taken to exclude extraneous muscular activity. Loewy's contrary results may be explained by the absence of this precaution.

In experiments with a bulky but nearly indigestible food (agar-agar) similar results were obtained in those cases where muscular efforts, fatigue, and headache were excluded.

These experiments were made on men, and tell against Zuntz's view that the activity of the digestive tract is an important factor in the total gaseous metabolism of the body. W. D. H.

**The Rôle of Electrolytes in the Action of Certain Animal Ferments.** H. BIERRY (*Biochem. Zeitsch.*, 1912, 40, 357–369).—The pancreatic and intestinal juices of the dog entirely lose their

power of hydrolysing starch when submitted to dialysis against distilled water. The power can, however, be restored if chlorine or bromine ions are added, and these are absolutely essential for the production of the amylolytic action. Dialysed pancreatic juice does not attack maltose, neither does dialysed intestinal juice attack sucrose; the action can in both cases be partly restored on addition of chlorides. In this respect, the above-mentioned animal ferments differ from the amylases of vegetable origin, and also from lactase and emulsin of animal origin, which are capable of exerting their hydrolysing action even in the absence of chlorides. S. B. S.

**The Enzymes which Attack Mannans, Galactans, and Celluloses.** H. BIERRY and J. GIAJA (*Biochem. Zeitsch.*, 1912, 40, 370—389).—The authors give a general account of the polysaccharides which may be considered as anhydrides of mannose and galactose (mannans and galactans), of their botanical origin, and of the investigations on the ferments which act on them. They have been able to obtain from the alimentary tract of various invertebrates enzymes which are capable of hydrolysing polysaccharides of these characters; thus the hepato-pancreatic juice of *Helix pomatia* hydrolyses all the mannans and galactans which have been investigated. The gastric juice of *Astacus fluviatilis* acts on the manno-galactose of lucerne and Greek hay, giving rise always to galactose, and also to mannose, but the amount of the latter substance varies according to the concentration of the ferment. This appears to indicate that manno-galactan is a mixture of mannans and galactans. The action of this juice on mannans of different origin varies; thus, the soluble mannan from the seeds of lucerne or Greek hay is less readily attacked than the insoluble Corrozo mannan. The gastric juices of sea crustaceans can be employed for differentiating the mannans of various origin, attacking the Corrozo mannan, but not the mannans of lucerne and Greek hay. In the same way the mannans can be employed for differentiating the various gastric juices (of *Helix*, *Astacus*, *Maja*, and *Homarus*). It is assumed that the various mannans and galactans are substances formed by the condensation of different numbers of molecules of mannose and galactose. The various mannanases and galactanases differ from one another and also from other sucroclastic ferments. S. B. S.

**Ageing of Flour and its Effect on Digestion.** J. A. WESENER and GEORGE L. TELLER (*J. Ind. Eng. Chem.*, 1911, 3, 912—919).—The author discusses the work of Ladd, Bassett, Halliburton, Mann, and Hale on this subject, together with the criticism on the same by Rockwood. A description of numerous digestion experiments on (1) starch from flour which has been bleached with oxides of nitrogen; (2) on bread which had been impregnated during preparation with nitrous fumes, and (3) on fibrin which had been treated with a nitrite solution.

The conclusions of the author are (a) that nitrites do not interfere with diastase in its action on starch, even when present as sodium nitrite

to the extent of one part in 1000. (b) Nitrous and nitric acids do not inhibit peptic digestion, and may wholly replace hydrochloric acid; digestion by pepsin without acids will not take place. (c) Whilst pancreatic digestion will not take place in the presence of free acids, it is not inhibited by the presence of relatively large quantities of nitrites, neither is its action restrained on the protein which has been previously subjected to appreciable quantities of nitrous and nitric acids. (d) Other writers on this subject have not demonstrated the presence of mineral nitrite, nitrous or nitric acids in commercially bleached flour. (e) The nitrite-reacting material in flour appears to be due to the direct union of the colouring matter and the nitrogen oxide. (f) It has been shown by Vaughan that the substance which gives the nitrite-reacting material and responds to Liebermann's nitroso-reaction is not poisonous, neither has it any action on the blood.

F. M. G. M.

**Relative Digestibility of White and Wholemeal Breads.** L. F. NEWMAN, G. W. ROBINSON, E. T. HALNAN, and HENRY A. D. NEVILLE (*J. Hygiene*, 1912, 12, 119—143).—The experiments on four men, each lasting a week, deal with the digestibility of white and so-called standard breads. The two kinds of bread were eaten under strictly comparable conditions. The degree of absorption showed marked uniformity, except that in one individual the phosphorus absorption was considerably less than in the others. The results yield no support to the view that "standard" bread possesses any advantages as regards the availability of the main food constituents. In relation to protein there is a distinct advantage on the side of white bread, some 3½% more being absorbed. The phosphorus compounds are more abundant in bread of the standard type, and are no worse absorbed than those in white bread. In breads containing more of the whole wheat berry than "standard" bread, the availability of both nitrogen and phosphorus proved to be decidedly less. With regard to the possible importance and special nutritive influence of unknown constituents present in the cortex of wheat, the present experiments yield no evidence. The results can only be of practical importance in cases where bread forms a very large proportion of the total dietary.

W. D. H.

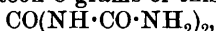
**A Nutrition Investigation on the Insoluble Carbohydrates or Marc of the Apple.** EDWARD C. SCHNEIDER (*Amer. J. Physiol.*, 1912, 30, 258—270).—The pectin prepared from apple marc yields on hydrolysis with hydrochloric acid 35·87% of pentosan and 45·83% of galactan. The intestinal bacteria destroy hemicelluloses and also the pectin. They do not form reducing sugars as an end product. They destroy almost equally the pentosan and the galactan of the pectin. Animal enzymes, malt diastase, and "taka" diastase do not hydrolyse the marc or its pectin. Weak solutions of hydrochloric acid split off from the marc, pectin and reducing sugars. From 79 to 84% of the hemicelluloses of the marc is either utilised or destroyed during digestion. Bacterial activity probably accounts for this disappearance. The coefficient of digestibility for the pentosan is 87, and for the galactan 77.

W. D. H.

**Protein-sparing Action of Ammonium Salts in the Diet.** E. GRAFE (*Zeitsch. physiol. Chem.*, 1912, 78, 485—510).—Experiments on dogs, some of which lasted some months, are described in detail. The results are that ammonium salts lessen protein waste, and are probably synthesised in the body into protein material. The addition of tryptophan to ammonium salts in the diet has no appreciable effect. The meaning and origin of tryptophan in the body are discussed.

W. D. H.

**The Utilisation of Carbonyldicarbamide.** KURT HENIUS (*Chem. Zentr.*, 1912, i, 1483; from *Zeitsch. exp. Path. Ther.*, 1912, 10, 293—295).—The author took 8 grams of this substance,



added to a constant purine-free diet, and found that it is burnt to urea, ammonia, and carbon dioxide.

W. D. H.

**The Influence of Calcium Salts in the Purine Metabolism of Mammals.** H. LUBIENIECKI (*Arch. exp. Path. Pharm.*, 1912, 68, 394—400).—In sixteen experiments on rabbits and dogs, the administration of calcium salts decreased the purine (allantoin) excretion in nine cases; in three cases there was no effect, and in the remaining four the excretion was lessened.

W. D. H.

**Uric Acid Formation from Nucleic Acid and Hypoxanthine under the Influence of Atophan.** E. FRANK (*Arch. exp. Path. Pharm.*, 1912, 68, 349—370).—In men, as a rule, not more than one-third of administered nucleic acid is represented by uric acid formation. Atophan (2-phenylquinoline-4-carboxylic acid) rapidly increases the amount of uric acid formed after feeding on purine substances (nucleic acid, hypoxanthine); no such increase occurs in cases of gout.

W. D. H.

**The Effects of Thyroid Feeding on Nitrogen and Carbohydrate Metabolism.** R. A. KRAUSE and WILHELM CRAMER (*Proc. physiol. Soc.*, 1912, xxiii—xxiv; *J. Physiol.*, 44).—In man thyroid feeding produces diuresis, and a rise in the output of nitrogen, especially in the form of urea. The ammonia of the urine also rises, but the uric acid and creatinine show no change, or only a slight increase. Similar results were obtained in dogs. In dogs, also, there was a marked lowering of the limit of assimilation of carbohydrates, that is, glycosuria is readily produced.

W. D. H.

**Absorption of Fat by the Stomach in the Salmon.** CHARLES W. GREENE (*Amer. J. Physiol.*, 1912, 30, 278—282).—A full account of work of which a preliminary notice has already appeared (this vol., ii, 272).

W. D. H.

**Blood-flow and Metabolism in the Submaxillary Gland.** JOSEPH BARCROFT and FRANZ MÜLLER (*J. Physiol.*, 1912, 44, 259—264).—The rate of blood-flow in the submaxillary gland of anaesthetised cats, when the nerves to the gland were cut, varies from 0.25 to 0.45 c.c. of blood per minute; the oxygen intake varies from 0.017 to 0.027 c.c.

per gram per minute. Yohimbine causes no secretion of saliva even when injected in concentrations of 1 to 1000—5000 Ringer's solution into the arterial supply, although the dilatation of the arterioles so produced admits of a ten-fold increase in the blood supply. Such increase causes no measurable change in the oxygen used by the gland. After this treatment stimulation of the chorda tympani nerve leads to a good secretion of saliva and a seven-fold increase in the oxygen used.

W. D. H.

**Physiology of the Pancreas.** OTTO COHNHEIM and PH. KLEE (*Zeitsch. physiol. Chem.*, 1912, 78, 464—484).—The amount secreted of pancreatic juice, of pancreatic juice and bile, and in some cases of gastric juice was investigated in fistula-dogs fed on various diets. The substances which excited the greatest flow of pancreatic juice were beef steak, white bread and butter, and potatoes. Oatmeal, which has been recommended in diabetes, produces the smallest effect.

W. D. H.

**The Presence of the Active Principles in the Thyroid and Suprarenal Glands Before and After Birth.** FREDERIC FENGER (*J. Biol. Chem.*, 1912, 11, 489—492).—It has been stated that the thyroid of new-born animals does not contain iodine. As this appeared highly unlikely the question was re-investigated, and a similar search was made for adrenaline. The material was obtained from the ox, pig, and sheep, and the result was that both active principles are present long before birth; the activity is increased shortly before birth, and a maximum is reached in the young growing animal.

W. D. H.

**Physiology of Glands. XVII. The Internal Secretion of the Suprarenal Bodies and their Innervation.** LEON ASHER (*Zeitsch. Biol.*, 1912, 58, 274—304).—If means are adopted to exclude all the organs supplied by the splanchnic nerve, except the suprarenals, then stimulation of that nerve leads to a rise of blood pressure. If the suprarenals are also excluded, no rise of blood-pressure occurs when the nerve is stimulated. The result is attributed to production of adrenaline, and the splanchnic nerve is regarded as the true secretory nerve of the suprarenal bodies.

W. D. H.

**Pituitrin and its Active Constituents.** HERMANN FÜHNER (*Chem. Zentr.*, 1912, i, 1586; from *Münch. med. Woch.*, 59, 852—853).—The action of an extract of the infundibular portion of the pituitary body (Parke Davis's pituitrin) is on intravenous injection into rabbit very similar to anaphylactic shock. Histamine ( $\beta$ -iminazolyethylamine) and methylguanidine have somewhat similar actions. The active substance in the extract is not yet identified, but it is suggested that it is allied to the substances mentioned.

W. D. H.

**Fasting Studies. X. A Glycogen-free Liver.** PHILIP B. HAWK (*J. Amer. Chem. Soc.*, 1912, 34, 826—828).—In connexion

with the author's fasting studies, the liver of a dog which had fasted for periods of 117 days and 104 days was examined, and found to be free from glycogen. Pflüger (Abstr., 1907, ii, 796) found that glycogen was still present in the liver of a dog after a fast of seventy-three days. It seems, therefore, that the liver of an animal subjected to repeated and very prolonged fasts may be rendered glycogen-free, whilst in the case of an animal subjected to a single protracted fast some glycogen will still remain.

E. G.

**Glycogen Formation in the Liver after Intravenous Injection of Sugar.** ERNST FREUND and HUGO POPPER (*Biochem. Zeitsch.*, 1912, 41, 56—70).—Part of the liver was analysed before injection, and part after injection. In the case of dogs it was found possible to increase the amount of glycogen after injection of sugar, especially after injection into a branch of the portal vein. For the experiment to succeed, it is necessary to exclude all form of cerebral stimulation, whether by narcotics or by an interruption of any of the centrifugal paths leading to the liver. The state of the digestive processes taking place in the animal at the time of the injection has no marked influence on the experiment. The addition of pancreas extract to the sugar solution, especially that obtained from an active pancreas (from an animal killed during the height of digestion), appears to especially favour glycogen formation.

S. B. S.

**The Utilisation of  $\beta$ -Hydroxybutyric Acid and the Meaning of Acetoacetic Acid in the Normal and Diabetic Livers.** I. BRUNO O. PRIBRAM (*Chem. Zentr.*, 1912, i, 1482—1483; from *Zeitsch. exp. Path. Ther.*, 1912, 10, 284—292).—The livers of freshly killed dogs were perfused with arterialised blood to which  $\beta$ -hydroxybutyric acid was added. There was a loss of the acid, and an increase of acetoacetic acid in the perfusion fluid; the latter, however, does not account for all the  $\beta$ -hydroxybutyric acid which disappears; some of the latter is probably synthesised in the liver with the formation of loose fatty acid-sugar complexes. In the livers of dogs made diabetic by phloridzin, the change is much smaller, as regards both reactions.

W. D. H.

**Autolysis and Metabolism. II. The Influence of Arsenic on Autolysis.** ERNST LAQUEUR and JAKOB ETTINGER (*Zeitsch. physiol. Chem.*, 1912, 79, 1—37).—Arsenic behaves in relation to autolysis much in the same way as it does to metabolism; in the latter case certain doses stimulate, and larger doses poison. In small doses autolysis is furthered, and in larger doses it is inhibited. The liver was the organ used. Full details in reference to dose and effect are given.

W. D. H.

**Autolysis and Metabolism. III. The Influence of Sodium Salicylate on Autolysis.** ERNST LAQUEUR [and, in part, KURT BRÜNECKE and E. CRAMPE] (*Zeitsch. physiol. Chem.*, 1912, 79, 38—64).—Sodium salicylate in large but not lethal doses increases the output of nitrogen, and similarly for a short time furthers autolysis of the liver.

After longer action, or in larger doses, it inhibits the process. It was found that the presence of the salt interferes somewhat with the removal of protein from the preparations investigated. Sodium fluoride is a good disinfectant in autolysis experiments, and interferes much less with enzyme action than toluene or chloroform. W. D. H.

**Autolysis and Metabolism. IV. The Influence of Sodium Benzoate on Autolysis.** ERNST LAQUEUR and KURT BRÜNECKE (*Zeitsch. physiol. Chem.*, 1912, 79, 65—81).—Sodium benzoate increases autolysis on the first day, just as in metabolism it increases the output of nitrogen. The presence of the salt increases the difficulty of removing proteins from the preparations. W. D. H.

**Autolysis and Metabolism. V. The Influence of Gases, Especially Oxygen and Carbon Dioxide, on Autolysis.** ERNST LAQUEUR (*Zeitsch. physiol. Chem.*, 1912, 79, 82—129).—Oxygen increases and carbon dioxide lessens the activity of the autolytic enzyme of the liver. The inhibitory influence of compressed oxygen is very great. The action of carbon dioxide is greater than that of corresponding strengths of other acids. Its furthering effect is quite marked at the tension in which it occurs in the blood. W. D. H.

**The Formation of Lactic Acid in Antiseptic Autolysis of the Liver.** GEORG VON STEIN (*Biochem. Zeitsch.*, 1912, 40, 486—497).—The quantity of lactic acid formed in autolysis increases from the forty-eighth to the seventy-second hours of incubation, and then diminishes. There appears therefore to exist in addition to the lactic acid-forming ferment, a ferment which destroys the acid. The antiseptic used exerts some influence on the amount of acid formed. Compared with chloroform water autolysis, water half saturated with salicylic acid, or one-eighth saturated with mustard oil, or 1% boric acid solution accelerate autolysis, whereas 10% alcohol inhibits it. The addition of carbohydrates does not increase the amount of lactic acid formed. S. B. S.

**Presence and Distribution of Manganese in Animal Organs.** GABRIEL BERTRAND and FLORENTIN MEDIGRECEANU (*Compt. rend.*, 1912, 154, 1450—1452. Compare this vol., ii, 459).—The authors have examined the digestive, respiratory, and genito-urinary organs, glands with internal secretion, muscular, nervous and osseous tissue, skin and teeth, adipose tissue, eyes, and finally the bile, milk or eggs of typical animals of the three classes, mammals, birds, and fishes. They find that, with the exception of the white of bird's eggs, manganese is present in all the organs examined, varying in amount from hundredths to tenths mgs. per 100 grams. For similar organs of the same species the variation in manganese content is very slight from one animal to another, and is but little greater amongst different species of the same class. The difference is, however, more marked from class to class, birds having a higher manganese content than mammals. Amongst the more important organs or tissues, the manganese content is highest in the uterus of birds (0.786—2.20 mgs.

per 100 grams), the lowest value occurring in the muscular and nervous tissues and the lungs. The grey matter of ox brain has a higher manganese content than the white matter; the heart and the muscles of the tongue than the muscles of the trunk and limbs. Milk is very poor in manganese, although slightly richer than blood.

W. G.

**The Potential Differences at Damaged and Undamaged Surfaces of Animal and Vegetable Organs.** JACQUES LOEB and REINHARD BEUTNER (*Biochem. Zeitsch.*, 1912, 41, 1—26).—The potential differences between the damaged and undamaged surfaces were measured in the usual way, the objects experimented on being amongst other things apples, tomatoes, and the finger-nails of human subjects. It was shown that the alteration of the concentration of an electrolyte at the undamaged surface alters conditions in such a way that the side with the decreasing concentration becomes more positive. The alteration in the concentration causes a change in accordance with Nernst's formula ( $E = RT/nT \cdot \log C_1/C_2$ ). The actual differences found, however, are somewhat smaller than those demanded by the formula, it being assumed that the membrane is permeable (reversibly) to cations. From these facts the conclusion is drawn that the intact membrane acts as a metal, with the distinction that it is not absolutely impermeable to anions. If the concentration of the salt solution is too high, changes appear to be caused in the membrane, the latter appearing to become more pervious to anions. With a suitable concentration of the salt (for example,  $m/20$ -sodium chloride), the potential difference is the same whether the solution is neutral, acid ( $m/1000$ -HCl), or alkaline ( $m/1000$ -NaOH). This shows that chains which are reversible as regards the hydrogen ions are not being dealt with. The addition of non-electrolytes exerts no influence on the potential difference. The fact that the alteration of the concentration of salts of different cations alters the electromotive force in the same way contradicts the hypothesis of Bernstein and Höber that the current of rest results from the diffusion of the salts of only one cation (potassium in the case of muscle). In this respect, also, the surface layers of organs differ from all other substances insoluble in water, such as the metals.

S. B. S.

**Purine Metabolism. IX. The Content in Purine Bases of the Muscles of Different Animals.** U. RINALDI (*Biochem. Zeitsch.*, 1912, 41, 51—55).—The content in purine bases in the striated muscles of different animals is smallest in the mantle of polyps; then come muscles of fish; the highest content is shown by the muscles of birds, which is greater than that in mammals. The breast muscles contain the largest quantity. The total and purine nitrogen, however, do not show very big variations when calculated as the percentage of the dried weight of tissue. Nevertheless, the purine nitrogen shows larger variations than the total nitrogen.

S. B. S.

**Toxicological Investigations on Bio-Electric Currents. II. The Pharmacological Specificity of Chemical Alterations in the Current.** L. HERMANN (*Zeitsch. Biol.*, 1912, 58, 261—273).—Certain substances affect the electrocardiogram, changing it into a

monophasic effect. The same substances affect the activity of the heart. A similar effect on skeletal muscle runs parallel with the effect of the reagents on its functional activity. The substances employed were lithium, ammonium, potassium, calcium, barium, strontium, and magnesium salts, strophanthin, antiarin, saponin, methyl-violet, veratrine, nicotine, eserine, aconitine, and guanidine; all of these have the double action on the heart except lithium salts, nicotine, and guanidine. The only ones in the list which have a similar action on skeletal muscle are ammonium and potassium salts, saponin, methyl-violet, veratrine, nicotine, and aconitine.

W. D. H.

**Nerve Degeneration.** HENRY O. FEISS and WILHELM CRAMER (*Proc. physiol. Soc.*, 1912, xx; *J. Physiol.*, 44).—Nerves kept in sterile Ringer's solution after removal from the body undergo a change similar to Wallerian degeneration, but so far the degenerated "myelin" has not given the Marchi reaction.

W. D. H.

**The Retina does not Contain the Chemical Constituents of the Optic Nerve.** N. ALBERTO BARBIERI (*Compt. rend.*, 1912, 154, 1367—1369).—Fresh retina obtained from the eye of the ox does not contain cerebroin or cerebrin.

H. W.

**Enzymes in Sterile Milk.** ARTHUR HARDEN and JANET E. LANE-CLAYPON (*J. Hygiene*, 1912, 12, 144—152).—The presence of peroxydase and catalase can be demonstrated in the milk obtained by catheter from both goats and cows. The catalase in goat's milk is more abundant than in cow's milk. The reduction of methylene-blue does not occur with catheter milk, at any rate within many hours. Schardinger's reagent is not reduced by goat's milk, but catheter milk from the cow frequently reduces it.

W. D. H.

**Spectrophotographic Investigation of Meconium.** LOUIS LEWIN (*Pflüger's Archiv*, 1912, 145, 393—400).—Acetone extracts a green pigment from meconium which shows two absorption bands ("meconium bands") which resemble those of acid hæmatoporphyrin. Their position, however, is not identical with those of hæmatoporphyrin, neither is the pigment convertible into alkaline hæmatoporphyrin by treatment with alkali. Variations in the position of the bands occur when other extracting agents are employed. Although the pigment is probably derived from bile pigment, it is not identical with any hitherto known substance. A yellow pigment soluble in benzene and in ether may also be present.

W. D. H.

**The Time of Secretion of Nitrogen, Carbon, Sulphur, and Phosphorus After Ingestion of Proteins and Their Hydrolysis Products. II. Experiments on the Dog.** CHARLES G. L. WOLF and EMIL ÖSTERBERG (*Biochem. Zeitsch.*, 1912, 41, 111—137).—Experiments similar to those carried out on the human subject (this vol., ii, 581) were carried out on dogs. The degradation of uncooked proteins takes place with greater difficulty in man than in

the dog. No fundamental difference could be observed, however, in the case of cooked proteins, except, perhaps, that in the case of man the curves representing the hourly excretion of nitrogen are somewhat steeper. In the case of the dog, as contrasted with man, the cystine group is not attacked before the nitrogenous parts of the protein molecule. Alanine also appears to be less readily attacked. There is, however, no very fundamental difference between the metabolism of man and dog. The dog appears in certain cases to secrete ammonia to neutralise the acid secretion products in the urine, whereas man under similar conditions excretes fixed alkalis. S. B. S.

**Undialysable Substance in Diabetic Urine.** HENRI LABBÉ and G. VITRY (*Compt. rend.*, 1912, 154, 1373—1375. Compare this vol., ii, 582).—The urine of diabetic patients contains a greater proportion of undialysable substances of more acidic character than does that of healthy persons. H. W.

**Presence of Radium in Some Carcinomatous Tumours.** W. S. LAZARUS-BARLOW (*Proc. Roy. Soc.*, 1912, B, 85, 170—173).—Acceleration of leak sometimes occurs when carcinoma tissue is introduced within an electroscope. Out of five non-malignant and twenty-eight malignant tissues examined, three cases of primary carcinoma and one of secondary carcinoma yielded sufficient evidence of the presence of radium in them. The amount in maximum corresponded with  $2.73 \times 10^{-5}$  mg. per gram of dried tissue. E. F. A.

**Sulphur Metabolism in Cancer Patients.** NAGATAKA MURECHI (*Biochem. Zeitsch.*, 1912, 41, 138—148).—After heating urine with hydrochloric acid and barium chloride, and filtering off the precipitated barium sulphate, a further precipitation can sometimes be caused by heating the filtrate with hydrogen peroxide. This reaction appears to be characteristic of cases of cancer; in normal cases only a trace of precipitate is produced, whereas in cancer cases the precipitation is marked; and the sulphur thus separated as barium sulphate can amount to as much as 3.8% of the total. It belongs to the "neutral" sulphur of the urine, and is partly derived from a  $\text{SO}_2$ -group. S. B. S.

**The Existence of a Proteolytic Ferment and the Detection of Amino-acids in Exudates.** KARL WIENER (*Biochem. Zeitsch.*, 1912, 41, 149—157).—In exudates from carcinomatous cases, a proteolytic ferment could be detected by its action on glycylglycine and leucylglycine, the glycine after scission of the polypeptide being isolated in the form of the hydrochloride of the ethyl ester. From carcinomatous exudates, furthermore, histidine, arginine, and leucine could be isolated. From an ascitic fluid, tyrosine, but not leucine, was isolated. Arginine and histidine could not be obtained from this material pure, the picrolonates isolated having too low a melting point. S. B. S.

**Asylum Dysentery.** HAMILTON TEBBUTT (*J. Hygiene*, 1912, 12, 218—226).—A number of dysentery bacilli of the mannitol-fermenting

type were isolated from cases in an English asylum. These may be divided into (1) those that do, and (2) those that do not ferment sorbitol and form indole in peptone-beef broth in six days. Several attempts to infect a monkey with sorbitol-fermenting strains failed. No dysentery bacilli were found in the flies infesting the surroundings of chronic and acute cases of bacillary dysentery. W. D. H.

**The Causation of Œdema.** LUDWIG PINCUSOHN (*Chem. Zentr.*, 1912, i, 1479—1480; from *Zeitsch. exp. Path. Ther.*, 1912, 10, 308—316).—In relation to Martin Fischer's view that the swelling of tissues is determined by the presence of acids produced by metabolic processes, the swelling of gelatin under the influence of a large number of acids was studied, and these are arranged in order of activity. Bile which lessens surface tension, diminishes the amount of swelling. Gelatin, muscle, and cartilage swell more in dilute acid than in distilled water. Liver, spleen, kidney, and lung behave in the opposite way. There are all gradations; thus the medulla of the kidney swells less than the cortex. W. D. H.

**The Synergic Action of Local Anæsthetics.** BÉLA VON ISSEKUTZ (*Pflüger's Archiv*, 1912, 145, 448—454).—Bürgi's teaching that the action of drugs of the same pharmacological group in combination is only an additive one, is not confirmed. The increased action is greater than this, and is seen in local anæsthetics in various combinations; thus antipyrine increases the action of cocaine by 46%, of eucaïne-B by 39%, and of novocaine by 19%. Eucaïne-B increases the action of novocaine by 32%. The action of cocaine on eucaïne-B and on novocaine is negligible. W. D. H.

**Pyruvic Acid Glycosuria, and the Behaviour of Pyruvic Acid in the Animal Body.** PAUL MAYER (*Biochem. Zeitsch.*, 1912, 40, 441—454).—In view of the fact that pyruvic acid is similar to dextrose in that it undergoes fermentation with yeast, its behaviour in the animal body (of rabbits) was investigated. The sodium salt administered *per os* or intravenously was found to be highly toxic, but relatively large doses (7—8 grams) could be tolerated when given subcutaneously. After such doses, the urine of animals in a state of normal nutrition contained dextrose, unchanged pyruvic acid (as salt), which was isolated in the form of the phenylhydrazone (m. p. 192°), lactic acid, and small quantities of protein. In the case of starving animals, injection of pyruvate only caused a slight glycosuria, but the livers of such animals contained appreciable quantities of glycogen, whereas the livers of animals which had not received pyruvate, and which had fasted for a similar period (eleven days), were free from glycogen. Hyperglycæmia was found in the case both of normally fed and fasting animals. The author discusses the reason of this fact, mentioning two possible hypotheses, namely, the synthetic formation of dextrose from pyruvic acid, and the toxic action of the latter.

S. B. S.

**Metabolism of Oxalic Acid and Oxalates.** JACQUES M. ALBAHARY (*Compt. rend.*, 1912, 154, 1370—1373).—Oxalic acid and sodium oxalate are not destroyed by the action of pepsin or of

pancreatic juice. When a slightly alkaline solution of oxalic acid is injected into a dog, the acid appears to be eliminated in the urine in two forms, one of which is precipitable immediately as magnesium oxalate, the other only after it has been submitted to the action of mineral acids.

H. W.

**The Physiological Action of Some Pyrimidine Compounds of the Barbituric Acid Series.** ISRAEL S. KLEINER (*J. Biol. Chem.*, 1912, 11, 443—470).—The administration of barbituric acid by the mouth causes only diarrhœa; given subcutaneously, the local effects seen are due to acid; the sodium salt has no such local action. Malonylguanidine, 5-aminomalonylguanidine hydrochloride, 2:4-diaminodihydro-6-pyrimidone sulphate, and 2:4:5-triaminodihydro-6-pyrimidone sulphate have no action. Subcutaneous injection of 5-aminomalonylguanidine hydrochloride leads to grave changes in the renal epithelium, albuminuria, and frequently death. All the series give a Prussian-blue colour with ferrous sulphate. Evidence is adduced which indicates that 2:4-diaminodihydro-6-pyrimidone and cyanoacetylguanidine are deamidised in the body.

W. D. H.

**The Synergic Action of the Opium Alkaloids.** BÉLA VON ISSEKUTZ (*Pflüger's Archiv*, 1912, 145, 415—439).—Certain drugs increase the action of others. Burgi showed that chloral hydrate and urethane or urethane and pyramidone do not act in this way, but morphine increases ("potentiert") considerably the narcotic action of urethane and of chloral hydrate. The present research deals with the question in relation to the numerous alkaloids of opium, and it is found that this potential action is present in varying degrees (20 to 50%) when dealing with alkaloids of different chemical composition (morphine, narcotine, papaverine), but is absent when the chemical composition of the toxophore group is similar (morphine, codeine, dionine, heroine, thebaine).

W. D. H.

**The Antagonism between the Opium Alkaloids and apomorphine.** BÉLA VON ISSEKUTZ (*Pflüger's Archiv*, 1912, 145, 440—447).—The emetic action of apomorphine is antagonised by codeine, heroine, thebaine, and morphine in doses small enough to produce no narcotic action.

W. D. H.

**Actions of Pilocarpine and Nicotine.** HENRY H. DALE and PATRICK P. LAIDLAW (*Proc. physiol. Soc.*, 1912, xii—xiii; *J. Physiol.*, 44).—The sympathetic effects on the eye produced by nicotine, hordenine methiodide, and cytisine are partly due to their direct action on ganglion cells, but occur even when the superior cervical ganglion is excised, provided that the suprarenal bodies are intact. If these bodies are removed or shut off from the circulation, the effects fail. Similar results occur with pilocarpine. These alkaloids have therefore, in part an indirect action by increasing the secretion of adrenaline. Anomalous effects on the cat's uterus *in situ* compared with the results seen in the isolated organ are probably susceptible of the same explanation.

W. D. H.

**Phosphorus Poisoning in a Dog with Partial Exclusion of the Liver (Eck's Fistula).** F. FISCHLER and K. BARDACH (*Zeitsch. physiol. Chem.*, 1912, 78, 435—463).—In a dog with Eck's fistula, the liver still continues to play its part in protein, carbohydrate, and fat metabolism. There is no poisoning due to the entry of protein cleavage products into the general circulation. The urine, however, has an alkaline reaction, and contains excess of amino-acids. Such dogs resist more phosphorus than normal dogs, and jaundice is not so readily induced. The pathological anatomy of the liver does not differ from that ordinarily produced by phosphorus. W. D. H.

**The Action of Atoxyl in vitro on the Animal Body.** M. ROTHERMUNDT and J. DALE (*Zeitsch. Immunitätsforsch. exp. Therapie*, 1912, 12, 565—594).—The action of atoxyl on trypanosomes is a direct one. The atoxyl soon after it enters the parasitic cell is reduced and makes a "trypanocide" compound. The reduction does not take place in the animal body first, and there is no evidence that toxic protein compounds are formed and liberated in the body which act on the parasites. W. D. H.

**The Therapy of Antimony Poisoning by Potassium Hexatantalate.** FELIX ROSENTHAL and JOSEPH SEVERIN (*Arch. exp. Path. Pharm.*, 1912, 68, 275—296).—Morgenroth and Rosenthal showed that the lethal action of antimony compounds on trypanosomes can be inhibited by tantalum. Potassium hexatantalate and antimony compounds react in the blood, and the former neutralises the poisonous action of the latter. The same antidote is also efficacious whether given by the mouth or subcutaneously, and can be employed in antimony poisoning generally. Full details as to doses and suggestions as to the chemical reactions involved are given. W. D. H.

**The Toxicity of Alkali Salts of Thiocyanic Acid.** FR. FRANZ (*Chem. Zentr.*, 1912, i, 1482; from *Arbb. Kais. Gesundh.-Amt.*, 1912, 38, 435—449).—Potassium, sodium, and ammonium thiocyanates were tested on rabbits and other animals. No hydrocyanic acid was split off, and these salts did not act as poisons. W. D. H.

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### Chemistry of Vegetable Physiology and Agriculture.

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The Intestinal Flora. Isolation of a Microbe Capable of Producing  $\beta$ -Iminazolyethylamine from Histidine. ALBERT BERTHELOT and D. M. BERTRAND (*Compt. rend.*, 1912, 154, 1643—1645).—Only one of the various micro-organisms isolated from human intestines when injected into a guinea-pig caused symptoms characteristic of  $\beta$ -iminazolyethylamine; the micro-organism is

distinct from those hitherto described, and is given the name *Bacillus aminophilus intestinalis*.

After the growth of this micro-organism in media containing histidine, it is possible to extract a base (as the picrate), the hydrochloride of which from its chemical and physiological behaviour must be that of  $\beta$ -iminazolyethylamine.

There is also present in human faecal matter a micro-organism quite distinct from *B. aminophilus intestinalis*, capable of producing  $\beta$ -iminazolyethylamine from histidine.  
D. F. T.

**Decomposition of Carbohydrates by Bacteria.** B. KLEIN (*Centr. Bakt. Par.*, 1912, i, 63, 321—333).—Instead of the usual method employed in experiments on the decomposition of carbohydrates by bacteria, in which relatively large amounts of nutritive media are used, the following process is recommended. Two loops of an agar culture (twenty hours) of the desired bacteria are added to 1 c.c. of Barsiehoff's sugar-peptone solution. Under these conditions the decomposition of dextrose by *B. coli commune* takes place after one hour, and of mannitol and lactose after two to three hours. The method is also suitable for demonstrating known facts, such as the action of heat, the effect of the age of a culture, etc.

Coli cultures may be differentiated in the following manner. In the case of a twenty-hour coli culture, two loops are added to 1 c.c. litmus-lactose-peptone solution, and two loops are placed in an Einhorn tube ( $1\frac{1}{2}$ —2 c.c.) filled with sugar broth. The decomposition of the lactose and the production of gas from dextrose can generally be observed in two or three hours.  
N. H. J. M.

**Detection of Indole in Cultures of Bacterium coli.** D. RIVAS (*Centr. Bakt. Par.*, 1912, i, 63, 547—550).—The author recommends the substitution of trypsinised peptone water for ordinary peptone water or peptone beef broth as used in the cultivation of *Bact. coli* for the Salkowski test for indole.

The medium is prepared by adding a solution of 0.5 gram trypsin in 10—20 c.c. water to 10 grams of Witte's peptone dissolved in 200—300 c.c. of water; the mixture is stirred gently every fifteen to twenty minutes, and allowed to digest at 38—40° for two to three hours.

Such a medium contains compounds more closely approximating to indole than does ordinary peptone water; the organism grows better, and a distinct and characteristic indole reaction can be obtained with cultures of *Bact. coli* after incubation at 37° for only five to six hours.  
H. B. H.

**The Degradation of Polypeptides by Bacteria.** I. TAKAOKI SASAKI (*Biochem. Zeitsch.*, 1912, 40, 174—179).—*Bacterium coli* in Fränkel's solution was capable of hydrolysing glycyl-L-tyrosine and glycyl-glycine.  
S. B. S.

**Bio-chemistry of Micro-organisms. VI. The Fermentation of Formic Acid by Bacillus prodigiosus in a Medium of Constant Composition.** HARTWIG FRANZEN (*Zeitsch. physiol. Chem.*,

1912, 79, 177—214).—The paper consists mainly of tabular results of experiments carried out on the lines of the author's previous work.

W. D. H.

**Bacteriological Studies\* of the Fixation of Nitrogen in Certain Colorado Soils.** WALTER G. SACKETT (*Centr. Bakt. Par.*, 1912, ii, 34, 81—115; *Agric. Exper. Stat. Colorado Agric. Coll. Bull.* 179, 1911. Compare Stewart, this vol., ii, 595).—Experiments on fixation of free nitrogen, both in solutions and in the soil itself, in connexion with Headden's investigation of sterile patches of soil in Colorado (*Bull.* 155, *Colorado Agric. Coll. Exper. Stat.*).

The results indicate that the fixation of nitrogen is sufficiently vigorous to account for the nitrates found, provided that it is nitrified, whilst the rate of nitrification observed is sufficient in most cases.

Whilst the power of fixing nitrogen is not limited to any particular area or class of soils, it was found that the adobe soils have very little, if any, power of fixing nitrogen. Excessive amounts of nitrates either destroy the nitrogen-fixing organisms or greatly reduce the numbers present in the soil. The dominant nitrogen-fixing organisms in the soils examined seems to be *Azotobacter chroococcum*, and to this organism is due the characteristic dark brown colour of the nitre soils. The pigment is produced in presence of nitrates and to a less extent in presence of nitrites, whilst ammonium chloride and sulphate, asparagine, and peptone are without effect.

N. H. J. M.

**Some Bacteriological Effects of Liming.** PERCY E. BROWN (*Centr. Bakt. Par.*, 1912, ii, 34, 148—172).—Pot experiments on the effect of ground limestone on ammonifying, nitrifying, and nitrogen-fixing bacteria in a typical Wisconsin drift soil

Applications up to three tons per acre increased the number of bacteria developing on "modified synthetic" agar, and increased ammonification, nitrification, and nitrogen-fixation, as tested by the beaker method. The increases are in proportion to the amount of the application. The ammonification of dried blood or cottonseed runs parallel with the number of bacteria, whilst with peptone the results show very little relation to numbers.

The yield of oats was considerably increased by applications of two or three tons of limestone per acre, and applications up to three tons increased the nitrogen in the crop more rapidly than the crop itself.

N. H. J. M.

**The Mechanism of Alcoholic Fermentation.** ARTHUR HARDEN and WILLIAM J. YOUNG (*Biochem. Zeitsch.*, 1912, 40, 458—478).—According to the conception of the authors, the action of phosphates when added to a fermentation mixture can be represented by the equation:

$2C_6H_{12}O_6 + 2Na_2HPO_4 = 2CO_2 + 2C_2H_5O + C_6H_{10}O_4(PO_4Na_2)_2 + 2H_2O$ .  
This is quite different to the conceptions of von Lebedeff, who assumes that the hexose is first converted into dihydroxyacetone, which then reacts with the phosphates. The authors, in support of their own view,

now show that in experiments with the maceration juice of Schroder's dried yeast the added phosphate causes an increase of carbon dioxide in the fermentation mixture which is equivalent to the amount of hexosephosphate formed in accordance with the above equation, and that the increased carbon dioxide is not derived from the already formed phosphate, as would be expected from von Lebedeff's equations representing the action. The same phenomena was observed when zymine and expressed juice were employed. Furthermore, the authors also show that dihydroxyacetone ferments more slowly than sugars, but it does not inhibit sugar fermentation. There is no evidence that it is of an intermediary product of fermentation; on the contrary, it is more likely that it is itself converted into sugar before undergoing fermentation.

S. B. S.

The Chemical Reactions Occurring in Alcoholic Fermentation. V. EDUARD BUCHNER and JAKOB MEISENHEIMER (*Ber.*, 1912, 45, 1633—1643).—Mainly polemical. Boysen-Jensen (*Abstr.*, 1909, ii, 172; Dissertation, Copenhagen, 1910) has made the statements that "Kahlbaum's" pure dextrose when kept at 20° for three weeks in presence of phenylmethylhydrazine yielded the phenylmethylsazone of dihydroxyacetone, and that the same compound was obtained in a similar manner from dextrose after fermentation with yeast. A repetition of these experiments gave in both cases only phenylmethyl-dextrosazone. Boysen-Jensen's further observation that dihydroxyacetone is decomposed by animal charcoal into carbon dioxide and alcohol could also not be confirmed. It is shown that 0.1 gram of dihydroxyacetone in 5 c.c. of water with or without the addition of boiled yeast-juice is fermented by 1 gram of living yeast almost as completely as, but more slowly than, dextrose under similar conditions (compare Sclator, *Abstr.*, 1912, i, 162). A discussion of von Lebedeff's results (*Abstr.*, 1911, ii, 816, 1122) and of the probability of dihydroxyacetone being an intermediate compound in alcoholic fermentation is also given.

W. J. Y.

The Supposed Formation of Dihydroxyacetone During Fermentation and the Action of Animal Charcoal and Phenylmethylhydrazine on this Substance. FRANCES CHICK (*Biochem. Zeitsch.*, 1912, 40, 479—485).—In dilute solutions, dihydroxyacetone forms with phenylmethylhydrazine a substance which differs from the typical glycerosephenylmethylsazone, melts at 146—147°, and is obtained in the form of either yellow or green needles. Dihydroxyacetone could not be obtained from dextrose either before or after fermentation with English top-yeast under the conditions described by Boysen-Jensen. The pure substance does not undergo scission into alcohol and carbon dioxide on treatment with charcoal at 37°. The experiments were carried out with the main object of verifying certain recent statements of Boysen-Jensen, which the author fails to confirm.

S. B. S.

Nature of the Fixation of Calcium by *Aspergillus niger*. (Mlle.) ROBERT (*Compt. rend.*, 1912, 154, 1308—1310).—When *Aspergillus niger* is grown in a solution containing calcium, it fixes this

as calcium oxalate and retains it in the mycelium. The presence of calcium does not determine the formation of oxalic acid ; part of the acid produced normally by the action of the mould and present in the culture fluid is removed as calcium oxalate. In consequence, the mould when grown in presence of calcium salts increases in weight and contains more oxalic acid ; on the contrary, in the culture fluid there is less acid present when calcium salts are added to it. E. F. A.

**Bactericide and Antiparasitic Properties of Carbonyl Chloride.** SEMIBRATOFF (*Centr. Bakt. Par.*, 1912, i, 63, 479—482).—A 20% solution in toluene was employed. In concentrations above 10%, carbonyl chloride has bactericidal properties, and small amounts kill rats and insects. The substance is, however, too costly and too poisonous and irritating to be of practical use for disinfecting or for the destruction of rats. N. H. J. M.

**Formation and Assimilation of Ammonia in Dead Plants.** WLADIMIR I. PALLADIN and N. N. IWANOFF (*Bull. Acad. Sci. St. Pétersbourg*, 1912, [vi], 573—594).—The authors have studied the formation and consumption of ammonia during the autolysis of dead yeast (hefanol, zymín).

Autolysis in water is accompanied by the formation of considerable quantities of ammonia and of substances which readily yield ammonia. The addition of phosphates to the water causes marked retardation in the formation of ammonia, the effect of potassium dihydrogen phosphate in this respect being decidedly more pronounced than that of the dipotassium salt. Dextrose produces still greater retardation. The methylation of the aporrhagma (compare Ackermann and Kutscher, *Abstr.*, 1910, ii, 1089 and following abstracts) probably takes place at the expense of the dextrose or of the intermediate products of its decomposition by zymase, and the same is the case with other syntheses from the amino-acids and their aporrhagma. The very small amounts of ammonia formed during autolysis afford an indirect proof that the formation of ammonia is a reversible process. The introduction of leucine has no influence on the quantity of ammonia formed in the autolysis of yeast in water. Lactose retards the formation of ammonia only to a very slight extent. The influence of oxygen on the formation of ammonia is difficult to ascertain. Oxidising reactions retard the functions of proteolytic enzymes (compare this vol., ii, 291) and also the formation of ammonia. Investigation of the process of formation of ammonia leads to the establishment of the dependence of fermentation and respiration on the degradation of the proteins. T. H. P.

**Synthetic Processes in Plants. I. Sucrose Synthesis.** P. BOYSEN-JENSEN (*Biochem. Zeitsch.*, 1912, 40, 420—440).—In view of the fact that the heat developed by a plant is less than the quantity which should be expected from the oxygen consumption and the carbon dioxide output, and also in view of the fact that the concentration of sucrose is too great in comparison with that of reducing sugars for a synthetic action of the enzymes to be expected from the

in vitro experiments on the synthesis of disaccharides from monosaccharoses, the author draws the conclusion that part of the energy of the plants is employed in synthetic processes. There should, therefore, be some relationship between the energy of respiration and the amounts of sucrose in a plant. In the author's experiments, the energy of respiration was altered in the following ways: (1) by bringing the plants into an atmosphere of hydrogen, (2) by alteration of the temperature, (3) by autolysis, (4) by direct in vitro experiments. In the case of autolysis, the respiratory enzymes are destroyed. In the in vitro experiments, dextrose and lævulose were brought together in the presence of yeast and an oxydase, both of which enzymes the author has shown to be necessary for respiratory processes. In the presence of these, synthesis takes place. If one is wanting, the respiratory process does not take place and synthesis fails. The results of the experiments are regarded as confirming the author's views. The method of estimating the non-reducing sugars was as follows. The reducing power of Barfoed's solution was estimated. From the amount of cuprous oxide, the amount of dextrose could be ascertained, as maltose has but very slight (practically negligible) reducing power. By the reduction of Fehling's solution, the combined amounts of maltose and dextrose could be found. From the reduction of Fehling's solution after inversion with hydrochloric acid (5 c.c. of *N*/10-acid to 10 c.c. of solution, which strength does not invert maltose), the amount of sucrose could be ascertained when the amounts of maltose and dextrose had been already obtained.

S. B. S.

**Comparison of "Total" and "Nitric" Nitrogen in Parasitic and Saprophytic Plants.** L. LUTZ (*Compt. rend.*, 1912, 154, 1247—1249).—The author has shown previously (*Bull. Soc. bot. France*, 1908, 55, 104) that plants of these types all contain nitrates, and that the quantity of nitrate accumulated in a parasitic plant depends on the extent to which the plant is parasitic, the richness of the host plant, and the presence or absence of chlorophyll. In the present paper it is shown that (1) complete parasites, especially those containing chlorophyll, contain less total nitrogen, and, as a rule, much less "nitric" nitrogen than partly parasitic plants; (2) completely or partly parasitic plants containing chlorophyll have high "total" nitrogen and low "nitric" nitrogen, whilst for plants of these types free from chlorophyll the reverse is the case.

T. A. H.

**Distribution of Oxydases in Plants and their Rôle in the Formation of Pigments.** FREDERICK KEEBLE and E. FRANKLAND ARMSTRONG (*Proc. Roy. Soc.*, 1912, B, 85, 214—218).—A method of application of benzidine and of  $\alpha$ -naphthol as reagents for the detection in situ of oxydases in plant tissue is described: it may be used micro- or macro-chemically. In the case of *Primula sinensis* it is shown that the distribution of pigment in the flower coincides exactly with that of a peroxydase. Two peroxydases are present in this plant. One, indicated by benzidine, occurs in the epidermis; the other, indicated both by  $\alpha$ -naphthol and by benzidine, is localised in the cells constituting the bundle sheath. These are separated

widely in the stem, but they come in close proximity in the flower petals.

White flowers, which by breeding tests are known to be dominant whites, fail to give the epidermal peroxydase reaction. The peroxydase is, however, present, since after treatment of the flower with hydrogen cyanide and subsequently with the reagent, the characteristic peroxydase colorations are produced. This confirms the presence in dominant whites of an inhibiting substance which prevents the formation of pigment, a supposition which has been made repeatedly by breeders.

Recessive white flowers are shown to possess peroxydase and presumably to be colourless, owing to the lack of chromogen.

The observations are extended to explain a number of problems in genetics and plant physiology.

E. F. A.

**The Distribution of Urease in the Higher Plants.** GÉZA ZEMPLÉN (*Zeitsch. physiol. Chem.*, 1912, 79, 229—234).—Urease has been previously noted in various fungi, the Soya bean, and in lupin seedlings. Its presence also in *Robinia pseudacacia* led the author to discover it in the seeds of many other plants, the names of which are given. Most Papilionaceæ contain it, although in variable degree, but its presence in most graminaceæ is difficult to detect.

W. D. H.

**Cyclamen Europæum.** GEORGES MASSON (*Chem. Zentr.*, 1912, i, 1225; from *Bull. Sci. Pharmacol.*, 18, 477—482).—The bulbs contain a saponin-like substance, cyclamic acid, and a carbohydrate, cyclamose, together with uncharacterised substances.

The bulbs on extraction with light petroleum yield a mixture of fats, which is separated by dry alcohol into a green oil and a solid mass. The fat-free bulbs on extraction with 95% alcohol furnish a syrupy extract, which gelatinises in the cold, forms an emulsion on addition of water, reduces Fehling's solution, and is precipitated by tannin, baryta water, or lead acetate solution. It contains a saponin-like substance, *cyclamic acid*, which was separated as a colourless, pseudo-crystalline powder, yielding amorphous alkali salts and gelatinous salts with copper, barium, or lead. It forms with tannin a *compound*, m. p. 212—214°, insoluble in water, but soluble in alcohol. When boiled with dilute sulphuric acid, it furnishes dextrose and a colourless, amorphous substance insoluble in ether, soluble in dry alcohol, and in solutions of alkali hydroxides.

On further extraction with 65% alcohol, the bulbs yield *cyclamose*,  $[\alpha]_D - 18.90^\circ$ , as a colourless, amorphous, hygroscopic powder, having a taste recalling that of gum arabic. This reduces Fehling's solution slowly in the cold, and forms an *osazone*, m. p. 208—210°, which crystallises in short, yellow needles, and is insoluble in methyl alcohol. Cyclamose on hydrolysis furnishes dextrose. The latter is also present in the bulbs in a free state.

T. A. H.

**Chemical Constitution of the Latex of Euphorbia Species. Relation between Chemical Constitution and Systematic Classification of Plants.** J. VON WIESNER (*Monatsh.*, 1912, 33, 461—483).—The latex of *Euphorbia lactiflua* from Chili is shown to

contain about 3·88% of rubber and 28—30% of resin. It also contains euphorbone,  $C_{15}H_{24}O$ .

*Euphorbia* species are characterised by containing rubber only in small quantities, together with a considerable proportion of resin. Some euphorbone is also always present. E. F. A.

Oil from the Seeds of the Hybrid *Juglans nigra* x *Juglans cinerea*. A. FOUCHET (*Chem. Zentr.*, 1912, i, 1321; from *Bull. Sci. Pharmacol.*, 1912, 18, 529—534).—The kernels on extraction with light petroleum yield 50% of a yellow oil,  $D_4^{20}$  0·925,  $n_D^{20}$  1·4765,  $[\alpha]_D^{20}$  0°, acid number 0·37, iodine number 151, saponification number 191, acetyl number 11, containing 70% of linolein together with glycerides of stearic, oleic, and linolenic acids and traces of volatile and soluble acids. T. A. H.

Presence of Mandelonitrile-glucoside in *Photinia serrulata*. HENRI HÉRISSEY (*Compt. rend.*, 1912, 154, 1249—1251; *J. Pharm. Chim.*, 1912, [vii], 5, 574—577.\* Compare Guignard, *Abstr.*, 1906, ii, 795).—From an alcoholic extract of the mature leaves of *Photinia serrulata*, mandelonitrile-glucoside has been isolated and identified by means of its rotation, conversion into prulaurasin by dilute alkali, and its decomposition products. T. A. H.

The Fat of *Picramnia Lindeniana*. CLEMENS GRIMME (*Chem. Rev. Fett. Harz. Ind.*, 1912, 19, 51—55).—The tree *Picramnia Lindeniana Tulasne*, a native of Guatemala, bears a fruit which was found to consist roughly of water 10·25%, ash 5·83%, protein 12·87%, fat 39%, raw fibre 13·94%, and an extract 18·11%. The crude fat is yellow with a granular, somewhat crystalline structure and an aromatic odour,  $D^{50}$  0·888,  $D^{15}$  0·9125, m. p. 40—41°, acid number 3·34; the fat has the following composition: phytosterol 1·08%, unsaturated fatty acids 41·41% (oleic acid 20·9%), stearic acid 2·72%, myristic acid 21·06%, and palmitic acid 31·52%. F. M. G. M.

The Evolution of Nitrogen, Phosphorus, and Sulphur During the Growth of Barley. GUSTAVE ANDRÉ (*Compt. rend.*, 1912, 154, 1627—1630. Compare Joulie, *Mon. sci.*, 1894, [iv], 8, 886).—During the growth of barley the amounts of dry material, of nitrogen, phosphorus, and sulphur in a plant reach a maximum at the stage of complete maturity. After this the phosphorus is constant, but the other three show a decrease, which is, however, only slight in the case of the sulphur. D. F. T.

Wheaten Flour. I. Influence of the Hydrogen Ion Concentration on the Baking Value of Flour. H. JESSEN-HANSEN (*Compt. rend. lab. Carlsberg*, 1912, 10, 170—206).—The hydrogen ion concentration of dough made from wheaten flour and distilled water has been determined in a number of cases both from the electrical conductivity and by Sørensen's colorimetric methods. Experiments made to show the effect of the addition of increasing quantities of acid on the size of a loaf in which parallel baking tests were made have

\* and *Bull. Soc. chim.*, 1912, [iv], 11, 680—683.

led to the following conclusions. For every dough there is a certain optimum hydrogen ion concentration with which the best risen loaves will be obtained; this is greater than that naturally shown by freshly milled flour and distilled water. The optimum concentration is approximately  $10^{-5}N$ ; it is a little higher for the best quality flour, and slightly lower for low grade or bad flours. In flour from the same wheat the top grade from the centre of the grain is the most acid, the seconds and the bran have the smallest hydrogen ion concentration. The various flour improvers are considered to act in virtue of their increasing the acidity of the flour.

Extraction of gluten by washing is considered worthless as a means of testing the baking value of flour. E. F. A.

**The Effect of Phosphorus Manuring on the Amount of Inorganic Phosphorus in Flat Turnip Roots.** BURT L. HARTWELL and FREDERICK S. HAMMETT (*J. Ind. Eng. Chem.*, 1911, 3, 831—832).—The author has shown previously that the percentage of total phosphorus in turnips is influenced by the amount of available phosphorus in the soil, as a result of further study it appears as if the inorganic phosphorus is influenced even more than the total phosphorus content of the root, and the present paper contains an account of experiments instituted to discover methods of differentiating between these and of estimating the inorganic phosphorus present in the roots at various stages of growth and under different cultural conditions. Impregnation of the tissues with magnesium sulphate and ammonium chloride with microscopic search for crystals of magnesium ammonium phosphate was abandoned as unsatisfactory, and the following method was subsequently devised.

Grated portions of fresh turnips were treated with acetic acid (about 2% on the moisture content of the root), the juice extracted by pressure, filtered, treated with barium chloride, neutralised with ammonium hydroxide, allowed to remain about a day, then filtered, and as much of the insoluble matter as possible dissolved with hot water and dilute nitric acid. The phosphorus was then determined in the filtered liquid with molybdenum and magnesium mixture in the usual way.

The results showed that although the total content of phosphorus in turnips was nearly doubled by the application of an acid phosphate to the soil, the inorganic phosphorus content was increased about six-fold. F. M. G. M.

**The Quantity of Nitrogen Compounds in Wines.** FRIEDRICH SCHAFFER and E. PHILIPPE (*Chem. Zentr.*, 1912, i, 1238; from *Mitt. Lebensmitterunters. Hygiene*, 3, 1—11).—The quantities of various kinds of nitrogen compounds present in natural and artificial wines have been determined.

The total nitrogen (N) was determined by Kjeldahl's method, the ammonia ( $N_a$ ) by distilling the wine with magnesia, the amides ( $N_p$ ) by boiling the wine with hydrochloric acid and then distilling with excess of magnesia, and the non-dialysable nitrogen compounds ( $N_r$ ) by dialysing the wine and determining the nitrogen in the residue by

Kjeldahl's method. The quantity of nitrogen compounds precipitated by alcohol ( $N_3$ ) was obtained by neutralising the wine with alkali, adding twice its volume of 95% alcohol, and determining the nitrogen in the washed precipitate by Kjeldahl's method.

The results are expressed in terms of nitrogen. In natural wines, N varies from 0.1450 to 0.3836,  $N_a$  0.0042 to 0.0168,  $N_p$  0 to 0.0098,  $N_y$  0.028 to 0.092,  $N_s$  0.0147 to 0.035. The ratio  $N/N_3$  for natural wine varies between 5.6 and 41.2. For artificial, sweetened, and residual (tresterweinen) wines the ratio varies from 1.25 to 26.3, but in sweetened wines does not, as a rule, differ much from that of natural wines.

T. A. H.

**Biological Absorption of Phosphoric Acid in Soils.** A. DUSCHETSCHKIN (*Bied. Zentr.*, 1912, 41, 305—306; from *J. exper. Landw.*, 1911, 666).—Black soil (300 grams) to which starch (6 grams) and phosphoric acid (0.1827 gram) were added was kept for about nine weeks, and the phosphoric acid soluble in water in 2% acetic acid and in 1% citric acid estimated. The results showed that in presence of starch a good deal of the phosphoric acid is rendered insoluble by micro-organisms. When chloroform was added to the soil the phosphoric acid remained in soluble forms. The biological fixation of phosphoric acid is increased by addition of sodium nitrate to the soil.

N. H. J. M.

**Exchange of Bases in the Soil.** GEORG WIEGNER (*J. Landw.*, 1912, 60, 111—150).—The interaction of an amorphous silicate gel containing water with ammonium ions may be expressed by the equations employed for adsorption reactions, the most suitable being  $x/m = \beta \cdot c^{1/p}$ .

N. H. J. M.

**Mica as Source of Potassium for Plants, and its Weathering.** EDWIN BLANCK (*J. Landw.*, 1912, 60, 97—110).—Sand culture experiments in which oats were manured with muscovite and biotite as sources of potassium in addition to ammonium nitrate and the usual minerals. Both minerals gave increased amounts of dry matter as compared with the yields without potassium. Biotite yielded a much greater amount of potassium than muscovite. Both minerals are more suitable as sources of potassium than potassium feldspar.

N. H. J. M.

**Flocculating Power of Some Soluble Salts on the Clayey Substances of Soils.** GIULIO MASONI (*Chem. Zentr.*, 1912, i, 1496; from *Staz. sper. agrar. ital.*, 45, 113—159. Compare Hall and Morison, *J. Agric. Sci.*, 1907, 2, 244).—Chlorides have greater effect than nitrates and sulphates; calcium salts more than potassium and ammonium salts, and the latter more than sodium salts. There is no simple relation between the amount of salt and its flocculating power. There are, however, exact relations between the flocculating power ( $P_f$ ) of salt solutions and between the concentration of ions ( $C_1$ ) and the degree of dissociation ( $\alpha$ ). The value,  $P_f$ , of each salt increases with the strength of  $C_1$ , whilst  $\alpha$  diminishes. Flocculation is

connected with cations, anions being without effect. The valency of the cation has a relative effect on the magnitude of  $P_f$ , whilst the atomic weight is without effect. When the value  $P_f$  for sodium is taken as 1, the values for potassium, ammonium, and calcium are respectively 2.4, 2.4, and 5.7.

The flocculating power of a salt is directly connected with the absorptive power of the soil for the salt, and may be considered as an exchange of the radicle concerned with another present in the soil.

N. H. J. M.

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## Analytical Chemistry.

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**An Automatic Pipette.** T. O. SMITH (*J. Ind. Eng. Chem.*, 1912, 4, 47).—The essential point is that to a three-way stopcock burette there is fitted by means of a cork a fine capillary tube long enough to reach from the zero reading of the burette to the top of the solution in the stock bottle. By raising or lowering the capillary tube the burette may be adjusted for the automatic delivery of any quantity of liquid desired.  
F. M. G. M.

**Automatic Filter.** C. C. WALLACE (*J. Amer. Chem. Soc.*, 1912, 34, 823—824).—An arrangement is described for effecting filtration automatically, which has been found very satisfactory for collecting silver halides in Munroe-Gooch crucibles. The apparatus consists of a wooden framework to hold the precipitating flasks and the suction filter flasks, and is suspended from a horizontal beam so that it can swing freely. The precipitation flasks are suspended by wires at the necks so that the lips of the flasks rest just inside the crucibles. By means of a clockwork arrangement, the framework is swung very slowly, so that the precipitation flasks gradually alter their position, and eventually they are completely drained. The special advantages claimed are that less dust than usual can enter the crucibles, that a considerable saving of time is effected, that the possibility of spilling the liquid is reduced, and that two or more filtrations can be carried out simultaneously.  
E. G.

**A Drying Oven.** JOHN H. COSTE (*J. Soc. Chem. Ind.*, 1911, 31, 471).—The oven consists essentially of a double-walled, cylindrical copper vessel, placed horizontally. The chamber formed by the double walls is fitted with a reflux condenser, and contains a suitable quantity of a pure liquid, the boiling point of which approximates closely to the desired temperature. A flattened tube lying under, but not in contact with, the inner, drying chamber opens into the bottom of the chamber at the end farthest from the door, and connects with the external air or with a reservoir of carbon dioxide or nitrogen. Air, or other gas, which may be previously dried, is passed through this tube into the drying chamber, escaping through a special outlet arranged in the door of the oven.

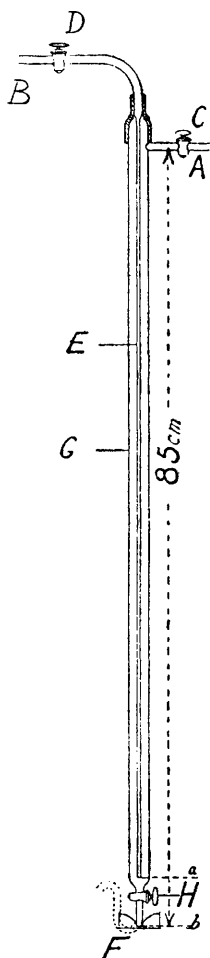
Drying goes on equally well in any part of the oven, and substances placed in it quickly attain a temperature within  $1^{\circ}$  of that of the vapour.  
T. S. P.

**I. Apparatus for the Continuous Extraction of Liquids with Immiscible Solvents Lighter than Water. II. Apparatus for Quantitative Reactions which Depend on the Measurement of an Evolved Gas.** RAYMOND F. BACON and P. B. DUNBAR (*J. Ind. Eng. Chem.*, 1911, 3, 930—932).—The continuous liquid extractor consists of four parts: (1) a jacket flask; (2) an extraction thimble; (3) an ordinary Gooch crucible funnel, and (4) a condenser; the Gooch funnel is so placed that the condensed vapour of the extracting liquid drops into it, and is carried to the bottom of the extraction thimble containing the liquid to be extracted, through which it rises and overflows at the top.

In the apparatus for the measurement of an evolved gas, it is unnecessary to remove the air before the reaction involving the evolution of a gas takes place, the volume of gas evolved being measured by the increase in volume of the total gas after the reaction, and by this means the method described by Spica (*Abstr.*, 1910, ii, 1120) for the estimation of citric acid by measuring the carbon monoxide evolved when it is heated with concentrated sulphuric acid can be considerably shortened. The apparatus consists of: (a) a graduated funnel tube; (b) a reaction chamber; (c) an absorption tube filled with glass beads; (d) a eudiometer, and (e) a levelling tube.

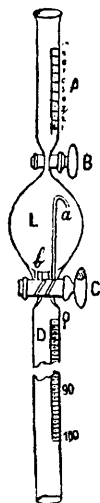
F. M. G. M.

**Apparatus for Obtaining an Average Sample of Gas and for Regulating the Flow of a Gas into an Evacuated Vessel.** FRANK STURDY SINNATT (*Analyst*, 1912, 37, 250—251).—The apparatus will be easily understood from the figure. *G* is a long burette of small diameter. The capillary *E* is about 1—1.5 mm. in bore, the walls being of stout glass, and its end is brought as close to the bottom of the main tube as possible. The exit of the main tube is short or bent into a seal as indicated by the broken line. The reservoir *F* may be replaced by a levelling bottle during the evacuation of the apparatus, but this must be removed before the actual working begins. The gas sampler is attached at *A* by pressure tubing and by a second opening to a vacuum pump. When the apparatus is required for use, tap *D* is closed and the whole exhausted, mercury being allowed to enter the



main tube from *F*. When the mercury level has reached the required point in the main tube, the sampling vessel is closed to the vacuum pump and then disconnected. Tap *H* is then closed. The sample of gas is obtained by connecting the gas supply to *B* and slowly opening tap *D*, when, owing to the difference in pressure between the gas vessel and the capillary *E*, gas is drawn down the latter and passes through the column of mercury into the gas vessel; if the distance between *a* and *b* is great, the tap should be opened very cautiously. When the diminished pressure in the gas-vessel has reached that represented by the height of the mercury column from *a* to the surface of the mercury in the main tube, gas no longer enters the gas vessel. *D* may now be opened fully. Mercury is now allowed to flow from the main tube drop by drop into the reservoir, thus causing the gas to enter into the gas-vessel. When the tap is set, the rate at which the mercury falls into the reservoir is constant, as it depends on the height of the column of mercury *a* to *b*; this flow is constant until the end of the capillary no longer dips into mercury. The distance *a* to *b* may be altered by moving the capillary tube, and consequently the gas may be drawn from a source at any diminished pressure required. By arranging for the mercury to run from the tube in a certain time, a representative sample of the gas throughout that period is collected in the samples. It is essential that during the operation the temperature of the collecting vessel should be as constant as possible in order to prevent any variation in pressure from that cause.

L. DE K.



**A New Universal Gasometer.** E. ROCHEREAU (*Chem. Zentr.*, 1912, i, 1074; from *Bull. Sci. Pharm.*, 18, 398—402).—The gasometer is shown in the accompanying diagram. The graduated tube, *A*, serves for measuring the liquids used in the analyses. The reactions, occurring with evolution of gas, take place in *L*, the gas passing through *a* into the measuring cylinder *D*, which dips into a vessel of water. By appropriate manipulation of the stopcock *C*, *L* can be put into communication with *D*, either through the tube *a* or through the opening *b*.

The apparatus can be used in all gasometric estimations, either in the presence of, or in the absence of, air. Examples are given of the determination of urea in urine, of nitrogen in nitrates, and of oxygen in water.

T. S. P.

**Simple Seal to Vessel containing Standard Stannous Chloride.** S. CHUMANOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 566—567).—The vessel is connected with one limb of a small U-tube, on a constriction of which rest lumps of marble. The other limb of the U-tube, which contains acid, is closed by means of an ordinary bulb trap. The apparatus may be used also for obtaining hydrogen in small quantities.

T. H. P.

**Simultaneous Estimation of Chlorine, Bromine, and Iodine.** F. SARVONAT (*J. Pharm. Chim.*, 1912, [vii], 5, 494).—The liquid is

acidified with nitric acid, and excess of silver nitrate added. The precipitate is collected in a centrifuge tube, dried, and weighed. It is then digested with ammonia solution, a crystal of potassium bromide and a piece of platinum wire having been added, during twenty-four hours in the dark. At the end of that time, excess of nitric acid is added, and the precipitate of silver bromide and silver iodide is collected, dried, and weighed. The digestion is then repeated, a crystal of potassium iodide being used in place of potassium bromide, and the precipitate of silver iodide weighed. From the three numbers thus obtained, the quantities of the three halogens in the original liquid can be calculated.

T. A. H.

**Quantitative Estimation of Perchlorates.** ARTHUR B. LAMB and JOHN W. MARDEN (*J. Amer. Chem. Soc.*, 1912, 34, 812—817).—During the study of some cobaltamines, it was necessary to analyse certain perchlorates. As no satisfactory method has hitherto been described for this purpose, the following has been devised.

A thin, hard glass test-tube of 25—30 c.c. capacity is fitted with two plugs of asbestos wool, one of which is placed 50 mm. and the other 95 mm. from the bottom of the tube. The perchlorate is weighed into the tube, the plugs are inserted, the tube clamped in a nearly horizontal position, and the lower end gently heated. The white fumes formed as the oxygen is evolved are retained by the first plug. When effervescence has ceased, the tube is heated more strongly until all the chloride has fused. When cold, the contents of the tube are washed on a filter with warm water, and the chloride is precipitated as silver chloride. The estimation may be carried out either gravimetrically or volumetrically. The method has been applied to the analysis of a new pentamminecobalt perchlorate with excellent results, and has been found to be very accurate as well as simple and rapid.

E. G.

**Methylene-blue as Indicator in Iodometric Titrations.** FRANK S. SINNATT (*Analyst*, 1912, 37, 252—254).—In a previous paper (*Abstr.*, 1910, ii, 747) a solution of pure methylene-blue was recommended instead of starch solution in the titration of iodine with standard thiosulphate. The author now states that the commercial dye also answers the purpose. A solution is made containing 0.05 gram per litre, and 1 c.c. is then used in the titration.

When iodine solution is added to methylene-blue, a green colouring matter is formed, and this may even form a precipitate; addition of thiosulphate restores the colour. The reaction is not impaired by the presence of large quantities of alcohol, and when there is present a sufficient quantity of the latter, chloroform or carbon disulphide also do not interfere.

L. DE K.

**Detection and Estimation of Minute Quantities of Fluorine in Minerals, Waters, and Living Tissues.** ARMAND GAUTIER and PAUL CLAUSMANN (*Compt. rend.*, 1912, 154, 1469—1475).—An historical survey of the methods advocated for estimating fluorine, and their errors, when used for small quantities, are pointed out. The paper contains instructions for concentrating the fluorine prior to estimation.

In the case of waters, the water is rendered faintly alkaline, 0.3–0.4 gram of sodium sulphate is added, followed by slight excess of barium chloride. The whole is heated to 100°, evaporated to dryness, and the residue extracted with cold water until all soluble salts are removed. An equal volume of alcohol (96%) is added, and the precipitate separated by centrifugalising. From this precipitate the fluorine is liberated as hydrogen fluoride or silicon fluoride by warming with sulphuric acid in a specially designed gold crucible. The gases are absorbed in pure potassium hydroxide. Slight modifications are necessary if much sulphate is present.

Minerals which are entirely attacked by concentrated sulphuric acid are distilled straight away in the gold crucible. In other cases they are first fused with alkaline carbonate and silica, the fused mass extracted with water, the silica precipitated by ammonium carbonate, filtered off, and the filtrate concentrated ready for estimating the fluorine.

Animal or vegetable tissues are dried, calcined at 550–600° with calcium or barium oxide, the residue extracted with hydrochloric acid, and the liquid treated as in the case of a water. W. G.

**A Rapid Method for the Estimation of Sulphur in Roasted Blende.** C. C. NITCHIE (*J. Ind. Eng. Chem.*, 1912, 4, 30–32).—The details of a method with a sketch of apparatus employed for the estimation of sulphur in ores by heating them in a current of air at about 1000°, absorbing the resulting oxides of sulphur in an excess of standard alkali, and titrating the excess in the presence of phenolphthalein. It is claimed that the operation only requires about ten minutes to complete, is sufficiently accurate for control work in the operation of the plant, and requires but little training or chemical skill to carry out successfully. F. M. G. M.

**Estimation of Sulphur in Nitrocellulose.** CARL KULLGREN (*Zeitsch. Schiess. und Sprengstoffwesen*, 1912, 7, 89–91. Compare Abstr., 1901, i, 672; 1905, i, 512).—The substance was denitrified by evaporating with concentrated hydrochloric acid, burnt in a stream of oxygen, the evolved sulphuric acid absorbed by alkali, and subsequently estimated as barium sulphate. F. M. G. M.

**Estimation of Sulphurous Acid in White Wines.** MONIMART (*Ann. Chim. anal.*, 1912, 17, 170–171).—Fifty c.c. of the wine are treated with 3 c.c. of sodium hydroxide solution, D 1.38, and, after the lapse of twenty minutes, the mixture is acidified with sulphuric acid and titrated with *N*/50-iodine solution. The latter solution is conveniently prepared by placing 50 c.c. of potassium dichromate solution (containing 1.96 grams of the salt per litre), 10 c.c. of concentrated hydrochloric acid, and 5 c.c. of a 10% potassium iodide solution in a 100 c.c. flask, and diluting the mixture with water to the mark. W. P. S.

**Simplification of the Method of Estimating Nitrogen.** R. NEUMANN (*Chem. Zeit.*, 1912, 37, 613–614).—Results of experi-

ments carried out by the author show that it is not necessary to collect the ammonia in a receiver containing standard acid solution during the distillation part of the process; if a condenser is used, the ammoniacal distillate may be collected without loss and titrated at the end of the distillation (compare this vol., ii, 87). Litmus is recommended as indicator in the titration of the ammonia derived from proteins, but in the estimation of ammonia in ammonium salts, by distilling the latter with magnesium oxide, cochineal should be used.

W. P. S.

**Estimation of Ammonia in Urine.** OTTO FOLIN and ARCHIBALD B. MACALLUM (*J. Biol. Chem.*, 1912, 11, 523—525).—A pressure of 40—45 lbs. per square inch is quite sufficient to produce an effective air current in the Folin process. The time can be shortened by using small amounts of urine, and the ammonia estimated by Nessler's method, without any loss of accuracy.

W. D. H.

**Nitric Nitrogen in Mixed Fertilisers.** S. S. PECK (*J. Ind. Eng. Chem.*, 1911, 3, 817—818).—The estimation of total nitrogen in mixed fertilisers to which sodium nitrate has been added does not give satisfactory or concordant results, and for the purpose of elucidating the mystery a sample of a mixed fertiliser was prepared containing 3% of nitrogen as sodium nitrate and the same quantity in the form of ammonium sulphate, besides high-grade powdered dry tankage, superphosphate and potassium salts. Thirty-four portions were weighed out and set aside for various intervals of time and under different atmospheric conditions before analysis by several different processes. The results lead to the following conclusions: That in the presence of moisture the modified Gunning method gives incorrect results; that a mixed fertiliser containing sodium nitrate and acid phosphate does not lose nitrogen even during a four months' interval, and that the determination of moisture in such a complex mixture is uncertain and cannot be depended on as a basis for comparative purposes.

F. M. G. M.

**The Estimation of Nitrites in Potable Waters.** GEORGE D. ELSDON (*Chem. News*, 1912, 105, 243).—Contrary to the usual statement, ferric iron, even at a very high dilution, is sufficient to give a reaction with starch and potassium iodide. One part in 50,000,000 can just be detected, whilst 1 part in 10,000,000 gives an appreciable reaction. This is sufficient to interfere with the test for nitrites, and the action is the same whether nitrites are present or not. Ferrous iron, even in comparatively large amounts, is without action in the absence of nitrites, but in their presence it retards the action. The Griess-Ilosvay test for nitrites is not affected by the presence of either ferric or ferrous iron. The permissible limit of nitrites, calculated as nitrogen, in potable waters may be placed at 0.01 part per million.

C. H. D.

**Behaviour of Hydrogen Peroxide towards Ammonium Silicomolybdate and Phosphomolybdate.** PETR G. MELIKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 605—608).—The microchemical

detection of phosphoric acid in minerals, certain parts of plants and lower organisms by means of ammonium molybdate in an acid medium is sensitive and characteristic only in absence of soluble silicates, the latter giving ammonium silicomolybdate, which in crystalline form and solubility in ammonia is similar to ammonium phosphomolybdate. These two precipitates may be distinguished by their behaviour towards hydrogen peroxide solution. If a precipitate is formed by addition of 2—3 drops of a solution of ammonium molybdate in nitric acid to the substance to be tested, 2—3 drops of a 30% hydrogen peroxide solution are added, and the test left for twenty-four hours in a moist place; under these conditions the phosphomolybdate dissolves, whilst the silicomolybdate remains undissolved. Should the liquid dry up, a further quantity of hydrogen peroxide solution is added, and the solution examined after some time. This reaction may possibly be utilised in quantitative analysis.

T. H. P.

**Separation of Arsenic from Antimony and Other Metals with Some Applications in Toxicological Work.** STANLEY W. COLLINS (*Analyst*, 1912, 37, 229—238).—The process employed is based on the use of methyl alcohol, first proposed by Friedheim and Michaelis (*Abstr.*, 1895, ii, 415).

In one experiment quoted, 0.06 gram of arsenic pentoxide, 0.05 gram of antimony oxide, 0.04 gram of bismuth oxide, 0.03 gram of mercurous chloride, 0.03 gram of mercuric chloride, and 5 grams of ferrous chloride (unnecessary when dealing with arsenic trioxide) were placed in a distilling flask with 50 c.c. of pure methyl alcohol. In order to prevent volatilisation of other chlorides (antimony in particular), 10 c.c. of sulphuric acid (D 1.84) were added, and hydrogen chloride was passed through the solution before and during the distillation, which was repeated twice with 50 c.c. and twice with 20 c.c. of methyl alcohol. From the joint distillate, the arsenic was precipitated as sulphide. The precipitate corresponded with 0.0596 of arsenic pentoxide, and none of the other metals were present.

The process may be applied to the testing of viscera, etc., even when salvarsan is suspected. These should be subjected to a preliminary treatment with nitric and sulphuric acids.

L. DE K.

**Analysis of Sodium Arsenate.** H. CORMIMBOEUF (*Ann. Chim. anal.*, 1912, 17, 161—163).—The following method may be applied to the analysis of samples of sodium arsenate which are intended for use as insecticides. Five grams of the sample are ignited at a low temperature (in order to destroy the colouring matter which is usually present in the commercial product), and then dissolved in about 150 c.c. of water; this solution is titrated with *N*/1-sulphuric acid, Orange IV being used as the indicator. Let the number of c.c. of acid required be denoted by *X*. Phenolphthalein is now added, and the solution titrated with *N*/1-sodium hydroxide solution, the quantity required being expressed by *X'*. Then the percentage quantity of arsenic oxide present is  $X \times 0.115 \times 20$ . If the number *X* is equal to *X'*, the product is dibasic, and the percentage quantity of

sodium oxide present is  $2X \times 0.031 \times 20$ , but if not, the amount of sodium oxide is  $[(X \times 0.031 \times 20) + (X' \times 0.031 \times 20)] \times 2$ .

W. P. S.

**Trillich's Method for the Estimation of Free Carbonic Acid in Water.** HERMANN NOLL (*Zeitsch. angew. Chem.*, 1912, 25, 998—1005).—From a prolonged series of experiments the author finds that, not only do hydrogen carbonates have an effect on the results of the titration of free carbonic acid in water, using phenolphthalein as indicator (Trillich's method), but the concentration of the indicator also influences the result. He comes to the conclusion that Trillich's method gives good results only when the water contains no hydrogen carbonates, and the amount of free carbonic acid present is not sufficient to form appreciable amounts of hydrogen carbonate during the titration. If the water contains considerable amounts of hydrogen carbonates, correct results can only be obtained when phenolphthalein of a definite strength is used. The values found for the free carbonic acid may be either too high or too low, since hydrogen carbonates show an acid reaction towards weak, and an alkaline reaction towards concentrated, phenolphthalein solutions. For waters having up to 14° (German) of temporary hardness, the strength of the phenolphthalein solution should be 1 : 1000 to 1 : 2000, and 0.5 c.c. should be used for 200 c.c. of water. For harder waters, the strength of the phenolphthalein must be determined by appropriate experiments.

The estimation of normal carbonates by titration with sulphuric acid, using phenolphthalein as indicator, is affected by similar errors, and the results may be either too high or too low. The addition of sodium chloride, as recommended by Lunge and Lohöfer (*Abstr.*, 1902, ii, 105), does not do away with this variation, and has no beneficial effect.

T. S. P.

**Method of Analysis without the Use of Hydrogen Sulphide.** HANS TRAPP (*Zeitsch. anal. Chem.*, 1912, 51, 475—480).—The process is, briefly, as follows: After reducing the higher oxygenated compounds with sulphur dioxide (insoluble sulphates may be formed), the first group is precipitated as usual with hydrochloric acid, and, after oxidising with nitric acid, the solution is neutralised with ammonia and at once digested with excess of yellow ammonium sulphide, which precipitates every metal with the exception of those of the arsenic group and the alkalis and alkaline earths. Addition of hydrochloric acid to the filtrate precipitates the metals of the arsenic group.

The undissolved precipitate when treated with nitric acid dissolves, with the exception of any mercuric mercury. Lead is precipitated by sulphuric acid and alcohol. Bismuth is left behind when the acid is evaporated and the residue taken up in water. On now adding excess of sodium hydroxide, zinc, aluminium and chromium are dissolved; copper, cadmium, nickel, and cobalt, also iron and manganese, are left undissolved. These are then digested with ammonium sulphide and then treated with dilute hydrochloric acid, which dissolves the iron and manganese only. The residue is then dissolved in nitric acid and the copper and cadmium separated by zinc dust. In the solution then remains nickel and cobalt.

L. DE K.

**Qualitative Detection of Alkali Hydrogen Carbonates.** R. T. HASLAM (*J. Amer. Chem. Soc.*, 1912, **34**, 822—823).—The following method has been devised for the detection of hydrogen carbonates in presence of large quantities of normal carbonates, and particularly for ascertaining the purity of sodium carbonate prepared from sodium hydrogen carbonate for standardising acids.

The substance under examination is dissolved in freshly-boiled water, and excess of calcium chloride is added. After four or five minutes, the precipitated calcium carbonate is removed by filtration. A few drops of ammonia are then added to the filtrate, and if hydrogen carbonate is present, a further quantity of calcium carbonate will be precipitated. If the substance contains much hydrogen carbonate, precipitation takes place in about half a minute, whilst with a very small amount, eight to ten minutes may be required. The test is capable of detecting 0.1% of sodium hydrogen carbonate in sodium carbonate.

E. G.

**Detection of Potassium as Cobaltinitrite.** HEINRICH SAL-KOWSKI (*J. Amer. Chem. Soc.*, 1912, **34**, 822).—With reference to Bowser's work (*Abstr.*, 1911, ii, 1031) on the detection of potassium, it is pointed out that, although the cobaltinitrite reaction has not been employed so largely as it deserves, it has been used both by de Koninck and also by the author for many years.

E. G.

**Reduction of Potassium Platinichloride by Magnesium.** ALBERT ATTERBERG (*Zeitsch. anal. Chem.*, 1912, **51**, 483).—A controversy with Trnka as to the first proposer of this method.

L. DE K.

**A Spectroscopic Method for the Estimation of Small Quantities of Rubidium in Presence of Much Potassium.** ERNST WILKE-DÖRFURT (*Zeitsch. anorg. Chem.*, 1912, **75**, 132—140).—The usual methods of producing spectra are useless for quantitative estimations. A new burner is described. The glass burner-tube has two air-openings, just below which a capillary for the gas is sealed on inside. A porcelain tube is fitted on above as a burner, and the salt is introduced, as in Beckmann's and Riesenfeld's burners, by electrolysis in a glass vessel through which air is drawn into the air-openings of the burner. A 10% solution of the alkali chlorides is used.

The blue lines of potassium and rubidium are more suitable for photographic comparison than the red lines, so the visible spectrum between 396 and 435 $\mu$  is selected, the remainder being cut off by filters. Dust must be excluded in order to prevent the formation of a luminous flame, and the inner blue cone of the Bunsen flame must be screened off. An exposure of thirty minutes is given, using extra-rapid plates. Standard plates are prepared by using artificial solutions containing from 1% to 0.005% of rubidium chloride, with potassium chloride to make 10%, and the salt solutions to be investigated are treated in the same way, the intensities of the rubidium lines on the negatives being compared visually. It is thus

easy to determine whether in carnallite and similar deposits the quantity of rubidium is of the order of 0.1, 0.01, or 0.001%.

C. H. D.

**Application of Physicochemical Volumetric Methods to the Estimation of Substances in Water.** F. DIENERT and A. GUILLERD (*Compt. rend.*, 1912, 154, 1504—1506).—Dutoit's method (Abstr., 1910, ii, 342) for determining the end-point in a precipitation process by means of conductivity measurements has been applied to the estimation of calcium, magnesium, and sulphuric acid in potable waters. The details for each determination are given, and a high order of accuracy is claimed for the results.

W. G.

**Separation of Glucinum from Aluminium [Iron, Chromium].** M. WUNDER and T. WENGER (*Zeitsch. anal. Chem.*, 1912, 51, 470—472).—About 0.3 gram of the mixed oxides is fused with 5 grams of sodium carbonate for two to three hours, first in a covered then in an open crucible. The fused mass is boiled with water and another gram of sodium carbonate, and after filtering the undissolved matter is subjected to a second fusion. Finally, the aluminium is precipitated from the united filtrates by boiling with excess of ammonium nitrate.

Iron, if present, may be separated from glucinum by fusing the insoluble residue with potassium pyrosulphate, dissolving the fused mass in water, and pouring this in a solution of 10 grams of sodium hydroxide in 150 c.c. of water. The glucinum is recovered from the solution by acidifying with hydrochloric acid and addition of ammonia. The impure ferric oxide is dissolved in acid and reprecipitated by ammonia.

The filtrate from the alumina may contain chromium as chromate, which may then be reduced by alcohol in the presence of acid and precipitated as usual by ammonia.

L. DE K.

**Detection of Zinc.** FRANZ F. WERNER (*Zeitsch. anal. Chem.*, 1912, 51, 481).—As is well known, potassium ferrocyanide yields a white precipitate in a solution of zinc sulphide in dilute hydrochloric acid. To confirm the presence of zinc further, the precipitate should be treated with bromine water, which yields a deep yellow oxidation product.

L. DE K.

**Rapid Estimation of Zinc.** V. HASSREIDTER (*Zeitsch. angew. Chem.*, 1912, 25, 1005—1006); K. VOIGT (*ibid.*, 1006).—Polemical (compare Voigt, this vol., ii, 298).

T. S. P.

**Analysis of Lithopone.** W. L. AUSTIN and CHARLES A. KEANE (*Analyst*, 1912, 37, 238—242).—The following process is recommended: 5 grams of the powdered sample are treated with strong hydrochloric acid and a little potassium chlorate, and the insoluble matter (barium sulphate) is collected. The filtrate and washings are made up to 250 c.c., and in 50 c.c. the total zinc is estimated by Voigt's method (titration with standard ferrocyanide in ammoniacal solution in the

presence of ferric tartrate; acetic acid producing a blue colour serves as external indicator).

For the estimation of sulphur as sulphide, 0.5 gram of the sample is oxidised with bromine, hydrochloric acid is added, and the sulphuric acid formed is precipitated in the filtrate with barium chloride. By calculating the sulphur to zinc sulphide, the balance of the zinc other than sulphide is easily calculated. Zinc oxide may also be estimated by acting on 2 grams of the sample with 5% acetic acid. Other impurities, such as calcium, are determined in a separate portion of the acid filtrate.

L. DE K.

**Precipitation of the Copper-Arsenic Group and the Separation of its Divisions.** J. I. D. HINDS (*Chem. News*, 1912, 105, 265; *J. Amer. Chem. Soc.*, 1912, 34, 811—812).—To the solution is added hydrochloric acid until the acidity is about normal. After adding nearly 1% by volume of nitric acid, the liquid is boiled down to half its volume so as to oxidise any stannous compound; arsenious acid will also be partly oxidised. A rapid stream of hydrogen sulphide is now passed, the liquid being kept near the boiling point. When after some five minutes no further precipitate is noticed, enough water is added to make the volume double that of the original, and more hydrogen sulphide is passed until the liquid is cold.

The precipitate, after being washed, is transferred to a beaker, and instead of being digested, in the customary manner, with yellow ammonium sulphide (which causes a loss of copper), it is covered with strong ammonia and a current of hydrogen sulphide is passed; this causes the sulphides of the arsenic group to dissolve rapidly.

L. DE K.

**Some New Features in the Electrolytic Estimation of Lead.** JOHN G. FAIRCHILD (*J. Ind. Eng. Chem.*, 1911, 3, 902—903).—Good deposits of lead peroxide, free from flakes and of close texture, can be obtained on a smooth platinum cylinder in two hours time without rotation, and as much as 100—200 mg. in weight; this can be raised to 300 mg., but there is then danger of flaking off. The secret of success is a low amperage to begin with and a temperature of 50—60°.

For alloys rich in lead, two grams (or more) are weighed out, and a portion representing about 0.1 gram of metallic lead employed. The volume of the electrolyte is 200 c.c. in a 250 c.c. beaker, and it contains 30 c.c. of strong nitric acid. The solution is heated to 50—60°, using an anode of 25 sq. in. surface with a cathode cylinder of 12 sq. in. The anode must be frequently burnished, and is ignited before being placed in the electrolyte; split cover glasses are used to prevent loss by evaporation.

The current is started at 0.25 ampere and maintained during one and a-half hours, after which it is raised to 0.5 ampere for half an hour, when the last traces of lead will be removed.

The beaker is lowered and removed, replaced by one containing clean water, the current is disconnected, and the anode washed with alcohol, drawn through a flame to free it from alcohol, and dried by holding it about a foot above the flame and weighed.

The smaller the percentage of lead present, the higher the amperage employed, and by this method lead is readily separated from copper, manganese, silver, and antimony. When a large amount of copper is present, only 20 c.c of nitric acid need be employed, whilst the presence or absence of ammonium nitrate does not appear to effect the results. The voltage of the solution is 2—2.5 volts, and the process can be hastened by simply dissolving any lead sulphate present in ammonium acetate.

F. M. G. M.

**Effect of Calcium on the Ammonium Molybdate Method of Lead Assay.** C. O. BANNISTER and W. McNAMARA (*Analyst*, 1912, 37, 242—247).—The authors agree with other writers (Guess, Seamon, Low) that Alexander's molybdate method (Abstr., 1893, ii, 599) is unsuitable for ores yielding calcium sulphate unless the latter is by some means completely removed; if not, the results of the titration are in excess of the truth.

Barium and strontium sulphates do not act in the same manner, but owing to occlusion of lead sulphate, the results are a little too low.

L DE K.

**Iodometric Copper Titrations.** K. SUGIURA and PHILIP A. KOBER (*J. Amer. Chem. Soc.*, 1912, 34, 818—822).—In studying the copper salts of certain amino-acids (Kober, Abstr., 1911, i, 824), the copper was precipitated as the hydroxide by means of alkali hydroxide. After the precipitate had been well washed, it was dissolved in 20—25 c.c. of 10% acetic acid. The solution of copper acetate was then titrated with potassium iodide and sodium thiosulphate in the usual manner, using starch as an indicator. It was found that these solutions gave a stable end-point, whilst titrations made in presence of nitrates gave an unstable end-point.

Kendall (this vol., ii, 93, 393) has described a method for removing the nitrites by means of sodium hypochlorite and phenol, but it is now shown that the method which has just been outlined will accomplish the same end, since all substances likely to interfere with the titration are removed by the precipitation with alkali hydroxide. Moreover, all the difficulties referred to by Peters (this vol., ii, 492) are obviated by the present method, which is both simple and accurate.

E. G.

**Estimation of Mercury in Smokeless Powder.** J. D. BERKHOUT (*Zeitsch. Schiess- und Sprengstoffwesen*, 1912, 7, 67—69. Compare Abstr., 1910, ii, 350).—A sketch of the furnace with a description of the method of estimating mercury in powders containing nitrocellulose or nitroglycerol. About 2.5 grams of the powder are gelatinised with about 20 c.c. of acetone in a mortar, mixed with copper oxide, and transferred to a glass combustion tube; the front of the tube is drawn out into a series of bulbs with constrictions of fine bore between them, and this portion cooled with running water. The rear of the tube is carefully heated, the mercury distils forward into the bulbs which are severed at the necessary constriction, and the mercury subsequently estimated as suggested by Raaschou (Abstr., 1910, ii, 350) or by other known methods.

F. M. G. M.

**Separation of the Rare Earths.** CHARLES JAMES (*J. Amer. Chem. Soc.*, 1912, 34, 757—771).—Since the author's scheme for the separation of the rare earths (*Abstr.*, 1908, ii, 498) was elaborated, several new methods have been introduced, whilst some of the old methods have been modified. The scheme has therefore been revised and brought up to date. E. G.

**Quantitative Estimation of Yttrium.** C. F. WHITEMORE and CHARLES JAMES (*J. Amer. Chem. Soc.*, 1912, 34, 772—774).—Experiments are described which have been carried out with a view to devising satisfactory methods for estimating yttrium in presence of sodium and certain other elements.

It has been found that yttrium can be quantitatively separated from sodium by precipitation with ammonium sebacate, and from potassium by a double precipitation with the same reagent. The separation of yttrium from iron, aluminium, lithium, and magnesium can be effected satisfactorily by its precipitation as the oxalate by means of oxalic acid in presence of ammonium chloride. E. G.

**The Bismuthate Method for Manganese.** D. J. DEMOREST (*J. Ind. Eng. Chem.*, 1912, 4, 19).—It has been supposed that the bismuthate method of estimating manganese is affected by the presence of chromium, and the author points out that this only occurs when excess of ferrous sulphate, followed by potassium permanganate, are employed as titrating reagents, but if the permanganic acid is directly titrated with sodium arsenite, any chromic or vanadic acids which may be present do not interfere with the results.

One gram of the sample is dissolved in 45 c.c. of water and 15 c.c. of nitric acid (D 1.42), and boiled until nitrous fumes cease to be evolved. After cooling, "bismuthate" is added in small portions until the permanganic acid (or manganese dioxide) persists after a few minutes boiling. Potassium nitrite is added to dissolve the manganese dioxide and nitrous fumes expelled by boiling, more bismuthate (about 0.5 gram) is added with shaking, the solution filtered, and the sodium arsenite run in from a burette until the pink tinge just disappears. There should not be a brown coloration at the end; if there is, it indicates insufficient acid. F. M. G. M.

**Estimation of Iron in Milk.** F. E. NOTTBOHM and W. WEISSWANGE (*Zeitsch. Nahr. Genussm.*, 1912, 23, 514—523).—Volumetric and gravimetric methods are unsuitable for the estimation of the small quantity of iron which is present in milk, and the colorimetric method, using thiocyanate, yields untrustworthy results, owing to the interfering action of phosphates and other constituents of the milk ash. If, however, the iron is first of all separated by means of "cupferron" (compare *Abstr.*, 1910, ii, 76; 1911, ii, 336), it may be estimated colorimetrically as thiocyanate. The ash obtained from 100 c.c. of milk is dissolved in hydrochloric acid, the iron is oxidised by the addition of nitric acid, and the solution is shaken for fifteen minutes with 2 c.c. of a 5% "cupferron" solution. The

mixture is then shaken twice with chloroform, the united chloroform extracts are evaporated to dryness, and the residue is dissolved in hydrochloric acid. This solution is oxidised with nitric acid, and the iron contained in it is estimated colorimetrically. W. P. S.

**Separation of Iron and Titanium.** FRANÇOIS BOURION (*Compt. rend.*, 1912, 154, 1229—1232).—The method is a simplification of that due to Friedel and Guerin (*Abstr.*, 1877, i, 168), which depends on the treatment of a mixture of the two oxides heated to a high temperature with a mixture of chlorine and hydrogen chloride, whereby the ferric oxide is converted into ferric chloride, which volatilises, whilst titanium dioxide remains unaltered. In the new process a mixture of hydrogen chloride and sulphur chloride vapour is employed as the chlorinating agent. Details of the method are given in the original. T. A. H.

**Analysis of Ferro-nickel containing Zinc, Aluminium, and Manganese.** E. C. CARRON (*Ann. Chim. anal.*, 1912, 17, 205—206).—A rapid commercial process, briefly as follows: Two grams of the sample are converted into sulphates, dissolved, and made up to 500 c.c. Twenty-five c.c. are then diluted to 100 c.c., and sodium peroxide is added until the liquid is strongly alkaline and the precipitate almost black. Iron, manganese, and nickel are precipitated, whilst zinc and aluminium are found in the filtrate and are separated by means of ammonium chloride, which precipitates the aluminium. The mixed oxides are redissolved in hot dilute sulphuric acid (1:2), and after adding a few drops of absolute hydrogen peroxide, the solution is heated to boiling and precipitated by excess of ammonia; the nickel remains in solution, and can be recovered and weighed as oxide by evaporating to dryness and repeatedly igniting the residue after moistening with strong nitric acid.

The iron and manganese oxides are dissolved in the smallest quantity of hydrochloric acid to which hydrogen peroxide has been added. The iron and manganese are then determined, jointly, iodometrically, and a separate estimation of the iron is made with standard permanganate, using 25 c.c. of the original solution.

L. DE K.

**Separation of Nickel and Palladium by Dimethylglyoxime.** M. WUNDER and V. THURINGER (*Ann. Chim. anal.*, 1912, 17, 201—202).—The solution of the two metals is slightly acidified with hydrochloric acid, and an excess of a 1% solution of dimethylglyoxime in 2% hydrochloric acid is added. The palladium is completely precipitated, and, after being washed with boiling water, it is ignited and weighed as metal.

The filtrate containing the nickel is heated to boiling and rendered slightly alkaline with ammonia. The rose-coloured precipitate is collected on a Gooch filter, washed first with boiling water, then with alcohol, and dried at 100° to constant weight. The weight multiplied by 0.2031 = metallic nickel.

L. DE K.

**The Estimation of Chromium, and its Separation from Vanadium in Steels.** JOHN R. CAIN (*J. Ind. Eng. Chem.*, 1912, 4, 17—19).—In the analysis of steel, if the solution containing chromium as chromate and vanadium as vanadate is titrated against ferrous solutions, using ferricyanide to indicate when reduction is complete, there is frequently an indefinite end-point, owing to the simultaneous reduction of some of the ferricyanide to ferrocyanide, which then gives the usual colour with the ferric salts present. The author advocates the precipitation of the chromium by boiling the nearly neutralised (ferrous) solution of the steel with either barium or cadmium carbonate, or zinc or magnesium oxide, the chromium being subsequently extracted from the precipitate by fusion, and separated from the vanadium by precipitating as lead chromate under the following conditions.

The drillings are dissolved in about 10 c.c. of concentrated hydrochloric acid per gram of steel employed; when hydrogen ceases to be evolved, the solution is diluted to a volume of 100—150 c.c. with water, nearly neutralised with saturated sodium carbonate solution, a slight excess of barium carbonate emulsion added, and the mixture boiled vigorously during ten to fifteen minutes with further small additions of barium carbonate, with the maximum exclusion of air possible.

The precipitate (which should not contain more than about two grams of excess of barium carbonate) is collected, washed with hot water, and fused in a platinum crucible with two grams of sodium carbonate and about 0.25 gram of potassium nitrate during twenty minutes.

The cooled fusion is digested with water, filtered, treated with hydrogen peroxide, and boiled during five to ten minutes, transferred to a separating funnel, and vigorously shaken with a slight excess of nitric acid, just neutralised with sodium hydroxide, and again acidified with an excess of 1 c.c. of nitric acid for each 100 c.c. of the solution. Lead nitrate (20 c.c. of a 20% solution) is then vigorously stirred in, the precipitate collected, and the lead chromate decomposed with hot hydrochloric acid, cooled, the volume made up to 150—200 c.c., and the chromium titrated with *N*/10-ferrous sulphate solution in the presence of potassium ferricyanide. F. M. G. M.

**Detection of Chromium Sesquioxide Insoluble in Acids.** UROSCH JANKOWITSCH (*Zeitsch. anal. Chem.*, 1912, 51, 483).—The oxide is treated with concentrated nitric acid and a little red lead. After heating gently and waiting for a few minutes, the liquid will turn yellow, owing to chromate being formed. L. DE K.

**Assay of Chrome-Iron Ore.** THEODOR ST. WARUNIS (*Zeitsch. anal. Chem.*, 1912, 51, 480—481).—0.5—0.4 Gram of the finely powdered ore is mixed intimately in a silver crucible with a mixture of 1 gram of sodium peroxide and 0.5 gram of potassium nitrate. After covering with a layer of 4.5 gram of this mixture, the whole is heated very gradually until the foaming ceases, when the mass is heated for a quarter of an hour at a bright red heat over a bunsen

burner. The molten mass should be stirred frequently with a stout silver wire.

The chromium is then fully attacked and completely soluble in boiling water. The further treatment is the usual one. L. DE K.

**Potassium Iodide and Mercurous Nitrate as a Delicate Reagent for Tungsten and Molybdenum.** ERWIN KAFKA (*Zeitsch. anal. Chem.*, 1912, 51, 482).—To the neutral solution of either compound is added a drop of saturated solution of mercurous nitrate, then 1 c.c. of strong hydrochloric acid, and further an excess of potassium iodide. When the precipitate of mercurous iodide has redissolved, mercury will deposit, and the supernatant liquid will gradually turn blue; very dilute solutions of molybdic acid are, however, not affected.

To distinguish between tungsten and molybdenum, potassium thiocyanate is added, when in the case of molybdenum the blue colour will change to blood-red. L. DE K.

**Sensitive Reaction for Molybdic Acid.** PETR G. MELIKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 608—609).—This reaction is based on the formation of the ammonium salt of permolybdic acid corresponding with the potassium salt,  $K_2O_2 \cdot MoO_4 \cdot H_2O_2$ , described by the author and Pissarjewsky (Abstr., 1899, ii, 31). The solution to be tested is evaporated to dryness on a water-bath and the cold, dry residue treated with concentrated ammonia solution until the reaction is strongly alkaline, 3—4% hydrogen peroxide solution being then added. If molybdic acid is present, a cherry-red or pale rose coloration, depending on the quantity of the acid, is instantly formed. Concentrated solutions must be employed and the test carried out in the cold. T. H. P.

**Occurrence of Tin in Canned Vegetables.** J. B. M. COEBERGH (*Pharm. Weekblad*, 1912, 49, 429—431, 489—495).—For special reasons the author confined his research to canned spinach. The amount of tin was estimated in the surrounding liquid (which is generally rejected), in the liquid obtained by pressing the mass, and in the residual cake, which after being weighed was dried and reduced to powder. The estimation was carried out by Schryver's process (destruction of organic matter by sulphuric acid and potassium sulphate). Some of the "tins" were protected by an inner coating of varnish, and in every case notice was taken of the amount of air present in the "tin." The results are communicated in a table, and a graphic representation is also added. The total quantity of tin in fifty specimens varied from 19 to 462 mg. per kilo.; in varnished "tins" from 63 to 126 mg.

The following conclusions were arrived at :

(1) Of a large number of old, unprotected "tins" of spinach, only a few were met with which contained tin in solution.

(2) The tin content in samples of the same origin can be very uneven. Consequently, the amount found in a single "tin" cannot be taken to represent the bulk in such a case.

(3) Spinach preserved in protected tins" did not show a high tin content, although that from non-protected "tins" frequently showed less still.

(4) Contrary to Lehmann's statements, no distinct relation was found between the presence of oxygen, or of nitrates, and the amount of tin dissolved.

(5) It is desirable to ascertain in how far the quality and the surface of the "tin" affect the solution of tin in canned vegetables.

(6) It is desirable to investigate the solubility of the combined (insoluble) tin in different liquids. L. DE K.

**A Method of Analysing Some Commercial Gold Alloys, Metals Present: Gold, Silver, Copper, and Occasionally Zinc and Tin.** JAS. O. HANDY (*J. Ind. Eng. Chem.*, 1911, 3, 804).—About 0.5 gram of the sample from which particles of steel have been removed with a magnet is dissolved in a mixture of 40 c.c. concentrated hydrochloric acid with 10 c.c. of nitric acid, and the silver separated as chloride.

The tin, copper, and gold are next precipitated as sulphide and separated as follows: the precipitate is boiled with a mixture of concentrated hydrochloric acid (15 c.c.) and water (35 c.c.), during ten minutes the tin dissolves, is reprecipitated in the partly neutralised solution ( $\text{NH}_4\text{OH}$ ), and weighed as oxide. The mixed gold and copper sulphides are ignited at a low temperature in a porcelain crucible, whereby the copper is converted into oxide and subsequently dissolved out of the porous gold by means of concentrated nitric acid (10 c.c.); the nitric acid is removed by heating with sulphuric acid, the copper converted into cuprous iodide, and titrated with sodium thiosulphate; the gold residue is weighed as an approximate check, but is separately estimated by a fire assay.

The zinc is precipitated with sodium carbonate from the sulphide filtrate and weighed as oxide.

**Gold.**—0.5 Gram of filings is scorified with 40 grams of test lead, 1 gram of borax glass, and 1 gram of powdered silica; if the resulting button is hard, the operation is repeated with the addition of 10 more grams of lead and 2 of borax-silica flux; after cupellation the gold and silver are weighed together, and the former estimated by difference.

A similar alloy of silver and gold must be prepared, the fire-assay of which indicates the correction for loss by volatilisation which it is necessary to employ. F. M. G. M.

**The Employment of the Formolite Reaction in the Analysis of Paraffins.** F. SOMMER (*Petroleum*, 1912, 7, 409—410).—It is found that the formation of formolite in paraffins offers a convenient method of sampling them.

About 20 grams of paraffin are fused in an equal weight of concentrated sulphuric acid, and slowly treated with formaldehyde; the mixture assumes an intense dark red colour; after warming for twenty minutes on the water-bath it is left until complete separation of the ingredients has taken place; the paraffin cake is removed, and, after

dilution, the liquid is extracted with chloroform, from which the formolite is recovered, dried at  $105^{\circ}$ , and weighed. From the examination of different samples of paraffin it was found that the more opaque samples yielded more formolite than the clear, the difference varying from 0.02 to 1.55% of formolite.

F. M. G. M.

**Paraffins.** F. ERSTEIN and H. POLONYI (*Petroleum*, 1912, 7, 594—596).—The author considers that the known methods of estimating oil in paraffins are untrustworthy, and advocates that the fused substance be treated with picric acid and the more or less intensive yellow (or red) colour produced be compared with that of a pure paraffin free from oil when similarly treated.

F. M. G. M.

**Detection of Methyl Alcohol in Ethyl Alcohol.** EUGEN AWENG (*Chem. Zentr.*, 1912, i, 1146; from *Apoth. Zeit.*, 1912, 27, 159).—One hundred c.c. of the alcohol to be tested are distilled, only the first 5 c.c. of distillate being collected; this distillate is oxidised with potassium permanganate, the excess of the latter is decomposed by the addition of oxalic acid, and the mixture is distilled. The first portion of the distillate contains acetaldehyde, which yields a red coloration with Jean's reagent (phenylhydrazine, sodium nitroprusside, and sodium hydroxide), whilst the formaldehyde distils later and gives a blue coloration with the reagent. The portion of the distillate yielding a blue coloration is collected separately, evaporated with an excess of ammonia, and the resulting hexamethylenetetramine tested with mercuric chloride or with potassium mercury iodide.

W. P. S.

**Direct Estimation of Extract in Wines.** KARL VON DER HEIDE and ERW. SCHWENK (*Zeitsch. anal. Chem.*, 1912, 51, 429—466).—The method of direct determination of the extract should be abandoned for the following reasons: acetic acid and its homologues are no longer present in the extract; lactic acid volatilises to an indefinite extent; tartaric acid is partly converted into the meta-acid (succinic acid remains unaltered); malic acid is partly converted into anhydromalic acid; non-volatile acids are for the greater part converted into esters of glycerol; the acid found by titration is consequently lower than that contained in the wine. Glycerol is but slightly lost on evaporation. Sugar is largely destroyed; consequently the solution of the extract will show a density lower than that of the dealcoholised wine.

When determining the density of the aqueous extract for the purpose of ascertaining the solid matter, this should be found by direct weighing and not by a calculation from the density of the original sample and that of the distillate. The difference between the two results should, however, be only trifling.

L. DE K.

**Estimation of Phenol in Urine.** MARIE HENSEL (*Zeitsch. physiol. Chem.*, 1912, 78, 373—381).—The urine is made faintly alkaline, concentrated, made acid with syrupy phosphoric acid as in Mooser's process, and 50 c.c. distilled over; 50 c.c. of water are added,

and the process repeated until Millon's reagent gives no reaction. The distillate is extracted with purified ether, and the ethereal solution washed first with 4% sodium hydrogen carbonate solution and then four times with *N*-sodium hydroxide solution. This is nearly neutralised and the phenols titrated with iodine solution. The method gives satisfactory results, even in urines containing much carbohydrate. Equally accurate results are given by Mooser's method (Abstr., 1910, ii, 1039), which has been adversely criticised by Neuberg and Hildesheimer (Abstr., 1910, ii, 1116).  
E. F. A.

**New Bromine Method for the Estimation of Thymol, Salicylates, and Similar Compounds.** ATHERTON SEIDEL (*Amer. Chem. J.*, 1912, 47, 508—526).—In an earlier paper (Abstr., 1909, ii, 1058) it was shown that salicylates cannot be estimated satisfactorily either by the bromate methods of Koppeschaar and Freyer, or by Messinger and Vortmann's iodine method. A study of the estimation of thymol by these methods has now been made, and as a result the following modification of Koppeschaar's method has been devised.

A weighed amount of thymol (0.1—0.5 gram) is placed in a 300 c.c. stoppered bottle with 1—2 c.c. of carbon tetrachloride and 100 c.c. of water. Bromine vapour is poured into the mixture until the colour, after thoroughly shaking, shows that bromine is present in considerable excess. After half an hour, 5 c.c. of carbon disulphide and 5 c.c. of 20% aqueous potassium iodide solutions are successively added, and the iodine liberated is titrated with 0.1*N*-thiosulphate. A further quantity of potassium iodide is added, and if no more iodine is liberated, the amount of thiosulphate used is noted. Five c.c. of 2% potassium iodate solution are then added, and, after shaking thoroughly, the titration with thiosulphate is continued until the colour of the iodine is again discharged. Further quantities of potassium iodide and iodate are added to ensure that the reaction is complete. The difference between the two readings of the burette corresponds with the amount of hydrobromic acid formed by the action of bromine on the thymol; 1 c.c. of 0.1*N*-thiosulphate represents 0.0075056 gram of thymol.

This method is also applicable to salicylates, and since, under the conditions specified, bromine does not react with benzoates, it also furnishes a means of estimating salicylic acid or salicylates in presence of benzoic acid or benzoates.

Attempts were made to apply the method to the estimation of several other organic compounds, but, in most cases, the results were not satisfactory.  
E. G.

**The Bromine and Iodometric Methods for the Estimation of Resorcinol.** C. M. PENCE (*J. Ind. Eng. Chem.*, 1911, 3, 820—822).—A discussion of numerous methods which have been advocated for the estimation of resorcinol with an account of the authors experiments, as a result of which he suggests the following procedure: 1.4563 grams of commercial resorcinol are dissolved in water, filtered, and diluted to 500 c.c. in a graduated flask; 25 c.c. are withdrawn, placed in a 500 c.c. glass stopped flask, treated with 50 c.c. of *N*/10-bromine

solution and 50 c.c. of water, followed by 5 c.c. of concentrated hydrochloric acid, and the mixture thoroughly shaken and allowed to remain one minute. The liquid is then diluted with about 200 c.c. of water, treated with 5 c.c. of 20% potassium iodide solution, shaken vigorously and left during about five minutes, and then titrated in the presence of starch as indicator.

The above concentrations were found to prevent the decomposition of the tribromoresorcinol by potassium iodide, which is a frequent source of error, and a blank experiment should also be made to ensure accurate results.

F. M. G. M.

**Direct Estimation of Geraniol in Essence of Citronella.** JUSTIN DUPONT and LOUIS LABAUNE (*Ann. Chim. anal.*, 1912, 17, 210—213).—Ten grams of the sample are shaken for two hours with a solution prepared as follows: 10 grams of hydroxylamine hydrochloride are dissolved in 25 c.c. of water and a solution of 12 grams of potassium carbonate in 25 c.c. of water is added. The oily product (citronellaloxime) is decanted, and after drying over anhydrous sodium sulphate it is acetylated by boiling in a reflux apparatus with double its volume of acetic anhydride. After washing and drying as usual, 2 grams of the acetylated oil are submitted to the ordinary saponification test (boiling with 20 c.c. of alcoholic  $N/2$ -potassium hydriodide). Supposing 12.6 c.c. of  $N/2$ -potassium hydroxide (= 6.3  $N$ -solution) had been absorbed, the geraniol content would be found from the formula  $154 \times 6.3/2 - (0.042 \times 63) = 55.92\%$ .

L. DE K.

**The Influence of the Presence of Peptones on Sugar Estimations by Fehling's Solution.** ALESSANDRO BERNADI (*Biochem. Zeitsch.*, 1912, 41, 160—164).—The author shows that the increase in the weight of cuprous oxide precipitated by Fehling's solution when sugars are estimated in the presence of peptones is probably due to the presence of copper sulphide. Correct results can be obtained, however, if the cuprous oxide is converted into the thiocyanate and the latter product weighed, and also if the peptone is previously precipitated as phosphotungstate before reduction of the sugars with Fehling's solution.

S. B. S.

**Colorimetric Estimation of Dextrose in Blood.** J. FORSCHBACH and SEVERIN (*Arch. exp. Path. Pharm.*, 1912, 68, 341—348).—The method of Autenrieth and Tesdorpf (colorimetric modification of Bang's process) was examined, and was found simple and speedy, and it can be used for small amounts of blood with good results. The question of the so-called residual reduction (Restreduction) of the blood is discussed.

W. D. H.

**Trommer's Test [for Sugar] in Urine.** ERNST SALKOWSKI (*Zeitsch. physiol. Chem.*, 1912, 79, 164—170).—Creatinine holds a considerable amount of cupric hydroxide in solution if the copper sulphate is added first and then the alkali in Trommer's test, but not when the reagents are added in the reverse order. In the first case,

reduction occurs on heating. Whether the amount of creatinine is sufficient in urine to account for the reduction so often seen in the absence of sugar appears doubtful. There is some danger in relying on the order in which the reagents are added, however, to distinguish between creatinine and sugar, especially when the latter substance is present only in small quantities. Other points in relation to this test and other tests for sugar in urine are discussed. W. D. H.

**Tabular Scheme for the Detection of Sugars and Their Derivatives in Urine.** MARIUS BLANC (*Ann. Chim. anal.*, 1912, 17, 168—169).—A table is given showing the characteristic reactions by means of which dextrose, lactose, lævulose, pentoses, inositol, alcaptones, and glycuronic acid may be identified when occurring in urine.

W. P. S.

**Estimation of Sugar in Beet by Warm Aqueous Digestion.** EMILE SAILLARD (*Rev. gen. Chim. pure appl.*, 1912, 15, 64—66).—Aqueous digestion when quantitatively carried out is considered the most satisfactory method of estimating sugar in beet.

Into a graduated flask of 201 c.c. capacity, 32.52 grams of well chopped root are placed, 7—8 c.c. of lead acetate (28—30 Bé) made up to 160—170 c.c. with water are added, and the mixture heated during fifteen to twenty minutes at 95°; the volume is made up to 201 c.c., and the mixture shaken during twenty minutes; on cooling, the volume is again adjusted, the liquid filtered, treated with 2—3 drops of acetic acid, and polarised.

F. M. G. M.

**Estimation of Formaldehyde.** ENRICO RIMINI and TEMISTOCLE JONA (*Chem. Zentr.*, 1912, i, 1147—1148; from *Giorn. Farm. Chim.*, 1912, 61, 49—56).—The authors have investigated methods which depend on the conversion of the formaldehyde into formalazine by means of hydrazine, and find that the following mode of operation yields the most trustworthy results: The volume of nitrogen which is evolved when 20 c.c. of a 1.1% hydrazine solution are treated with mercuric chloride is ascertained. Twenty c.c. of the hydrazine solution are then mixed with 5 c.c. of the formaldehyde solution under examination, and the excess of hydrazine is estimated gasometrically. The reactions proceed according to the equations:  $2\text{CH}_2\text{O} + \text{N}_2\text{H}_4 = \text{C}_2\text{H}_4\text{N}_2 + \text{H}_2\text{O}$  and  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4 + 6\text{KOH} + 2\text{HgCl}_2 = \text{K}_2\text{SO}_4 + 4\text{KCl} + 2\text{Hg} + \text{N}_2 + 6\text{H}_2\text{O}$ . When the excess of hydrazine is estimated by means of iodic acid, there is a danger that the formalazine may also be attacked, although trustworthy results may be obtained by decomposing the hydrazine by potassium iodate in alkaline solution.

W. P. S.

**Detection of Small Quantities of Chloral in the Presence of Chloroform.** TEMISTOCLE JONA (*Chem. Zentr.*, 1912, i, 1148; from *Giorn. Farm. Chim.*, 1912, 61, 57—59).—The solution of the substance is rendered slightly acid with sulphuric acid, and a small quantity of zinc is added. When hydrogen ceases to be evolved, a strip of filter-paper, which has been immersed in sodium nitroprusside solution and

a 5% piperidine solution, is suspended in the neck of the flask containing the mixture. On warming the contents of the flask the paper is coloured blue if chloral was present in the original substance, the coloration being due to the acetaldehyde produced. The test will detect 1 part of chloral in 20,000 parts of solution. W. P. S.

**Estimation of Malic Acid.** P. B. DUNBAR and RAYMOND F. BACON (*J. Ind. Eng. Chem.*, 1911, 3, 826—831).—A description of experiments on the rapid estimation of malic acid, based on the observation of Walden that under certain conditions uranium salts produce a marked increase in the specific rotation of *l*-malic acid.

The author finds that when a neutral solution of malic acid is treated with uranyl acetate, its rotation is increased approximately  $28^{\circ} V$  for each per cent. of malic acid in the solution; *d*-tartaric acid is the only other common acid affected in this manner by uranyl acetate, so that in its absence malic acid can be quantitatively determined by treating its solution with uranyl acetate, polarising, and multiplying the difference between this reading and that of the untreated solution by 0.036. The product equals the percentage of malic acid present.

In the presence of more than 10% of reducing sugars and less than 0.25% of malic acid, certain simple modifications are necessary, due to the action of uranyl acetate on the rotation of the sugar.

The most favourable concentrations of malic acid to employ are 0.2 to 0.25%, and the percentage error seldom exceeds more than 5% of the malic acid present. F. M. G. M.

**The Detection of Benzoic Acid in Coffee Extract.** HERMAN C. LYTHGOE and CLARENCE E. MARSH (*J. Ind. Eng. Chem.*, 1911, 3, 842).—On testing samples of coffee extract for benzoic acid by extracting with ether and testing the ethereal extract with ferric chloride, an acid was precipitated which differed from benzoic acid by giving precipitates with salts of manganese, nickel, magnesium, calcium, and barium, as well as (like benzoic acid) with those of iron and copper; from these results the following is suggested as a method for detecting benzoic acid in coffee extract.

The acidified extract is treated several times with ether, the ethereal extracts combined, washed with water, and extracted with ammonium hydroxide; the ammoniacal liquid is evaporated to small volume with the addition of ammonium hydroxide to prevent its becoming acid, treated with manganese sulphate, and the precipitate collected.

The filtrate is treated with ferric chloride, and yields a green precipitate if benzoic acid is present, the mixture is evaporated to dryness, and the contained benzoic acid isolated by sublimation. For quantitative results the method of E. Clark (*Science*, 1909, 253) was found convenient. F. M. G. M.

**Rapid Method for the Detection of Salicylic Acid.** L. STOECKLIN (*Ann. Falsif.*, 1912, 5, 220—223).—In the case of liquids, such as wine, beer, cider, etc., 10 c.c. of the sample are treated in

a test-tube with 1 c.c. of hydrochloric acid and then shaken with 5 c.c. of dichloroethylene, care being taken that the shaking is not sufficiently violent to cause the formation of an emulsion. The aqueous portion is then removed by means of a small siphon, and the dichloroethylene is washed twice by filling the tube with water and inverting it a few times. After the wash-water has been removed with the siphon, a drop of ferric chloride solution is added to the dichloroethylene and the mixture shaken thoroughly. Should salicylic acid be present, the small quantity of water remaining on the surface of the solvent is coloured violet; 0.05 mg. of salicylic acid yields a distinct coloration. When applying the test to beer, bread, etc., it is preferable to extract the salicylic acid as described, to evaporate the solvent, and to test the residue as described by Jorissen (addition of 10 c.c. of water, 5 drops of potassium nitrite solution, 3 drops of acetic acid, and 1 drop of copper sulphate solution; a red coloration develops when the mixture is heated to boiling if salicylic acid is present) in order to avoid confusing *isomaltol* with salicylic acid.

W. P. S.

**Estimation of *l*- $\beta$ -Hydroxybutyric Acid in Urine and Blood.** BRUNO O. PRIBRAM (*Chem. Zentr.*, 1912, i, 1509; from *Zeitsch. exper. Path. Ther.*, 1912, 10, 279—283).—The method proposed depends on the absorption of two atoms of bromine by the crotonic acid formed when hydroxybutyric acid is distilled from a sulphuric acid solution. The conversion of the hydroxybutyric acid is best attained by the use of 60% sulphuric acid; an excess of standardised bromine solution is added to the distillate, and the excess is then titrated with thiosulphate solution. The presence of phenols and sugars interferes with the estimation, but this may be avoided by saturating the urine with ammonium sulphate, adding sulphuric acid, and extracting the mixture with ether, the ethereal extract being employed for the estimation. Blood should be treated with six times its volume of alcohol in order to remove proteins before the estimation is carried out.

W. P. S.

**Colorimetric Estimation of Uric Acid [in Urine].** E. RIEGLER (*Zeitsch. anal. Chem.*, 1912, 51, 466—470).—The process is based on the formation of a blue colour when uric acid is added to a solution of phosphomolybdic acid in presence of disodium hydrogen phosphate. Into a tube holding 10 c.c. and divided to 0.1 c.c. is placed 1 c.c. of a solution of uric acid containing 0.1 gram in 100 c.c. (dissolved by means of sodium hydrogen carbonate), in another similar tube 1 c.c. of the urine to be tested, and into a third tube 1 c.c. of the same urine after the uric acid has been removed by means of ammonium chloride.

To each of the tubes is now added 2 c.c. of a 10% solution of phosphomolybdic acid, and then a 5% solution of disodium hydrogen phosphate up to the top mark. After mixing, the liquid is heated until small gas bubbles are noticed, and the tube is then rapidly cooled in cold water. The colours are then compared in a suitable colorimeter. Allowance must be made for the colour shown in the tube containing the urine deprived of uric acid.

L. DE K.

**Estimation of Uric Acid and Xantho-uric Compounds.** D. SAUZÉAT (*J. Pharm. Chim.*, 1912, [vii], 5, 164—168, 445—449, 485—490).—The various methods that have been proposed for the estimation of uric acid in urine are critically discussed, and modifications of a number of them are suggested. T. A. H.

**Study of the Guaiacum-guaiacol Test.** KURT SCHERN and WILLI SCHELLHASE (*Chem. Zentr.*, 1912, i, 1401; from *Berl. tierärztl. Woch.*, 1912, 28, 221—223).—The addition of guaiacol to guaiacum tincture intensifies the reaction of the latter with milk. Whilst guaiacum tincture alone yields but a feeble, if any, coloration with raw milk, the combined tincture at once gives a dark blue ring. Boiled milk does not give a coloration even after long contact with the reagent. The presence of hydrogen peroxide influences the guaiacum reaction, but not the guaiacol-guaiacum test unless the peroxide is present in considerable quantity (about 1.5% of a 3% hydrogen peroxide solution). W. P. S.

**The Loss of Fat on Drying Meat.** MUNEMICHI TAMURA (*Biochem. Zeitsch.*, 1912, 41, 78—101).—Meat can be dried over a water-bath with comparatively little loss of fat when only relatively small quantities (not over 200—300 grams) are dried at once, especially if the drying is facilitated by the addition of alcohol. In these cases the time required for drying is comparatively short. If larger quantities are dried at one time, the time taken is longer, and in this case there is appreciable loss in fat. The author shows that, as regards fat content, the tissues are by no means homogeneous, and he discusses the relative advantages in estimating the fat in tissues of drying large quantities at once, with the unavoidable fat loss, and thus obtaining a homogeneous powder, and of estimating the fat in small samples, where each sample must show some deviation from a mean. S. B. S.

**Estimation of Stearin and Olein in Fatty Acids.** HUGO DUBOVITZ (*Seifensieder-Zeit.*, 1912, 39, 298).—A satisfactory technical method of estimating the quantity of olein present in fatty acids is to remove it by graduated pressures at different temperatures which can be so arranged as to render the method approximately quantitative for the separation of fatty acids. F. M. G. M.

**The Kumagawa-Suto Method of Estimating Fat.** RINJI WATANABE (*Biochem. Zeitsch.*, 1912, 41, 71—77).—Analyses of various organs of the rabbit by this method are given. It is applicable to all; the blood, however, is not conveniently treated by this method, it being better in this case to extract the fats with alcohol. The suprarenals yield 27% of the weight of fresh organs of substance soluble in light petroleum, of which one-half is not saponifiable. If the fresh organ be treated with strong alkali, the solution thus obtained can be kept for a prolonged period before completion of the analysis.

S. B. S.

**A Method for Preparing Lecithin Emulsions and for their Quantitative Evaluation.** J. C. SCHIPPERS (*Biochem. Zeitsch.*, 1912, 40, 189—192).—The lecithin is dissolved in the quantity required in toluene, this solution is shaken with the requisite amount of saline solution or water for ten minutes, and the toluene is then driven off with steam, which is passed through the mixture for one to one and a-half hours, with constant shaking; the emulsion is then centrifuged and filtered through cotton wool. For the quantitative estimation of the lecithin in the emulsion, the latter is oxidised by an equal volume of a solution of dichromate and hydrochloric acid for six hours at 100° (5 grams of potassium dichromate; 300 c.c. of 38% hydrochloric acid diluted to 1 litre). The amount of dichromate used can be determined by titration with *N*/25-thiosulphate solution in the presence of potassium iodide and starch. One c.c. *N*/25-thiosulphate solution = 1.12 mg. lecithin.  
S. B. S.

**Sources of Error in the Estimation of the Polenske Number of Fats.** W. ARNOLD (*Zeitsch. Nahr. Genussm.*, 1912, 23, 389—391).—The apparatus used in this estimation must comply in all its measurements with those given in Polenske's original paper (*Zeitsch. Nahr. Genussm.*, 1904, 7, 273). The distillation flask must have a capacity of 300 c.c.; if it is larger, the results obtained are too high. The flask should be supported on an asbestos ring, the hole in which is 6.5 cm. in diameter, but a wire-gauze must not be used. Exactly 20 grams of glycerol should be employed in the saponification of the fat, and the volume of the distillate must be 110 c.c. During the distillation, the flame of the burner should be as large as possible without rendering the edges of the asbestos ring incandescent, and powdered pumice is employed in place of pieces of pumice to prevent the contents of the flask from bumping. Unless these details of procedure be adhered to, the method yields untrustworthy results. To ascertain whether an apparatus is fitted up correctly, a blank estimation on a sample of pure fresh lard should be made; the number obtained in this case should lie between 0.4 and 0.6 and never exceed 0.65.  
W. P. S.

**A New Method for the Estimation of Total Nitrogen in Urine.** OTTO FOLIN and CHESTER J. FARMER (*J. Biol. Chem.*, 1912, 11, 493—502).—The principle of the method is that of Kjeldahl's process; it can be shortened and so made available for clinical work by taking small quantities (1 c.c. or less) of urine; then the ammonia liberated is forced by an air current into standard acid, and estimated colorimetrically by Nessler's reagent and a Dubosq colorimeter. The analyses given are satisfactory.  
W. D. H.

**Estimation of Urea in Urine.** OTTO FOLIN (*J. Biol. Chem.*, 1912, 11, 507—522).—The principle of the method is to replace magnesium chloride for the decomposition of urea either by phosphoric acid or potassium acetate at a high temperature, and the ammonia formed is finally estimated by titration or by Nessler's reagent. The results are quite good with small quantities of urine, and if diabetic

urine is diluted so that 1 c.c. contains about 0.1 mg. of urea nitrogen, any preliminary removal of, or allowance for, the sugar present is unnecessary.

W. D. H.

**New Methods for the Estimation of Total Non-protein Nitrogen, Urea, and Ammonia in Blood.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1912, 11, 527—536).—The methods described in the preceding papers and this vol., ii, 683 can with the necessary modifications be applied to the analysis of blood.

W. D. H.

**The Correction-factor in the Estimation of Urea in Urine.** THOR EKECRANTZ and S. ERIKSON (*Zeitsch. physiol. Chem.*, 1912, 79, 171—176).—In the estimation of urea by Riegler's reagent, the correction-factor should be 0.198 instead of 0.2141, so that the percentage of urea is the volume of nitrogen multiplied by the weight of 1 c.c. of nitrogen in mg. at standard temperature and pressure, and multiplied also by the new factor.

W. D. H.

**Estimation of Mono- and Di-metallic Phosphates in the Presence of Organic Substances of an Acid Character. Estimation of Total Urinary Acidity.** L. LEMATTE (*Compt. rend.*, 1912, 154, 1445—1447).—The acidity of urine is due to a group of organic substances with acid reaction and to the replaceable hydrogen in mono- and di-metallic phosphates present therein. Titration, with a suitable indicator, gives the amount of monometallic phosphate present; the total phosphate being determined by titration with uranium nitrate, the difference is dimetallic phosphate. The organic acidity is determined by another titration, phenolphthalein being the indicator. From these results, by means of a formula, the total acidity can be calculated.

W. G.

**Estimation of Indican in Urine.** O. SAMMET (*Pharm. Zentr.-h.*, 1912, 53, 585—589).—A modification of Folin's method is described; 10 c.c. of the urine are mixed with 2 c.c. of 10% copper sulphate solution and 12 c.c. of concentrated hydrochloric acid, the blue colour (indigotin) produced is shaken out with chloroform, and the intensity of the coloration compared with that of 10 c.c. of freshly-prepared Fehling's solution. Folin denoted the coloration of 10 c.c. of the latter reagent as 100, and expressed amount of indican found in a sample of urine in terms of this quantity, but the author prefers to express the result in grams of indigotin or indican. The value 100 in Folin's scale (10 c.c. of Fehling's solution) corresponds with 0.137 gram of indigotin, or 0.2228 gram of indican per litre of urine.

W. P. S.

**Analysis of Urine.** O. VON SPINDLER (*Chem. Zentr.*, 1912, i, 1254—1255; from *Schweiz. Woch. Chem. Pharm.*, 1912, 50, 97—100).—Methods are described for the estimation of the ammonia, acidity, total solids, ash, sulphates, combined sulphur, total sulphur, nitrogen, and specific gravity of urine. The physiological importance of the results is discussed.

W. P. S.

**Estimation of Mustard Oil in Mustard.** DÉSIRÉ RAQUET (*Ann. Chim. anal.*, 1912, 17, 174—178).—It is recommended that the mustard be mixed with dilute alcohol in the usual process of maceration previous to distillation; the use of alcohol prevents loss of mustard oil, due to the action of micro-organisms, should the maceration be too prolonged. Five grams of the mustard are mixed with 100 c.c. of water and 20 c.c. of 90% alcohol in a closed flask, maintained at 35° for one hour, and then distilled, the distillate being received in a flask containing 10 c.c. of ammonia. The ammoniacal distillate is heated with an excess of *N*/10-silver nitrate solution, and the excess is titrated in the usual way with thiocyanate solution. The quantity of mustard oil (allylthiocarbimide) is then calculated from the amount of silver nitrate which has been used in the reaction. W. P. S.

**Estimation of Ferrocyanides.** HERBERT E. WILLIAMS (*J. Soc. Chem. Ind.*, 1912, 31, 468—471).—0.5 Gram of the ferrocyanide is dissolved in 100 c.c. of water, the solution transferred to a 250—300 c.c. distilling flask, and then 0.05—0.1 gram of cuprous chloride, dissolved in a few drops of hydrochloric acid or in a saturated solution of sodium or potassium chloride, is added. After well mixing the contents of the flask, 25—30 c.c. of 4*N*-sulphuric acid are run in, and the mixture distilled through a condenser into absorption flasks containing sodium or potassium hydroxide. With gentle boiling, the ferrocyanide decomposes completely in about half an hour, all the cyanogen being evolved as hydrogen cyanide, and absorbed in the alkali hydroxide. The cyanide formed is then determined in the usual way.

A small quantity (about 2%) of cuprous chloride is sufficient to determine the decomposition of a large quantity of ferrocyanide. It is probable that cuprous cyanide is first formed, and then decomposed by the sulphuric and hydrochloric acids present with evolution of hydrogen cyanide and regeneration of cuprous chloride; this cycle of reactions is then repeated until decomposition of the ferrocyanide is complete.

The application of the above process to the estimation of the ferrocyanide contents of cyanogen mud or of spent oxides is given, and the results obtained discussed in detail. T. S. P.

**New Reaction for Tar Constituents (Pyridine) in Ammonia and Ammonium Salts.** ALFRED WÖHLK (*Ber. Deut. Pharm. Ges.*, 1912, 22, 285—288).—Very small quantities of pyridine may be detected in ammonium salts by grinding about 0.5 gram of the latter in a mortar with 1 gram of borax; if pyridine is present, its characteristic odour is noticed immediately. In testing ammonia, a portion of the solution is neutralised with hydrochloric acid and evaporated to dryness, the residue obtained being used for the test. W. P. S.

**Estimation of Nicotine in Tobacco.** EDWARD F. HARRISON and PERCY A. W. SELF (*Pharm. J.*, 1912, [iv], 34, 718—719).—The method proposed depends on the separation of nicotine from ammonia by precipitating the former with iodine. The tobacco is rendered alkaline with calcium hydroxide and steam-distilled until the distillate ceases to give a turbidity with iodine; the distillate is collected in a

definite volume of  $N/1$ -acid, and this solution is titrated at the end of the distillation, litmus being used as indicator. After the addition of 10 c.c. of  $N/1$ -acid, the solution is evaporated to a volume of 50 c.c., ten times the quantity of iodine required to combine with the nicotine (as calculated from the total alkalinity of the distillate) is added, the mixture is diluted to 100 c.c., and filtered. Seventy-five c.c. of the filtrate are now treated with an excess of thiosulphate, and the ammonia is estimated by distillation in the usual way. Allowance being made for the quantity of ammonia found, the remaining alkalinity of the distillate is calculated as nicotine. Results of experiments are given, showing that nicotine may be precipitated completely by means of iodine.

W. P. S.

**Analysis of Tannins.** LOUIS E. LEVI and AUGUST C. ORTHMANN (*Collegium*, 1912, 33—40).—An attempt to estimate tannin by means of chromium salts based on the employment of chromium chromate,  $\text{Cr}_2(\text{CrO}_4)_3$ , and basic sulphochromate,  $\text{Cr}_2\text{SO}_4\cdot\text{CrO}_4(\text{OH})_2$ , as mordants for textiles. It was thought possible that these complex chromium compounds would (in the presence of tannin) break up into insoluble basic chromium compounds, and be quantitatively precipitated according to the amount of tannin present.

Numerous experiments are described with different chromium salts; in some cases the tannin and gallic acids were precipitated alone, in others in combination with chromium, and the results are considered sufficiently promising to warrant a further continuation of the work.

F. M. G. M.

**The Chlorophyll Group. XV. Methods for Estimation of the Components of Chlorophyll (*allo*- and *neo*-Chlorophyll).** C. A. JACOBSON and LEON MARCHLEWSKI (*Biochem. Zeitsch.*, 1912, 40, 296—306).—It has already been shown that *allo*- and *neo*-chlorophylls both exist in the chlorophyll of different plants. Two methods have been devised by the authors for estimating the relative quantities of these two components. The first depends on the difference of the spectrum. The band  $\lambda$  436.5—442.8 is due to the *allo*-component, whereas the band  $\lambda$  391.8—399.7 is due to the *neo*-component. The second method depends on the difference in the extinction coefficients of the two components. The authors give plates showing the spectra of chlorophylls containing varying amounts of the components, and also a table of extinction coefficients for the same mixtures. They have analysed the chlorophyll of several plants, and the results show variations in the amounts of these constituents. The presence of other pigments do not influence the results. In order to obtain the spectra for varying mixtures it was necessary to prepare the pure *neo*-chlorophyll, for which purpose two methods are given. The one depends on the difference of behaviour of *neo*-chlorophyll to other substances when the ethereal solution is treated with varying strengths of hydrochloric acid, the *neochlorophyll* being but slightly basic and remaining in ethereal solution when the latter is treated with hydrochloric acid of relatively high concentration; the other method is a modification of Sorby's method of treating chlorophyll, and

depends on extraction of the carbon disulphide solution with graded strengths of alcohol.  
S. B. S.

**Analysis of Indigos Containing Starch.** G. H. FRANK and ARTHUR G. PERKIN (*J. Soc. Chem. Ind.*, 1912, 31, 372—373).—The authors confirm Thomson's statement (compare Abstr., 1911, ii, 346) that indigotin cannot be estimated accurately in samples of indigo containing starch by means of Rawson's method. They find, however, that the starch may be removed completely by boiling for thirty minutes with 4% hydrochloric acid, and recommend that, after the starch has been eliminated in this way, the indigotin should be estimated in the residue by Bloxam's tetrasulphonate method. Pure indigotin is not attacked when boiled with dilute hydrochloric acid. Care should be taken in carrying out the tetrasulphonate method not to boil the mixture of precipitant (potassium acetate) and tetrasulphonic acid solution; a clear solution is attained at a temperature of 90°, which is all that is required.  
W. P. S.

**Estimation of Small Quantities of Bilirubin.** E. HERZFELD (*Zeitsch. physiol. Chem.*, 1912, 78, 163. Compare this vol., ii, 612).—The bilirubin previously used was obtained from human gallstones. From ox gallstones, H. Fischer obtained 20% of bilirubin (Abstr., 1911, i, 803).  
E. F. A.

**Estimation of Gliadin or Alcohol-soluble Protein in Wheat Flour.** RALPH HOAGLAND (*J. Ind. Eng. Chem.*, 1911, 3, 838—842).—A discussion of the results of Osborne ("Proteins of the Wheat Kernel," Carnegie Inst., 1907) and other workers on the separation of wheat proteins by their solubility (or the reverse) in alcohol of varying concentrations. The author confirms the work of Teller, and considers that (1) shaking the sample vigorously with alcohol during sixty to ninety minutes extracts an equal amount of alcohol-soluble protein to that obtained by the usually more prolonged treatment of eighteen to twenty-four hours; (2) whilst boiling alcohol extracts slightly more protein than cold alcohol, there does not appear to be any advantage in its employment, and (3) alcohol varying in strength from 45 to 55% by weight extracts more protein than alcohol of any other strength, and it is recommended that alcohol of 50% by weight be employed for the determination of gliadin in wheat flour, and that the use of 70% alcohol, whether by weight or by volume, be discontinued.  
F. M. G. M.

**Assay of Digestive Ferments.** HOWARD T. GRABER (*J. Ind. Eng. Chem.*, 1911, 3, 919—921).—A description of numerous experiments on pepsin, pancreatin, rennet, papain, and bromelin. It is shown that (1) the composition of the white of egg has an important bearing on the apparent strength of pepsin, the albumin appearing more difficult to digest the first twenty-four hours after the egg is laid; a change then gradually takes place, until after about five to seven days it has reached its maximum solvent condition, after which period its digestibility again gradually diminishes; (2) in the assay of

pancreatin by starch hydrolysis, as well as in all diastatic ferments, the kind of starch employed is of great importance, and in stating the strength of each, it should be in terms of the particular starch employed; (3) papain appears to be equally active as regards any kind of raw beef when acting in acid media, but if the character of the beef is changed as by cooking, papain loses its solvent action on the protein; (4) rennet is influenced in its coagulating power by (a) the condition of the milk, its chemical composition such as the presence and quantities of inorganic salts, particularly those of calcium; (b) by the manner of mixing the rennet with the milk; (c) the kind of cow from which the milk is taken, and (d) the temperature at which the milk was kept before and during the test.

F. M. G. M.

**A New and Accurate Method for Determining the Tryptic Value of Pancreatin.** CLARENCE F. RAMSAY (*J. Ind. Eng. Chem.*, 1911, 3, 822—823).—No satisfactory method has yet been devised for estimating how much protein a given sample of pancreatin will digest, and the following is now suggested as giving results accurate to within 2 or 3%.

The material required is: 0.5 gram of pancreatin made up to 50 c.c. with distilled water; 900 c.c. of milk containing 1.8 gram of hydrogen sodium carbonate; two grams of rennin (1:30,000; time, ten minutes equivalent), and 1 c.c. of 6% acetic acid added to 50 c.c. of water.

The warmed milk is placed in a series of cylindrical tubes (50 c.c. in each) and maintained at a temperature of 40°. Five tubes are treated with the following amounts of the pancreatin solution: 8.33 c.c. (1:600), 7.69 c.c. (1:650), 7.14 c.c. (1:700), 6.66 c.c. (1:750), 6.25 c.c. (1:800), in each case the exact time of addition is noted, the contents well mixed, and after fifteen minutes' digestion 5 c.c. of the milk is removed and treated with 3 c.c. of the rennin solution. No precipitate indicates that the casein has all been peptonised, and that the pancreatin is stronger than is required to peptonise the milk; by this means two tubes are found in the series between which the strength of the pancreatin lies. A further series of experiments are then carried out with quantities of pancreatin between the amounts contained in the two limiting tubes until the exact quantity of pancreatin required to peptonise that quantity of milk is discovered.

Pancreatin deteriorates very rapidly in neutral solution, therefore the solution must be prepared and added immediately to the milk. Acid precipitates peptonised milk, therefore the quantity of acetic acid in the rennin must be exactly neutralised by the hydrogen sodium carbonate added to the milk.

F. M. G. M.

**A New Micro-chemical Reaction of Semen.** PESET ALEXANDRE (*Zeitsch. anal. Chem.*, 1912, 51, 473—475).—The author has tried the gold bromide reaction recommended by De Dominicis ("Risveglio Medico," May 15th, 1910). A trace of semen is heated on a slide with a drop of saturated solution of gold bromide to boiling, and then examined under the microscope with enlargement of

300—400. There are formed oblong, pointed, and quadrangular crystals, here and there also rectangular or cross-shaped, hemitropic crystals of garnet colour and 20—25 c.c. size. They are soluble in alkalis and alcohol, insoluble in acids and fairly permanent.

According to the author the reaction is successful if the solution of the semen contains 10% of the latter. The rectangular form of the crystals is but seldom found. Instead of gold bromide, saturated solutions of gold chloride and potassium bromide (kept separately) may be used. Quadratic crystals are almost exclusively obtained; crystals of potassium auribromide also separate, but on account of their size and different form they cannot be confounded with the semen compound.

Quadratic crystals are obtained from the part of the semen soluble in alcohol, whilst the insoluble portion often yields the pointed variety. The quadratic crystals may also be due to choline.

L. DE K.

#### A Rapid Gravimetric Method of Standardising Vaccines.

JAMES W. WILSON and CHARLES DICKSON (*J. Hygiene*, 1912, 12, 49—59).—Bacterial emulsions are rapidly evaporated to dryness in tared flasks or on tared platinum foil, and the strength of the emulsion determined by the increase in weight of the flasks or foil. The method is more rapid, less fatiguing, and more trustworthy than counting methods.

W. D. H.

**Organic Arsenic Products Recently Introduced into Therapeutics.** GIUSEPPE BRESSANIN (*Gazzetta*, 1912, 42, i, 438—440).—The following method given in the Italian Pharmacopoeia for the estimation of sodium cacodylate is based on the alkalinity of this compound to methyl-orange: 1.6 gram of the product is dissolved in water and the solution made up to 100 c.c.; 10 c.c. of this, to which a drop of phenolphthalein has been added, should be coloured by 0.5 c.c. of *N*/100-sodium hydroxide solution. If 3—4 drops of methyl-orange are added to the decolorised solution, at least 7 c.c. of *N*/10-hydrochloric acid should be required to produce a red coloration, a content of at least 70% of sodium cacodylate being indicated.

With pure products this method gives good results, the cacodylic acid set free by the hydrochloric acid being neutral to methyl-orange; but any admixture, such as sodium hydrogen carbonate, behaving towards these indicators in the same way as sodium cacodylate will naturally be estimated as the latter. In order to detect such admixture, the solution neutral to methyl-orange is heated to expel carbon dioxide, cooled, and titrated with *N*/10-potassium hydroxide in presence of phenolphthalein; with a pure product, the amount of alkali thus used corresponds with that of the hydrochloric acid required in the original titration.

Different samples of atoxyl contain widely varying proportions of water, and the author suggests that this substance should be administered in the anhydrous condition.

T. H. P.

## General and Physical Chemistry.

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**The Absorption and Refraction Methods.** ARTHUR HANTZSCH (*Ber.*, 1912, 45, 1742—1746).—Polemical (compare Auwers, this vol., ii, 505; Hantzsch, this vol., ii, 313).  
E. F. A.

**Molecular Refraction and Dispersion as Aids to the Organic Chemist.** FRITZ EISENLOHR (*Jahrb. Radioaktiv. Elektronik.*, 1912, 9, 315—354).—A summary of recent work on the influence of constitution on the refractive and dispersive power of organic compounds.  
H. M. D.

**The History of Spectrochemistry.** RAFFAELLE NASINI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 685—689).—The author claims priority over Brühl in respect to the discovery of the constitutive character of dispersion and of the influence of conjugation on optical properties.  
C. H. D.

**Intensity Measurements in the Spectra of Streaming Gases with Direct Current Discharge and High Current Densities.** JULIUS SCHWEDES (*Zeitsch. wiss. Photochem.*, 1912, 11, 169—204).—Measurements of the intensity of emission have been made in the spectra of hydrogen, oxygen, and carbon monoxide under conditions which permit satisfactory photometric records to be obtained. For this it has been found necessary to pass the gas continuously through the discharge tube, and to employ the constant current yielded by a high potential accumulator battery. The measurements are also facilitated by the use of quartz discharge tubes and of specially designed Wehnelt cathodes, the construction and preparation of which is described.

The photometric data show that the intensity of the lines in the first subsidiary series of hydrogen increases more rapidly than the strength of the current. On the other hand, the intensity of the lines of the second hydrogen spectrum increases less rapidly than the current. In the case of oxygen, both the first and second subsidiary series behave like the first subsidiary hydrogen series. At low pressure, this is not accompanied by any displacement of the energy maximum, although this is displaced towards the red end at higher pressures when the current strength is increased.

The bands of carbon monoxide show a linear increase in intensity with increase in the current, and this holds, not only for the edges, but also for other parts of the bands.  
H. M. D.

**Nature of the Luminosity of Phosphorus.** MIECZYSLAW CENTNERSZWER and A. PETRIKALN (*Zeitsch. physikal. Chem.*, 1912, 80, 235—240).—The luminous glow of phosphorus in an organic solvent gives a continuous spectrum in the visible region. By means of a special arrangement it was found possible to obtain the spectrum in the

invisible region ; in the ultraviolet it shows fourteen sharp lines and a band in the neighbourhood of 3252 Ångström units. The approximate wave-lengths of the lines are given. No lines or bands were observed in the ultraviolet absorption spectrum.

It is known that phosphorus affects a photographic plate through black paper. The authors find, however, that when the apparatus is so arranged that the products of oxidation are removed as fast as they are formed, the plate is not affected, so that the effect in question is due to a volatile product of the oxidation of phosphorus, perhaps hydrogen peroxide. G. S.

**Vacuum Tube Spectra of the Vapours of Some Metals and Metallic Chlorides. I. Cadmium, Zinc, Thallium, Mercury, Tin, Bismuth, Copper, Arsenic, Antimony, and Aluminium.** JAMES H. POLLOK (*Sci. Proc. Roy. Dubl. Soc.*, 1912, 13, 202—218).—A comparison has been made of the vacuum tube spectra of the metals and their chlorides with the corresponding spark spectra. For this purpose, photographic records have been obtained with the aid of quartz vacuum tubes, and wave-length measurements are recorded for each of the metals investigated.

From the observations it appears that the lines shown by the vacuum tube spectra of metallic vapours consist of some or all of the lines exhibited by the spark spectrum. Those lines which are continuous in the spark spectrum are invariably the strong lines of the vacuum tube spectrum, whereas discontinuous lines are frequently not found in the vacuum tube spectrum, especially if a condenser is not placed in the circuit.

When a condenser is introduced into the vacuum tube circuit, certain lines are enhanced, this being very frequently the case with the more prominent discontinuous lines of the spark spectrum.

The same lines are obtained with the chloride as with the vapour of the metal, although in certain circumstances the lines of chlorine are obtained in addition. As a rule, the chlorine lines are not exhibited unless a condenser is introduced, and even then the lines are rather faint in the case of certain chlorides. When a line is enhanced by the insertion of a condenser, it is found that the same change occurs both with the vapour of the metal and that of the chloride. Lines which appear in the arc spectrum, but not in the spark spectrum, are not seen in the vacuum tube spectra, either with or without a condenser.

When a large amount of chloride vapour is present in the tube and no condenser is used, bands are developed which appear to be quite independent of the lines of the spark spectra of the elements, and probably owe their origin to the molecules of the compounds under observation. H. M. D.

**Vacuum Tube Spectra of Some Metals and Metallic Chlorides. II. Lead, Iron, Manganese, Nickel, Cobalt, Chromium, Barium, Calcium, Strontium, Magnesium, Potassium, Sodium, and Lithium.** JAMES H. POLLOK (*Sci. Proc. Roy. Dubl. Soc.*, 1912, 13, 253—268).—The general conclusions

arrived at from the previous observations (compare preceding abstract) were confirmed by the results obtained in the investigation of this further series of metals. Except in the case of manganese and magnesium, bands are not so readily formed by the chlorides of this series as by those of the first series.

As a general rule, the strongest lines in the spark spectrum are also the strongest in the vacuum tube spectrum. In general, the ultimate lines in the vacuum tube spectrum appear to be identical with the ultimate lines of the spark spectrum, but this is not always the case. For instance, manganese gives a characteristic group in the vacuum tube spectrum which is extremely persistent, namely, the lines of wave-length  $\lambda = 2801.3$ ,  $2798.5$ , and  $2795.3$ , whereas the wave-lengths of the ultimate lines in the spark spectrum of manganese are  $\lambda = 2605.8$ ,  $2594.0$ , and  $2576.2$ .  
H. M. D.

**The Ultimate Lines of the Vacuum Tube Spectra of Manganese, Lead, Copper, and Lithium.** GENEVIEVE V. MORROW (*Sci. Proc. Roy. Dubl. Soc.*, 1912, 13, 269—287).—Photographs have been obtained of the spectra given by discharge tubes containing very small quantities of the vapours of the chlorides of the various metals. The wave-lengths of the ultimate lines of manganese are  $\lambda = 2801.3$ ,  $2798.5$ , and  $2795.3$ , those of copper  $\lambda = 3274.1$  and  $3247.6$ , and those of lithium  $\lambda = 6708.2$  and  $4602.4$ . In the case of lead, a tube containing 0.1 mg. of the metal as chloride was found to give a broad band extending from  $\lambda$  4068.2 to 4058.0. With a smaller quantity of the vapour, this band disappeared, but the line  $\lambda = 4068.2$  remained, and is apparently one of the ultimate lines.  
H. M. D.

**Series in the Spectra of Tin and Antimony.** T. VAN LOHUIZEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 31—45).—A new formula is suggested for the representation of the connexion between the wave-lengths of the lines in spectral series. The formula is such that if the parameters 1, 2, 3 . . . are used as abscissæ and the reciprocal values of the wave-lengths as ordinates, every series is represented by one and the same curve when the axes are suitably transferred. This curve is of the third degree.  $y = -N/x^2$ , in which  $y = 10^8\lambda^{-1}$ ,  $x = 1, 2, 3$ , etc., and  $N$  is the universal constant occurring in the formulæ of Rydberg, Ritz, and Hicks.

It is shown that the series lines of tin and antimony can be satisfactorily represented by means of this formula, and in this connexion the behaviour of the lines belonging to different series in a magnetic field is examined. The conclusion is drawn that lines belonging to different series are not necessarily resolved in a different manner by an applied magnetic field.  
H. M. D.

**Absorption Spectra of Aqueous Solutions of Salts of Neodymium and Praseodymium as Measured by means of the Radio-micrometer.** HARRY C. JONES and J. SAM GUY (*Physikal. Zeitsch.*, 1912, 13, 649—658).—A sensitive form of radio-micrometer is described in the form of a delicate moving coil galvanometer, the coil of which consists of a single loop of thin copper wire with a

blackened thermocouple at one end. The elements forming the couple consist of alloys, one of which contains 90% tin and 10% bismuth, and the other 97% tin and 3% antimony. When the coil, which with the couple and the attached mirror together weigh only 20 mg., is suspended between the poles of a strong magnet, a very sensitive radiometer is obtained, which has been employed in the investigation of the absorption spectra of aqueous solutions of neodymium salts between  $\lambda=5000$  and  $\lambda=10,000$ . From the radiometer readings, transmission curves have been plotted for the chloride, bromide, nitrate, sulphate, and acetate. According to these curves, the solutions in question exhibit sharply defined absorption maxima, and three of these at  $\lambda=7300$ , 7860, and 8605 have not been previously indicated in the experiments according to the photographic method.

With regard to the influence of concentration on the absorption, it is found that the bands are somewhat broader in the more concentrated solutions, but that the intensity of the bands increases with the dilution. This is interpreted in terms of the author's resonance theory.

H. M. D.

**Absorption Spectra of Isomeric Complex Salts. I.** ARNALDO PIUTTI (*Ber.*, 1912, 45, 1830—1834. Compare Ley and Winkler, this vol., i, 243).—The stereoisomeric croceo- and flavo-tetramminedinitrocobalt chlorides give different absorption curves, whereas there is no difference between the curves for xantho-nitropentamminecobalt chloride and isoxantho-pentamminenitritocobalt chloride.

The absorption curves for potassium ferro- and ferri-cyanides are very different from each other, but are the same for the  $\alpha$ - and  $\beta$ -isomerides of each salt. This agrees with the views of Bellucci (*Abstr.*, 1911, i, 430) as to the constitution of these salts, but is not in accordance with the structural formulæ put forward by Briggs (*Trans.*, 1908, 93, 1564; 1911, 99, 1019). The isomeric ferricyanides also give the same absorption curve in a solution containing oxyhæmoglobin.

T. S. P.

**Alkaloids and Ultraviolet Light.** GUSTAVE MICHAUD (*Arch. Sci. Phys. nat.*, 1912, 33, 498—499).—Photographs taken with a quartz objective rendered opaque to visible light by covering both faces with silver, show that certain colourless objects do not reflect the ultraviolet light, for which the silver is transparent. These include zinc oxide, bismuth nitrate, and cerium carbonate, whilst zinc carbonate appears grey. Black and dark-coloured inorganic substances behave practically alike to the visible and ultraviolet rays.

Alkaloids show great variation when photographed in this manner: papaverine, narceine, thebaine, narcotine quinine, cinchonine, cinchonidine, quinidine, brucine, and berberine appear black on the positive, whereas with the exception of berberine they all appear colourless by ordinary light. On the other hand, morphine, hyoscyamine, theobromine, caffeine, and strychnine appear colourless under all conditions of illumination.

E. F. A.

**Applications of the Electron Conception of Positive and Negative Valencies. IV. Fluorescence: Anthracene and Phenanthrene.** HARRY S. FRY (*Zeitsch. physikal. Chem.*, 1912, 80, 29—49).—The theory described in previous papers (compare Abstr., 1911, i, 431) is applied to explain the fluorescence phenomena in the case of anthracene and phenanthrene, on the basis of the absorption and fluorescence spectra of the vapours of these substances as measured by Elston (*Astrophysical Journal*, 1907, 25, 155). Electrodynamical formulæ for anthracene and phenanthrene are suggested, and the connexion between these and the absorption and fluorescence bands discussed in detail. G. S.

**New Example of the Coupling of Short- and Long-waved Fluorescence Bands.** M. GELBKE (*Physikal. Zeitsch.*, 1912, 13, 584—585).—The absorption and fluorescence spectra of ethyl-alcoholic solutions of acetone, diacetyl and ethyl oxalosuccinonitrile have been investigated. All three substances show an intense absorption band in the ultraviolet, and also a band of smaller intensity in the region of longer wave-lengths. If the ketones are excited by light rays corresponding with the short-wave absorption band, they emit fluorescent light of the wave-length of each of the absorption bands. If the exciting light consists, however, of rays corresponding with the long-waved absorption band, there is no fluorescence effect. The observations are considered to be in agreement with Stark's theory. H. M. D.

**Spectral Investigation of the Phosphorescence and the Distribution of the Excitation for Certain Phosphorescent Alkaline-earth Metal Sulphides.** ALBERT BACHEM (*Ann. Physik*, 1912, [iv], 38, 697—720).—The phosphorescence spectra of various active alkaline-earth metal sulphides have been examined, and the characteristic bands of the momentary and prolonged phosphorescent emission are described in detail. In order to obtain a uniform spectral distribution in the exciting light, use was made of the iron arc, and to ascertain the influence of temperature, observations of the phosphorescent emission were made at temperatures ranging from  $-180^{\circ}$  to  $200^{\circ}$ .

The examination of the distribution of the excitation or the relationship between the wave-length of the exciting light and the intensity of the phosphorescent light has shown that there are in general several excitation maxima. These maxima are not independent of the temperature, but their positions alter to some extent with the temperature of the phosphorescing substance. In the case of calcium and strontium sulphides containing bismuth as the active metallic "impurity," the maxima are displaced towards the long-waved region as the temperature rises.

A comparison of the wave-lengths which correspond with maximum and minimum absorption and excitation shows that these are not identical. The wave-lengths of the absorption maxima are smaller than those of the excitation maxima, whilst the reverse holds for the wave-lengths of the absorption and excitation minima.

H. M. D.

**Phosphorescence of Selenium Compounds.** W. E. PAULI (*Ann. Physik*, 1912, [iv], 38, 870—880).—It has been found that phosphorescent preparations of alkaline-earth metal selenides can be obtained by methods similar to those employed by Lenard and Klatt (*ibid.*, 1904, 15, 225, 425, and 634) for the preparation of the active sulphides. The phosphorescent selenides actually obtained are represented by the formulæ:  $\text{Ca}(\text{Bi})\text{Se}$ ,  $\text{Sr}(\text{Cu})\text{Se}$ ,  $\text{Sr}(\text{Bi})\text{Se}$ ,  $\text{Sr}(\text{Pb})\text{Se}$ ,  $\text{Ba}(\text{Pb})\text{Se}$ , and  $\text{Ba}(\text{Cu})\text{Se}$ , where the bracketed symbol refers to the metallic "impurity" present.

The sensitiveness of the selenides, in so far as their phosphorescent properties are concerned, to small variations in the conditions of formation, for instance, in the temperature to which they are heated, the period of heating, the admission or exclusion of air, and the rate of cooling, is much more pronounced than that of the active sulphides.

For the same metallic "impurity," the number of bands in the spectra of the selenides is smaller than in the spectra of the corresponding sulphides.

The upper temperature limit, above which the active substances do not show any after-luminosity, is also much lower for the selenides than for the sulphides.

Certain heavy metals which act as the photo-electrically sensitive constituents in the case of the alkaline-earth metal sulphides appear to be incapable of exciting phosphorescence if present in the selenides.

H. M. D.

**The Existence of Four Inactive Tartaric Acids; the Law of Mass Action with Reference to the Work of Darzens and Chatelier.** ALBERT COLSON (*Compt. rend.*, 1912, 154, 1801—1803).—A theoretical paper in which the author again draws attention to the views already set out by him on the stereochemistry of the tartaric acids (compare Abstr., 1892, 669, 758; 1893, i, 553; ii, 105).

W. G.

**Mercury Lamp for Quantitative Photochemical Investigations in the Ultraviolet.** FRITZ WEIGERT (*Zeitsch. physikal. Chem.*, 1912, 80, 67—77).—The lamp differs from others recently described in not being directly connected with the reaction vessel. It is composed essentially of an inverted U-tube of quartz, the discharge passing between two mercury surfaces in the usual way. The U-tube is surrounded by a cylindrical quartz tube, which extends some distance above the top of the former tube, and is cooled by water circulation round the upper part. The top of the cylindrical tube is closed by a quartz plate, so that the light is thrown from below upwards, and has not to pass through water, which would absorb a large proportion of the ultraviolet rays. The reaction vessel is provided at its base with a quartz plate, through which the light reaches the reaction mixture. When only qualitative results are required, the gas can be passed directly into the cylindrical tube surrounding the glowing tube, in which circumstances the light is completely absorbed.

The arrangement is figured and described in full detail in the original paper.

G. S.

**Chemical Action of Light. VII. Decomposition of Ozone in Ultraviolet Light.** FRITZ WEIGERT (*Zeitsch. physikal. Chem.*, 1912, 80, 78—106. Compare previous abstract).—By means of the mercury vapour lamp described in the previous paper, the rate of decomposition of ozone in ultraviolet light has been investigated. The results with freshly prepared mixtures of oxygen and ozone are reproducible with an accuracy of about 30%. The observed rate of decomposition is the sum of the spontaneous decomposition which also takes place in the dark, and the reaction under the influence of light. The "order" of the dark reaction exceeds 2, and in some cases is as high as 4, but as it is quite subsidiary to the light reaction it has not been further investigated.

The order of the light reaction in the course of an experiment is approximately unimolecular. When, however, the gas is subjected to alternate illumination and periods of darkness—a method which eliminates certain sources of error—the order of the reaction lies between 1 and 2. When a thick layer of gas is used, and the absorption is therefore complete, the reaction is very nearly unimolecular; when the layer is only 0.5 cm. thick, the order rises to 1.4. This change is the only photochemical action hitherto investigated which gives an order exceeding one.

The velocity coefficient diminishes with diminishing thickness of the layer of gas subjected to the action of ultraviolet light, and with a layer of 0.5 cm. thickness is about 50% of the value with the thickest layer used—43 cms.

The results are most easily accounted for on the hypothesis that under the influence of light a heterogeneous catalyst is formed, which accelerates the decomposition of ozone. The reaction velocity is determined by the concentration of this catalyst and by the rate at which the ozone reaches it by diffusion. This theory also accounts for some of the results obtained by von Bahr (compare Abstr., 1910, ii, 949) for the same reaction.

The reaction velocity increases with the intensity of the light, and the temperature-coefficient of the reaction is small. No induction period was observed. G. S.

**Wave-length of the Active Radiations in the Photochemical Synthesis of Ternary Compounds.** DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1912, 154, 1803—1805).—A concentrated aqueous solution of formaldehyde is decomposed by the light from a quartz-mercury lamp, even when the rays of wave-length less than  $0.19\mu$  are cut off. The products of decomposition consist of a mixture in almost equal volumes of carbon monoxide and hydrogen, together with some (10%) methane and carbon dioxide. Sunlight also slowly brings about the same decomposition.

Formaldehyde cannot be synthesised from a mixture of carbon monoxide and hydrogen by the action of sunlight, even in the presence of catalysts, such as spongy platinum, although it is formed to some extent when the mixture is exposed to the ultraviolet rays from a quartz-mercury lamp (compare Abstr., 1910, i, 543; ii, 814).

In the photochemical reaction  $\text{CO} + \text{H}_2 \rightleftharpoons \text{CH}_2\text{O}$ , the equilibrium

point is more markedly on the side of the decomposition products than it is in the case of the reactions  $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$  and  $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$ .  
T. S. P.

**Fatigue Effects and Initial Velocities in the Photo-electric Action in a Vacuum.** KARL HERRMANN (*Ber. Deut. physikal. Ges.*, 1912, 14, 557—572).—An apparatus has been designed which permits the investigation of the photo-electric effect on metallic surfaces which have been freshly prepared by means of a hard steel scrubber which can be made to operate on the metal under examination in the highly exhausted apparatus. Experiments were made with aluminium, magnesium, platinum, silver, lead, and tin, and in all cases the newly formed metal surfaces were found to exhibit fatigue effects when subjected to the action of ultraviolet rays. In general, the rate of decay of the emission of electrons increases with the electro-positive character of the metal. The changes in activity are such, however, that the relative positions occupied by a given pair of metals may vary with the period of exposure to the action of the exciting rays. This is the case with aluminium and magnesium and with lead and silver.

In the case of platinum, anomalous results were obtained, in that the activity diminishes at first to a small extent and then increases slowly, the values obtained for the activity after two hundred minutes' exposure being appreciably greater than the initial value. This anomalous behaviour is attributed to the action of the traces of gas which are still present in the exhausted apparatus.

When the magnitude of the photo-electric effect in the case of a metal surface prepared by scrubbing in a vacuum is compared with that exhibited by the same surface prepared in the same way at atmospheric pressure, the latter is found to be appreciably smaller.

With surfaces mechanically produced in the above manner there is no evidence of the existence of the high initial velocity effect which has been found in the case of metal surfaces cleaned by the action of a high potential discharge.  
H. M. D.

**The Photo-electric Effect in Antimony Cadmium Alloys.** KARL HERRMANN (*Ber. Deut. physikal. Ges.*, 1912, 14, 573—575. Compare previous abstract).—The fact that the thermal and electrical conductivity of antimony cadmium alloys vary to an enormous extent with the composition has led the author to examine these alloys in respect of their photo-electric behaviour. The results show that the photo-electric activity changes in an approximately linear manner with the composition of the alloy, and differs therefore entirely from the thermal and electric conducting power. This result indicates that the electrons set free from the metal by the ultraviolet rays are not the same as the "free" electrons which are responsible for the thermal and electrical conductivity.  
H. M. D.

**The Definition of the Vienna Radium Standard Preparations.** STEFAN MEYER and VIKTOR F. HESS (*Monatsh.*, 1912, 33, 583—611).—The heat development, the  $\gamma$ -radiation, the  $\alpha$ -radiation, and the emanation from the Vienna standard radium preparations have been exactly measured and defined. The heat development was

measured by means of two similar copper cylindrical calorimeters, gilded and polished externally, in one of which was placed the radium standard, and in the other a resistance coil, through which a carefully measured electric current was maintained. The two calorimeters were contained in a large outer vessel, in a room electrically heated to constant temperature, and the heating current was adjusted until a thermocouple recorded no difference of temperature between the two calorimeters after equilibrium of temperature had been obtained. Several preparations agreed in showing that the heat development per gram of radium chloride was 100.66, and per gram of radium, 132.26 calories per hour, the maximum departure from the mean value of any experiment being 0.3%. It is estimated that the whole of the  $\alpha$ - and  $\beta$ -, and 18% of the  $\gamma$ -radiation were absorbed and produced heat within the calorimeter. The energy of the  $\alpha$ -radiation, calculated from data as to the number and the velocities of the  $\alpha$ -particles expelled, is 127.7 (calories per hour per gram of radium). Estimating for the energy of the  $\beta$ -rays and of the recoiling atoms, and for 18% of the  $\gamma$ -rays brings up the figure to 133.46, or for the whole of the  $\gamma$ -radiation, 138. These figures refer to radium in equilibrium with its products as far as radium-C, but free from later products, and indicate that no appreciable part of the energy of disintegration escapes transformation into heat. The polonium (radium-*P'*) in equilibrium with 1 gram of radium would produce a further 25.86 calories per hour, the amount present after one year's accumulation being estimated to produce about 1 calorie per hour.

The ionisation produced by the  $\gamma$ -rays in cylindrical and spherical ionisation vessels of exactly defined construction and dimensions was determined, and a revision of the total radium extracted (3.68 grams) showed that the loss in the manufacturing processes to have been about 13%. The saturation current produced by the  $\alpha$ -rays from flat films containing known minute quantities of radium, free from its products, measured  $1.22 \times 10^6$  E.S.U., or twice this counting the  $\alpha$ -rays absorbed in the supporting plate, which is somewhat less than that calculated (1.28 under the conditions of measurement), owing probably to absorption in the film. The saturation current due to one curie of emanation is estimated from different data to be 2.67, 2.7, and 2.75 ( $\times 10^6$  E.S.U.). The total thorium extracted from 10,000 kilograms of mineral was about 330 grams, and the mesothorium corresponding to this, which is necessarily present in the radium, is too small to exert any influence on the results. If it is supposed that a maximum quantity of 500 grams was present, and that all this thorium was in reality ionium, the period of the latter is between 200,000 and 250,000 years.

A quartz tube in which 1 gram of radium chloride had been kept for two years had become full of cracks and quite rough on its inner surface. Glass tubes, with sealed-through platinum wires, are recommended for the preservation of radium preparations. F. S.

**The Coefficient of Absorption by Air of the  $\beta$ -Rays from Radium-C.** ARTHUR S. EVE (*Trans. Roy. Soc. Canada*, 1911, 5, iii, 59—67).—Very lightly built electroscopes made of a frame-work of

thin steel wires, covered with paper or aluminium foil, were suspended in the centre of a room away from all surrounding bodies, and the ionisation produced in them, when test-tubes containing radium preparations were suspended at various distances from the electroscopes, was determined. The absorption of the complex  $\beta$ -rays of radium-*C* by air was found to be approximately exponential, the ionisation being multiplied by the square of the distance to correct for the effect of increasing distance alone. The absorption coefficient  $\mu$  was found to be  $0.0033 \text{ (cm.)}^{-1}$  at short ranges of 0.6 to 1.6 metres, and 0.0045 at longer ranges of 2 to 5 metres. For the  $\gamma$ -rays the absorption coefficient for air was estimated to be between 0.000021 and 0.000031. The reciprocals of these coefficients are 2.5 and 250 metres respectively, and represent the average length of path of a  $\beta$ - or  $\gamma$ -ray, considered as an entity, in air before it is absorbed. Some experiments with the radium active deposit gave a value for  $\mu$  of about 0.012, which is three or four times as great as that for the  $\beta$ -rays escaping from glass test-tubes. This coefficient did not decrease after the active deposit had been removed from the emanation, whilst the proportion of radium-*C* relative to radium-*B* was increasing, and it appears that radium-*C* may, like radium-*B*, emit slow  $\beta$ -rays in considerable proportion.

F. S.

**Secondary Radiation in Gases for High Speed Primary Rays.** SIMON BLOCH (*Ann. Physik*, 1912, [iv], 38, 559—587. Compare Kossel, this vol., ii, 315).—Quantitative measurements have been made of the secondary radiation generated in different gases when subjected to the action of the high speed  $\beta$ -rays of uranium-*X*. A method has been devised by means of which the measured conductivity can be corrected for the reflected and secondary radiation due to the action of the walls of the experimental vessel. It has also been found that a paraffin condenser can be conveniently employed for the quantitative measurement of the exciting beam of high speed rays.

From the data it appears that a single  $\beta$ -ray emitted by uranium-*X* gives rise to 54 secondary rays per cm. in air at atmospheric pressure. For the other gases examined the values are: carbon dioxide 86, coal-gas 34, and hydrogen 7. The value for carbon dioxide, when compared with air, is in agreement with that required by the mass relationships, but the value for hydrogen deviates appreciably from the theoretical number.

When these results for high speed primary rays are combined with those of Kossel (*loc. cit.*) for low speed rays, a curve is obtained which shows the dependence of the secondary radiation on the velocity of the primary rays.

H. M. D.

**Absorption of  $\gamma$ -Rays by Gases and Light Substances.** G. CHADWICK (*Le Radium*, 1912, 9, 200—202).—By means of a compensation method of measurement, in which the  $\gamma$ -ray ionisation in a fixed chamber is made exactly equal to the  $\alpha$ -ray ionisation of a uranium oxide compensating ionisation chamber, by varying the distance of the source of  $\gamma$ -rays from the first-named chamber and cal-

culating the intensity of the  $\gamma$ -rays from the law of inverse squares, the absorption coefficients of air, hydrogen, and carbon dioxide have been directly determined. For air, a layer of liquid air was used as the absorbent, and the density was calculated from its composition as determined by analysis and the tables of Behn and Kiebitz. For the other gases, and also for air, a long cylinder of iron containing the gas compressed to 60 or 90 atmospheres was employed as the absorption vessel. The value for  $\mu/D$  ( $\mu$ =the absorption coefficient and  $D$ = the density) for air was 0.048 for  $\gamma$ -rays that had traversed 3 mm. of lead, and 0.046 when 1 cm. of lead was used. For carbon dioxide the values for 3 mm. and 1 cm. of lead were respectively 0.051 and 0.047, and for hydrogen for 3 mm. of lead, 0.047. For air at 0° and 760 mm. the value of  $\mu$  is 0.0000624. Eve's results on the number of ions produced by  $\gamma$ -rays (Abstr., 1911, ii, 956) are reduced about 30% by the use of this coefficient. Values are given for  $\mu/D$  for wood, aluminium, iron, lead, water, and various aqueous solutions, and it is found that this value is a minimum for substances of intermediate density, the more pronounced as the  $\gamma$ -rays employed are less penetrating, as found by Russell and Soddy. The values of  $\mu/D$  vary from 0.0401 to 0.599.

F. S.

**The Number of  $\delta$ -Particles Expelled Concurrently with each  $\alpha$ -Particle Emitted by Polonium.** W. T. KENNEDY (*Trans. Roy. Soc. Canada*, 1911, 5, iii, 29—35).—The number of  $\alpha$ -particles expelled per second from a certain plate coated with polonium was estimated from the magnitude of the saturation current and the data of Geiger on the number of ions produced by one  $\alpha$ -particle of polonium, allowing for the decay of the activity of the polonium during the experiments. The number of  $\delta$ -rays emitted from the polonium was evaluated by measuring the rate at which it charged up positively when insulated in a silvered vessel as completely as possible exhausted of air. Making allowance for the positive charge carried from the polonium by the  $\alpha$ -particles, it was deduced that for each  $\alpha$ -particle expelled about 125  $\delta$ -particles left the polonium. A considerable portion of this must be due to the bombardment of the polonium coated plate by  $\alpha$ -particles, so that before the number of  $\delta$ -particles emitted per  $\alpha$ -particle can be deduced, it is necessary to know how many  $\delta$ -particles are expelled from the plate when struck by one  $\alpha$ -particle. This number is being determined.

F. S.

**Pulverisation by Cathode Rays.** VOLKMAR KOHLSCHÜTTER (*Jahrb. Radioaktiv. Elektronik.*, 1912, 9, 355—418).—This is a report in which a full account is given of the phenomena of pulverisation under the influence of cathode rays and of the theoretical interpretation of the observations. The author has collected and classified the literature on the subject.

H. M. D.

**Röntgen Radiation from Substances of Low Atomic Weight.** CHARLES A. SADLER and PAUL MESHAM (*Phil. Mag.*, 1912, [vi], 24, 138—149).—Experiments have been made to determine the nature of the radiation emitted by carbon when excited by homogeneous

rays. The absorption data indicate that the radiation excited in carbon in these circumstances is heterogeneous and less penetrating than the primary exciting beam. As the penetrating power of the exciting radiation increases, the intensity of the scattered radiation is found to increase, and at the same time the change in quality becomes more pronounced.

H. M. D.

**Emission of Series Lines by Solid Metallic Compounds Under the Influence of Canal Rays. Limiting Value of the Exciting Energy.** JOHANNES STARK and GEORG VON WENDT (*Ann. Physik*, 1912, [iv], 38, 669—689).—It has been found that colourless compounds of all the alkali and alkaline-earth metals, of thallium, zinc, and aluminium emit the characteristic series lines when acted on by canal rays. It seems probable therefore that this property is common to the colourless compounds of all metals, but it is not exhibited by those which absorb visible light rays.

The seat of the phenomenon is not the solid surface of the metallic compound, but has been found to be located in the adjacent layer of the surrounding gas, the thickness of this layer, which may be as much as 1 millimetre, depending on the nature of the metal and the energy of the exciting canal rays. The nature of the phenomenon is independent of the particular elements with which a given metal is chemically combined.

For the emission of series lines by a metallic compound it is necessary that the energy of the exciting rays shall exceed a certain limiting value. This value varies considerably with the nature of the metal, and in the groups of the alkali and alkaline-earth metals it increases as the atomic weight increases. The limiting value of the canal-ray energy is the same for different compounds of a given metal.

The absence of the Doppler effect on examination of the emitted light rays indicates that the particles which are the source of the luminosity are projected with velocities which are very much smaller than those of the exciting canal rays.

Other experiments show that the pulverising action of the rays is not in any way connected with the emission of the series lines, and also that the thickness of the luminous gas layer can be increased or diminished by the application of an electric field with its lines of force at right angles to the surface of the metallic compound under investigation.

To explain the observations, it is supposed that the impact of the high-speed canal rays with the atoms of the metal leads to the emission of slowly-moving metal ions from the solid surface. The luminosity is due to the vibrations set up in the metal ions by the impact. The intensity of the emission gradually diminishes as the distance traversed increases, and the later stages of the motion of the ions are not characterised by any luminous effect. The emission of the series lines is conditioned by the non-absorption of rays of these frequencies by the solid surface. If such absorption occurs, the energy corresponding with the luminous emission is abstracted from the metal ions before they leave the surface, and in this case, although pulverisa-

tion may take place to a large extent, there will be no accompanying luminous effect. H. M. D.

**Emission of Bands by Solid Metallic Compounds under the Influence of Canal Rays.** JOHANNES STARK and GEORG VON WENDT (*Ann. Physik*, 1912, [iv], 38, 690—695).—In addition to the emission of series lines (compare preceding abstract), it has frequently been observed that the bombardment of metallic compounds by canal rays leads to the emission of banded spectra. The seat of this luminous effect is not confined to the part of the surface of the compound which is directly acted on by the canal rays, but extends considerably beyond this region. The banded emission is supposed to be due to the absorption of the light energy of the carriers, which are excited by the canal rays, by the molecules of the metallic compound. The phenomenon is therefore of the nature of a fluorescence effect.

As in the case of the series emission, there appears to be a limiting value of the speed of the canal rays which must be attained before banded emission takes place. This limiting value depends on the nature of the metal, and in the substances examined was found to correspond with cathode falls of potential varying from 500 to 1100 volts.

Since the metallic compounds which show the banded emission are not excited by light of wave-length exceeding  $\lambda = 300\mu\mu$ , it follows that the light which is absorbed by the compound as the result of the canal ray impact, and the absorption of which gives rise to the bands, must be of smaller wave-length than this. From this it would appear that such compounds are characterised by absorption bands in the remote ultraviolet and that the long-waved fluorescence bands in the visible spectrum are coupled with short-waved bands in the ultraviolet.

It is possible that the absorption of the light emitted by the carriers excited by the canal rays is not due to molecules of the compound, but to foreign molecules due to the presence of traces of impurities. Otherwise it is necessary to assume that the absorptive power of the compound itself must be very limited, for the region from which banded emission is observed extends far beyond that which is directly subjected to the impact of the canal rays. H. M. D.

**Ionisation of Gases by Light and the Spark Spectrum of Aluminium in the Schumann Region.** THEODORE LYMAN (*Physikal. Zeitsch.*, 1912, 13, 583—584).—In reference to the question of the ionising efficiency of light from different sources, the author has compared the ultraviolet spectra obtained from the spark discharge between aluminium electrodes in air and hydrogen with that from the tube discharge in hydrogen at a pressure of about 2 mm.

The photographic records show that the discharge through a hydrogen tube gives a very much larger number of short-waved lines than the aluminium spark in air, and is therefore to be preferred as a source of ultraviolet light in experiments on the ionisation of gases. Whereas the light energy appears to be nearly uniformly distributed in the region from  $\lambda = 1300$  to  $\lambda = 1600$  in the case of the hydrogen

spectrum, the aluminium spark spectrum shows only a few strong lines in this region.  
H. M. D.

**The Law of the Ionising Ranges of the Successive Radiations of Radioactive Substances.** F. BUTAVAND (*Le Radium*, 1912, 9, 203—205).—The atom conceived by Sir J. J. Thomson is assumed, and it is supposed that on disintegration the external ring of electrons is broken suddenly and some of them condense into a secondary atom, which leaves the primary at the tangential velocity at which the ring was moving. It is supposed that for each  $\alpha$ -particle, 6 electrons, and for each  $\beta$ -particle, 1 electron, are involved, and that the speeds within the atom obey the third law of Kepler as in the solar system. The ranges of the  $\alpha$ -rays expelled in successive changes multiplied by the number of electrons remaining in the external ring should remain constant. Out of 17 products emitting  $\alpha$ -rays, 12 obey this law and 5 do not.  
F. S.

**The Existence of Chemical Compounds of Short-lived Radioactive Elements.** HANS SCHRADER (*Phil. Mag.*, 1912, [vi], 24, 125—134).—Actinium-*B* was deposited on a platinum wire, which was then clamped between terminals and heated to various temperatures in a vacuum. Volatilisation commenced at 600°, and was nearly complete at 900°. The wire before heating was then exposed to the action of various gases or vapours. Hydrogen chloride did not affect the volatility of the radioactive material when the wire was subsequently heated, but bromine increased the amount volatilised, in one case from 18% to 77% at 675°. The same effect was observed when the active material was deposited on quartz instead of platinum. Chlorine and hydrogen iodide also had a similar effect. After exposure to hydrogen chloride an increase occurs in the amount of actinium-*B* dissolved from a platinum plate by water, although hardly any actinium-*C* is so dissolved.

To avoid effects due to the nature of the surface, experiments were carried out in which the volatilised material was condensed on surfaces at definite temperatures. A long, vertical quartz tube, heated at the bottom above 900°, was arranged to have a gradient of diminishing temperature upwards from the bottom, and a strip of mica was inserted into the tube. On dropping to the bottom a wire made strongly active with actinium-*B*, volatilisation occurred, followed by condensation at definite points on the mica strip. In air, condensation on the mica occurred mostly at places heated above 1000°, although volatilisation commences in a vacuum at 600°. In hydrogen the maximum amount of actinium-*B* was deposited at a temperature between 615° and 675°, whilst with thorium-*B* and -*C* the *B*-member was deposited almost pure on the hotter, the *C*-member on the cooler, parts of the strip. The explanation is advanced that in presence of air the active material forms compounds which are less volatile, whilst in hydrogen the active material may be the element itself, which is in agreement with the behaviour of the common metals and their oxides, the latter being usually less volatile than the former.

F. S.

**The Volatility of Radium-C.** ALEXANDER S. RUSSELL (*Phil. Mag.*, 1912, [vi], 24, 134—137).—Makower has shown that radium-A, -B, and -C cannot remain on a platinum surface heated in air to 900°, 600°, and 1200° respectively. On the other hand, in a sealed quartz tube containing radium emanation with an excess of hydrogen, radium-A, -B, and -C were found completely to volatilise at 650°. The difference is explained by Schrader's results (preceding abstract). In an atmosphere containing radium emanation and oxygen no volatilisation of radium-C occurred from a quartz surface at 1200°, whereas the -A, -B, and -C members are all non-volatile below 700°. In hydrogen it was found that radium-C commences to volatilise in considerable amount at 360°. There is thus a difference of 800° in the volatilisation points of a substance present only to the extent of  $7 \times 10^{-10}$  gram, and this can only be explained by supposing that two different compounds of radium-C are present in the two atmospheres.

F. S.

**Transformation Constant of Radium-D.** PAOLO ROSSI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 462—467).—Measurements of the diminution in activity of Vesuvian cotunnite activated by radium-D indicates that the period of half transformation of the latter does not differ widely from seventeen years.

T. H. P.

**Determination of Radium in Minerals and Rocks.** ERICH EBLER (*Zeitsch. Elektrochem.*, 1912, 18, 532—535).—The usual methods of determining radium are not quite suitable for determining the radium content of rocks and ores. A modified method, which gives good results, is as follows. A weighed amount of the material is fused in order to free it completely from emanation; it is then transferred to a quartz tube connected with a mercury pump, kept for a definite time until emanation has again collected, again fused, the emanation pumped off, transferred to an ionisation chamber, and the activity determined by measurement of the saturation current in the usual way.

G. S.

**The Disintegration Scheme of the Active Deposit of Thorium.** LISE MEITNER (*Physikal. Zeitsch.*, 1912, 13, 623—626).—New experiments have shown that thorium- $C_1$  and thorium- $C_2$  (these names refer to the two  $\alpha$ -ray giving members of the thorium active deposit, which give  $\alpha$ -rays of ranges respectively 4.8 and 8.6 cms. of air) are in different branches of the disintegration series, and that, not both, but one only (probably thorium- $C_1$ ) produce thorium-D. A partial separation of the two C-members has been effected. Thorium-B is obtained pure by evaporating the slightly acid solution of the active deposit to dryness after boiling it first with nickel foil, and the  $\alpha$ - and  $\gamma$ -radiations from this preparation increase with time similarly, the curves running parallel. But if before treatment with nickel, stannous chloride is added to the solution, the  $\alpha$ -rays from the evaporated solution increase much less than the  $\gamma$ -rays, and attain their maximum somewhat earlier. The range of the  $\alpha$ -rays of thorium- $C_2$  shows that the period must be of the order of  $10^{-12}$  second, so that the non-

parallelism of the  $\alpha$ - and  $\gamma$ -curves shows that the two *C*-members cannot stand in direct genetic connexion, and that thorium-*D* (the  $\gamma$ -ray member) cannot be the product of both, for then the  $\alpha$ - and  $\gamma$ -curves must necessarily be practically parallel. When stannous chloride is added, at least part of that one of the two *C*-members which does not give thorium-*D* must remain in solution instead of being precipitated by the nickel.

Other experiments are indicated in which, from the solution containing stannous chloride, part of the thorium-*B* and that *C*-member not giving thorium-*D* are precipitated. The solution, after evaporation, showed a steady fall of  $\alpha$ -rays for several hours at a rate somewhat less than the sixty minute, but much faster than the 10.6 hours, half-periods, whilst the  $\gamma$ -rays increase for several hours to more than double the initial value. After five hours both activities decay with the 10.6 hours period. F. S.

**The Radioactivity of Rubidium and Potassium Compounds.** ERNST H. BÜCHNER (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 22—26).—Of each of the three salts of rubidium, the chloride, sulphate, and nitrate, two samples were taken, the one of which had been kept in the dark for four or five months, and the other had been exposed to broad daylight. No difference in their action on photographic plates, due to exposure to light, was observed. The action was strongest with the chloride and weakest with the sulphate. Attempts to detect an  $\alpha$ -radiation from potassium and rubidium chlorides were unsuccessful. No scintillations could be observed when these substances were mixed with zinc sulphide and examined in the dark under the microscope. No difference of temperature was observed between two quantities, each about 2 kilograms, of sodium and potassium chlorides respectively contained in two vacuum flasks and immersed in a calorimeter surrounded with ice. The thermocouple employed could have detected a difference of 0.001°. F. S.

**Apparatus for the Determination of the Radioactivity of Springs.** FERDINAND HENRICH and FRITZ GLASER (*Zeitsch. angew. Chem.*, 1912, 25, 1224—1225).—A reply to Loewenthal (this vol., ii, 417). The factor used for correction is erroneous, as the quantity of emanation remaining dissolved in the water is already allowed for. A comparison of the Loewenthal fontaktoscope with that of Engler-Sieveking shows that the former gives distinctly low results. C. H. D.

**Determination of the Fixed Radioactive Elements in the Waters of La Toja and Lérez.** FAUSTINO DÍAZ DE RADA (*Anal. Fis. Quím.*, 1912, 10, 175—179).—Ten litres of the water of La Toja contain  $0.356 \times 10^{-5}$  mg. of radium in solution. One gram of the ferruginous deposit from the Lérez water contains  $0.349 \times 10^{-5}$  mg. of radium. G. D. L.

**The Presence of Uranium in Italian Rocks.** Granites from the Island of Montecristo and Radioactive Tufa from Fiuggi. RAFFAELLE NASINI and F. AGENO (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 689—692. Compare Millosevich, this vol., ii, 569; and Nasini and Levi, *Abstr.*, 1910, ii, 1026).—Only slight radioactivity has been

observed in the granites from Montecristo. Small quantities of uranium mica are present. Uranium is present in the highly radioactive tufa of Fiuggi.

C. H. D.

**The After-luminosity of Electric Discharge in Hydrogen Observed by Hertz.** (Hon.) ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1912, A, 86, 529—533).—The blue after-luminosity, first observed by Hertz in the passage of the jar discharge through hydrogen, has been found to be due to the presence of traces of sulphur in the gas. The glow is of very short duration, and its spectrum is identical with that obtained when active nitrogen is passed over heated sulphur. If the discharge tube is provided with an annexe and this is cooled in liquid air, the hydrogen sulphide (or other sulphur compound) is condensed, and the glow disappears after a very short time. On removing the liquid air, the glow is restored with the original brilliancy.

Special experiments have shown that the blue glow is not dependent on the presence of nitrogen, and the spectrum is therefore attributed to sulphur, although it cannot be obtained in sulphur vapour alone. It is probable that the luminosity is due to the combination of sulphur and hydrogen, and if this is the case, the sulphur must be in the form of a chemically active modification after it leaves the charge.

Similar after-glow effects are obtained in the discharge through hydrogen in presence of selenium and tellurium, but no result is obtained with arsenic.

H. M. D.

**Distribution of the Light in the Stratified Discharge in Vapours of the Alkali Metals.** JAKOB KUNZ and JAKOB G. KEMP (*Physikal. Zeitsch.*, 1912, 13, 594—595).—When a little hydrogen is admitted into a discharge tube containing potassium vapour, it is possible to obtain stratified discharge, and on examination of the luminous layers it is found that these are blue towards the cathode end and violet towards the anode. With a tube containing the liquid alloy of sodium and potassium, the strata obtained each exhibit a succession of colours, yellow, red, blue, and violet, from the cathode to the anode end. When the temperature is raised sufficiently, the same tubes show only yellow layers of luminosity, in which no separation can be detected. The distribution of the colours in the strata is discussed in reference to Planck's theory of radiation.

H. M. D.

**Absorption in Geissler Tubes and Allied Phenomena.** B. HONGSON (*Physikal. Zeitsch.*, 1912, 13, 595—609).—The author has investigated the diminution in pressure which occurs on continued passage of the current through a discharge tube. In the case of a tube containing nitrogen and fitted with aluminium electrodes, the quantity of gas absorbed per coulomb increases as the pressure diminishes. If  $p$  represents the mean pressure during one of the periods of observation,  $d$  the reduction in pressure per coulomb, and  $v$  the volume of the discharge tube, then the data show that  $p.d.v.$  remains constant.

Experiments with various metallic electrodes and tubes containing hydrogen, oxygen, nitrogen, and helium show that, in general, the

relationships involved are more complicated than in the case of nitrogen and aluminium electrodes. The product *p.d.v.* varies considerably with the mean pressure during discharge, and abnormally high values are frequently obtained at the commencement of a series of measurements. The actual behaviour in the various cases examined is shown by a series of curves in which the gas pressure is plotted as a function of the quantity of electricity which has been passed through the tubes.

It is supposed that gas is present in the electrodes in two different conditions, namely, condensed in the surface layer and occluded throughout the mass of the electrodes. These are in equilibrium with one another, but since the passage of the discharge causes the evolution of gas at the cathode and absorption at the anode, the equilibrium is disturbed and the observed changes in pressure in the tube are dependent on the rate of emission and absorption, and also on the time factor involved in the re-adjustment of the equilibrium between the condensed and occluded gas. When the rate at which the gas is emitted by the cathode is greater than that of the absorption at the anode, the initial period of discharge may be accompanied by a marked increase in pressure.

H. M. D.

**Significance of Maximum Specific Electrical Conductivity in Chemistry.** JOHN GIBSON (*Trans. Roy. Soc. Edinburgh*, 1912, 58, 117—136).—From the consideration of a variety of chemical changes occurring in homogeneous systems, it has been found that a tendency towards increase of specific electrical conductivity represents a common characteristic of such reactions, the tendency being measured by the magnitude of  $(K_{max} - K)$ , where  $K$  is the actual and  $K_{max}$  the maximum value of the specific conductivity of the system. The apparent existence of this general tendency leads to the enunciation of the hypothesis that homogeneous chemical systems, in which a reaction occurs either spontaneously or under the influence of light, are transformed in such a way that the specific electrical conductivity is increased, unless this tendency is counteracted by the operation of stronger chemical affinities.

By way of illustration, the behaviour of aqueous hydrochloric acid solutions may be considered. If the conductivity of such solutions is plotted as a function of the concentration, a curve is obtained which has a maximum at about 18%. Solutions less concentrated than this are termed premaximal, those more concentrated, ultramaximal, and it is shown that the chemical properties vary in a marked manner according to whether the one group or the other is involved. In premaximal solutions, the acid is very stable, but in ultramaximal it is readily oxidised and behaves as a reducing agent. In premaximal solutions it favours hydrolysis, whilst in ultramaximal concentrations it favours the abstraction of water and changes which are accompanied by the formation of water, such as esterification. Characteristic of all these processes is the tendency to increase in specific conductivity.

Saturated solutions of certain chlorides may be used as indicators of this tendency, for if small quantities are added to hydrochloric acid solutions, it is found that precipitation occurs only when the concentration of the acid solution is ultramaximal. A difference of  $\pm 1\%$

may be thus recognised, precipitation not being observed with 17% acid, but invariably so with 19%.

In respect of the tendency towards increase in specific conductivity, the following chemical changes are considered more closely: the behaviour of aqueous hydrochloric acid towards dissolved oxygen and chlorine; its oxidation by chromic acid, and its behaviour as an esterifying agent; the action of hydrochloric acid on acetaldehyde, aldol and crotonaldehyde, and on solutions of cobalt chloride; the reaction between hydrogen sulphide and iodine in aqueous solution; the decomposition of aqueous nitric acid under the influence of light, and the action of aqueous sulphuric acid on sucrose and on formic acid. The changes occurring in these different systems are all in accordance with the above generalised statement, and the author considers that it probably holds for all homogeneous systems.

In the concluding section, its application to the complex changes of plant and animal chemistry is considered, and various observations consistent with the validity of the hypothesis are noted.

H. M. D.

**Electrical and Mechanical Displacement Surfaces in Metals.** JOHANNES STARK (*Physikal. Zeitsch.*, 1912, 13, 585—589).—The author's theory of the nature of electrical conduction in metals (compare this vol., ii, 621) is further discussed, and attention directed to the probable existence of a connexion between the electrical conducting power of a metal and its tendency to flow under the influence of mechanical stress. This is to be expected, since the electrical conductivity is determined by the circumstance that the valence electrons are situated on the electrical displacement surfaces, whilst by serving as the units which bind together the positive spheres of surrounding molecules, the electrons determine the cohesion.

Observations are cited which appear to support the view that the two properties are related in the manner anticipated by the theory.

H. M. D.

**The Electrical Properties of Copper-Tin Alloys.** R. LEDOUX (*Compt. rend.*, 1912, 155, 35—37).—The author has made a number of electrical and thermo-electrical measurements on copper-tin alloys, using some twenty rods, each 10 cms. long and 5 mm. in diameter. The results and curves, which are set out, confirm those obtained by the study of other physical properties. Several of the curves indicate a singular point corresponding with an alloy  $\text{Cu}_4\text{Sn}$ .

W. G.

**Conductivity of Solid Mixtures of Salts.** MAX LE BLANC (*Zeitsch. Elektrochem.*, 1912, 18, 549—552).—The conductivity of the fluorides of lead, potassium and barium, and of lead fluoride containing 2% and 5% of potassium fluoride and 3% of barium fluoride respectively has been measured at 18°. The salts and mixtures were pressed into pastilles, and great care was taken in removing moisture. The results were only moderately satisfactory, as the treatment of the salt before measurement has considerable influence. The conductivity of lead fluoride is doubled by the addition of 5% of barium fluoride,

and becomes about five times as great by the addition of 5% of potassium fluoride. These increases are much smaller than those found by Fritsch (compare Abstr., 1897, ii, 301) under similar conditions. They may be due to the effect of the additions in bringing lead fluoride nearer to its melting point, and thus causing a diminution of viscosity.

G. S.

**Physico-chemical Investigation of Soft Soap.** FRANZ GOLDSCHMIDT and L. WEISSMANN (*Zeitsch. Elektrochem.*, 1912, 18, 380—396. Compare Farrow, Trans., 1912, 101, 347; McBain and Taylor, Abstr., 1911, i, 349).—The dependence of the viscosity and electrical conductivity of soap solutions on concentration and temperature was investigated. In most of the experiments, a soap made from potassium hydroxide and a mixture of fatty acids from palm oil was used.

The viscosity of a soap solution increases with concentration more rapidly than does an electrolyte solution; the temperature-coefficient of the viscosity does not differ much from that of normal electrolytes. The addition of potassium hydroxide or chloride in small concentration lowers, in large concentration enormously increases, the viscosity; above a certain concentration these substances enormously increase the temperature-coefficient of viscosity.

The results obtained for the variation of the conductivity of soap solutions with dilution exactly correspond with those obtained by McBain and Taylor (*loc. cit.*). In the presence of electrolytes the conductivity is smaller than the sum of the conductivities of the constituents, and with high concentrations of alkali the conductivity is less than for alkali solutions of the same concentration in the absence of soap.

In explanation of the effect of electrolytes, it is suggested that they continuously alter the state of the soap in solution as the electrolyte concentration is progressively increased. In dilute solution they diminish the hydrolysis and degree of dissociation of the potassium salts of the fatty acids, and in higher electrolyte concentration the soap is largely present as a hydrophil colloid (similar to gelatin).

G. S.

**Electric Potential of Cyanogen Iodide.** LAURA KOVÁČH (*Zeitsch. physikal. Chem.*, 1912, 80, 107—116).—An attempt was first made to determine the potential of cyanogen iodide by measuring the *E.M.F.* of a cell, one electrode of which was in contact with an equilibrium solution of cyanogen iodide, potassium iodide and cyanide, and free iodine. No satisfactory results were obtained, however, owing to hydrolysis of cyanogen iodide. The object of the investigation was then attained indirectly by equilibrium and potential measurements of the system  $\text{HI} + \text{ICN} \rightleftharpoons \text{HCN} + \text{I}_2$ . The equilibrium constant  $k_3 = [\text{HCN}][\text{I}_2]/[\text{ICN}][\text{H}^+][\text{I}^-]$  at 25° is 1.37, and the constant  $k = [\text{I}_2][\text{CN}^-]/[\text{ICN}][\text{I}^-]$  is  $1.37k_2$ , where  $k_2$  is the dissociation constant of hydrogen cyanide. From these data and the potential measurements, the potential,  $\epsilon_0$ , of the cyanogen iodide electrode at 25°, as defined by the equation  $\pi = \epsilon_0 + RT/2F \cdot \log [\text{ICN}]/[\text{I}^-][\text{CN}^-]$ , is  $\epsilon_0 = 0.6087 - RT/2F \cdot \log k_2$ . The potential of the iodine electrode at the same temperature is 0.6048 volt.

G. S.

**Normal and Liquid Potentials of Non-aqueous Solutions.** N. ISGARISCHEFF (*Zeitsch. Elektrochem.*, 1912, 18, 568—573).—As reference electrode, a calomel electrode, in which methyl alcohol was used in place of water, was employed. Its potential was determined by combining it with an ordinary calomel electrode; the *P.D.* at the junction of the aqueous and alcoholic solutions was calculated by means of Henderson's equation (compare Abstr., 1907, ii, 426). The normal potentials of a number of metals in methyl alcohol have been determined by combination with the new calomel electrode in the usual way. The results are as follows:  $\text{Cu} \rightarrow \text{Cu}^{++} = 0.320$ ;  $\text{Cd} \rightarrow \text{Cd}^{++} = -0.40$ ;  $\text{Zn} \rightarrow \text{Zn}^{++} = -0.6013$ ;  $\text{Ag} \rightarrow \text{Ag}^+ = 0.807$ ;  $\text{Ni} \rightarrow \text{Ni}^{++} = -0.247$  to  $+0.20$ . Cadmium, zinc, and especially nickel became passive in methyl alcohol, and this accounts for the rapid change in potential of the latter metal. G. S.

**The Isoelectric Point of Gelatin.** LEONOR MICHAELIS and W. GRINEFF (*Biochem. Zeitsch.*, 1912, 41, 373—374).—The isoelectric point, determined by the electrical cataphoresis method, lies between  $[\text{H}^+] = 1.6 \times 10^{-5}$  and  $3.5 \times 10^{-5}$ ; the mean of which is  $[\text{H}^+] = 2.5 \times 10^{-5}$ , which agrees well with that of the imbibition minimum as determined by Chiari. S. B. S.

**Electro-osmosis.** J. O. WAKELIN, BARRATT and ALBERT B. HARRIS (*Biochem. J.*, 1912, 6, 315—332. Compare this vol., ii, 420).—The media in which electro-osmosis was studied were of three kinds: (1) porous plugs of filter paper, cotton wool, naphthalene, or sulphur enclosed in glass tubes; (2) colloids in the form of hydrogel or colloidal solid; (3) living tissues. The results obtained with colloids have already been published (*loc. cit.*). The degree of osmosis is considerably greater in aqueous than in alcoholic solution under the same conditions.

For observations on living tissues, the human forearm was used, the tissues being emptied of blood as far as possible by the use of bandages. The extent of osmosis was estimated from the movement of the meniscus in a narrow tube attached to the upper part of a glass bowl, the mouth of which was applied to the skin. The direction of osmosis was from anode to cathode; the amount transported was about 11.9 c.mm. per hour per sq. cm. of surface of skin for a potential gradient of 1 volt per cm. The results will be described in a later communication. In similar experiments with non-living materials, the transport of dissolved dextrose through a bulb packed with filter paper and of iodine through a thin diaphragm of gelatine was demonstrated. G. S.

**Dielectric Constants of Liquid Mixtures of Non-associated Organic Solvents.** DIMITRI K. DOBROSERDOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 679—760. Compare Abstr., 1910, ii, 94; 1911, ii, 458).—The author has investigated the dielectric constants, specific gravities, and refractive indices of a number of binary mixtures, in various proportions, of non-associated organic solvents. According to the form of the curve expressing the dielectric constant

in relation to the compositions of the mixtures, the latter are divided into three groups: (A) Benzene and ether; carbon tetrachloride and carbon disulphide; carbon disulphide and ether; toluene and carbon disulphide; carbon tetrachloride and *m*-xylene; ether and ethylene bromide; ethylene bromide and chloroform; heptane and toluene; ethyl amyl ether and chlorobenzene. (B) Ether and chloroform; carbon tetrachloride and ether; ether and  $\alpha$ -bromonaphthalene; ethyl amyl ether and chloroform; carbon tetrachloride and ethyl amyl ether. (C) Carbon disulphide and bromobenzene; benzene and chloroform; carbon disulphide and chloroform; carbon tetrachloride and chloroform; pentane and ether; pentane and chloroform; carbon disulphide and ethylene bromide; benzene and ethylene bromide; carbon tetrachloride and ethylene bromide; heptane and ethylene bromide; heptane and carbon disulphide; heptane and  $\alpha$ -bromonaphthalene; heptane and chlorobenzene; benzene and bromobenzene; amylene and chloroform; amylene and ethylene bromide; *m*-xylene and chlorobenzene; heptane and chloroform. In group (A), the dielectric constant curve is a straight line, whilst in (B) it is concave, and in (C) convex towards the axis of concentrations.

None of the formulæ as yet proposed for the dielectric properties of solutions agrees with all the results obtained, and none of the views advanced of the cause of the abnormal behaviour of certain solutions are satisfactory. For the nine mixtures of group (A), Silberstein's formula,  $K = (V_1 K_1 + V_2 K_2) / (V_1 + V_2)$ , when corrected for the change of volume occurring on mixing the solvents, is satisfied, so that the dielectric constants are additive with respect to the volumes of the components. In certain cases the results are in agreement with Bouty's empirical formula,  $K = (m_1 K_1 + m_2 K_2) / (m_1 + m_2)$ , where  $m_1$  and  $m_2$  represent the weights of the two constituents; but this is only occasional.

The abnormal results are explainable on the assumption of chemical combination between the two solvents of a mixture. In some cases evidence of such combination is afforded by heat effects on mixing the solvents.  
T. H. P.

**Vapour Pressure Lines of Binary Systems with Widely Divergent Values of the Vapour Pressures of the Components.** PHILIPP KOHNSTAMM and J. R. KATZ (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 96—113).—The general character of the vapour pressure lines of binary systems is discussed for the case in which the two components have widely divergent vapour pressures. The data for substances of limited imbibition capacity, such as inulin and casein, are shown to be in accord with theoretical requirements. For systems of this kind, it is found that van't Hoff's vapour pressure formula does not hold even in the case of very dilute solutions. The volume contraction and the heat of mixing are also examined from the point of view of van der Waals' theory.  
H. M. D.

**Solvents with Small Dielectric Constants.** AL. N. SACHANOFF (*Zeitsch. physikal. Chem.*, 1912, 80, 13—19).—From a consideration of the available experimental data it is shown that the solvents in which

a diminution of molar conductivity with increasing dilution is observed have all small dielectric constants and slight dissociating power. Important deviations from the Nernst-Thomson rule are also observed only for solvents with small dielectric constants. G. S.

**Finely Divided Metals.** VOLKMAR KOHLSCHÜTTER and ALFRED NOLL (*Zeitsch. Elektrochem.*, 1912, 18, 419—428).—Silver cathodes were electrically dispersed in hydrogen, nitrogen, and argon at low pressures, and the resulting metallic layers were examined microscopically and their electrical resistance determined. It was found that the metal was most finely divided in argon, and that the particles were largest in hydrogen. After a time the particles undergo a kind of condensation to form larger particles, and if the metallic layer is very thin, the final result of this change is a rupture of the layer.

The electrical measurements show that from hydrogen through nitrogen to argon increasing amounts of the metal are necessary in order to obtain the same resistance, and, further, the deposits soon undergo a spontaneous change leading to a greatly diminished resistance. This diminution of the resistance can be greatly retarded by a high pressure of gas.

Even at 100° the finely divided silver undergoes oxidation in the air, and the action is the more vigorous the more finely divided the silver. G. S.

**Electrodes of the Third Kind (Correction).** JAMES F. SPENCER (*Zeitsch. physikal. Chem.*, 1912, 80, 125—127. Compare Abstr., 1911, ii, 364).—Owing to a mistake in the signs of the potentials, the formulæ and results given in the previous paper require correction. The formula for the  $P.D$  at a thallium electrode now becomes  $\epsilon = EP + RT/nF \log(c + 0.00487)$  instead of that previously given. The mean of a series of determinations gives for  $EP$  the value 0.4194 volt (referred to the hydrogen electrode as zero), so that the concentration of thallium ions is given by the expression  $E = 0.4194 + 0.0595 \log(c + 0.00487)$  from measurements of electrodes of the following type:  $Hg \cdot HgI, TlI \cdot Tl \mid N/10$ -calomel electrode.

G. S.

**Electro-affinity and Complex Formation as Factors of Electrolytic Dissociation.** AL. N. SACHANOFF (*Zeitsch. physikal. Chem.*, 1912, 80, 20—28. Compare previous abstract).—Electrolytic dissociation does not depend solely on the magnitude of the dielectric constant of the solvent, but also on the formation of solvates and complex ions. The formation of such ions favours electrolytic dissociation, because the electro-affinity of these ions is greater than that of the primary ions. In solvents with small dielectric constants, only complexes which yield ions of greatly enhanced electro-affinity can undergo electrolytic dissociation. The decomposition of such complexes on dilution explains the diminution of the molar conductivity in such solvents on dilution (compare Steele, McIntosh, and Archibald, Abstr., 1905, ii, 222). On account of the formation of complex ions with increased electro-affinity, the Nernst-Thomson rule is not applicable to solvents with small dielectric constants. G. S.

**Electrolysis of Fused Iodine Chloride and Bromide.** LUDWIK BRUNER and E. BEKIER (*Zeitsch. Elektrochem.*, 1912, 18, 368—373).—The specific conductivity of fused iodine bromide at 40°, measured with platinum electrodes, is 0.000302. Both iodine bromide and iodine chloride undergo continuous electrolysis in the fused state between silver electrodes, chlorine and bromine respectively being liberated at the anode (1 equivalent per faraday), whilst iodine is probably the primary product of electrolysis at the cathode. During the electrolysis of iodine chloride the silver electrodes were energetically attacked. G. S.

**Electrolytic Dissociation of Potassium Bromide.** KARL DRUCKER (*Zeitsch. Elektrochem.*, 1912, 18, 562—567).—On the basis of electrical conductivity measurements, it is shown that tribenzyl-methylammonium chloride and bromide, although strong electrolytes, follow Ostwald's dilution law up to a concentration of 0.02 mol. per litre. It was intended to determine the degree of dissociation of potassium bromide from its effect on the distribution of tribenzyl-methylammonium bromide between water and chloroform or bromoform, but the fact that the latter salt is partly polymerised in these solvents rendered the method inapplicable. The object was partly attained by finding the effect of the substituted ammonium bromide, potassium bromide, and a mixture of the two bromides on the *E.M.F.* of a concentration cell with silver bromide as electrode, and the conclusion is drawn that up to 0.02 molar concentration conductivity measurements give accurate results for the degree of dissociation of potassium bromide. The results were complicated by the fact that the complex bromide is adsorbed by silver bromide, as is also potassium bromide to a smaller extent. G. S.

**Apparatus for the Measurement of Transport Numbers.** OSCARRE SCARPA (*Nuovo Cim.*, 1912, [vi], 3, 308—312).—The conditions which should be fulfilled by a satisfactory transport apparatus are given, and two forms of apparatus which satisfy the conditions are described. The first form, which is used when the anode and cathode liquids and that from the central compartment have to be obtained separately, consists of a fairly wide tube of equal bore (diameter 10—20 mm.), bent several times upon itself, and the ends sealed to two wider tubes which form the anode and cathode compartments respectively. The final apparatus has the form of two inverted U-tubes, the inner limbs of which are in communication at the base, and the outer limbs bent upwards at the base and sealed to the wider vertical tubes. Two narrow vertical glass tubes,  $R_1$  and  $R_2$ , are sealed to the tops of the U-tubes; they coalesce at some distance above to a single tube, which can be closed by a tap. At the base of the central tube, where the inner limbs of the U-tubes join, is sealed a narrow glass tube,  $S$ , which is bent vertically. The apparatus is filled in such a way that the liquid partly fills the bases of the tubes  $R_1$  and  $R_2$ , and the tap is closed. After the electrolysis, the tap is opened and the solution in the tubes descends and separates the contents of the apparatus into three parts, the anode, cathode, and central solutions,

which can be removed separately, the central liquid being obtained through  $S$  by blowing through the single tube connecting  $R_1$  and  $R_2$  at the top.

The second apparatus consists of an inverted U-tube with the outer limbs bent round vertically, and rising above the top of the U-tube. To the upper part of the latter is sealed a narrow vertical tube provided with a tap. G. S.

**Influence of Pressure on the Position of Liquid Metals in the Thermo-electric Series.** ERNST SIEGEL (*Ann. Physik*, 1912, [iv], 38, 588—636).—The influence of pressure on the thermo-electric behaviour of liquid bismuth, tin, and mercury has been examined. In the case of mercury, measurements at temperatures from  $20^\circ$  to  $350^\circ$  show that the pressure effect is not independent of the temperature, but increases at first with rise of temperature and then diminishes. For liquid bismuth and tin, the pressure effects are less than 2% of the value obtained for mercury over the interval  $0$ — $100^\circ$ . The thermo-electrical behaviour of liquid bismuth in its dependence on pressure is therefore very different from that of the solid metal, and it is suggested that the effects in the two cases are not of the same kind.

To facilitate the carrying out of the experiments at the high temperatures necessary in the case of bismuth and tin, the author has devised an electrically heated bath of Wood's metal, by means of which it was possible to maintain the temperature of the thermo-electric junctions constant within  $0.001^\circ$ . H. M. D.

**Magnetic Properties of a Graded Series of Nickel-Manganese Alloys.** JAMES G. GRAY (*Phil. Mag.*, 1912, [vi], 24, 1—14).—The magnetic properties of nickel and of a series of nickel manganese alloys, containing 5, 10 ... to 30% of manganese, have been investigated at the ordinary temperature and at  $-190^\circ$  in the conditions brought about by (1) the process of casting, (2) annealing at  $900^\circ$ , (3) quenching at  $900^\circ$ .

In the case of pure nickel, the effect of cooling is to diminish the susceptibility for low fields and to increase it for high fields. The strength of the field at which the magnetisation curves corresponding with  $15^\circ$  and  $-190^\circ$  cross is greater than 200 C.G.S. units. The effect of adding manganese to nickel is to diminish the susceptibility of the latter. The resulting alloy behaves normally, however, in that the magnetisation curve for  $-190^\circ$  lies initially below and later above the curve for  $15^\circ$ . This behaviour is characteristic of the material in all three conditions.

For the alloys containing 5, 10, and 15% of manganese, the magnetisation curves cross at points corresponding with field intensities of 45, 24, and 14 C.G.S. units respectively in the case of the annealed material, whereas the corresponding values for the quenched alloys are 20, 10 and 7.

The alloy containing 20% manganese has somewhat remarkable magnetic properties. In all three conditions the magnetisation curves for  $15^\circ$  and  $-190^\circ$  cross one another at points corresponding with very small magnetising forces, and the improvement in the magnetic

susceptibility, which is brought about by cooling to  $-190^{\circ}$ , is very large. When an alloy of this composition is quenched at  $900^{\circ}$ , it is non-magnetic at the ordinary temperature, but acquires a marked susceptibility when cooled to  $-190^{\circ}$ .

Alloys containing 25 and 30% manganese are only feebly magnetic in all three conditions. The magnetisation curves cross for very small field intensities.

The magnetic properties of the nickel-manganese alloys are not altered by previous cooling to  $-190^{\circ}$ , and in this respect they differ essentially from the manganese- and nickel-steels. H. M. D.

**Use of the Magnetic Field in Determining Constitution. XVI.** PAUL PASCAL (*Bull. Soc. chim.*, 1912, [iv], 11, 636—640. Compare this vol., ii, 326, 426).—An examination of the magnetic susceptibilities of a number of acetylenic compounds shows that the presence of the treble linking decreases the diamagnetism, the necessary correction in calculating the molecular susceptibilities of such compounds being  $+8 \times 10^{-7}$ . This correction is much less than that for the double linking, namely,  $+57 \times 10^{-7}$ . In the following cases the further corrections necessary are: conjugation of the treble linking with (1) a benzene nucleus,  $-16 \times 10^{-7}$ ; (2) ether oxygen,  $-12.5 \times 10^{-7}$ ; (3) carbonyl oxygen,  $+11 \times 10^{-7}$ ; (4) acid hydrogen, as in phenyl acetylene,  $-12 \times 10^{-7}$ . It is noteworthy that conjugation with the benzene nucleus has an opposite effect to conjugation with carbonyl oxygen, in contradistinction to the effect these conjugations have on the refractometric constants.

If the carbon chain is branched or arylated, the presence of the treble linking prevents the radicals on either side of it affecting each other as far as their magnetic properties are concerned. T. S. P.

**Gravity and the Molecular and Atomic Energy of Gases.** E. LÖW (*Zeitsch. physikal. Chem.*, 1912, 80, 192—205).—Simple mathematical deductions are given of the effect of gravitational attraction on the molecular and atomic energy of diatomic gases, and of the work done by the particles against this attraction. The condition of affairs in a gas column of uniform temperature and of a gas column in connective equilibrium is also considered. Owing to the effects in question, a column of oxygen, which has the absolute temperature  $273^{\circ}$  at the base, is at a temperature of  $261.51^{\circ}$  at a level of 1064.7 metres. In a gas column of maximum density, for which the work of expansion is zero, the conditions are particularly simple. The modifications required to render the equations applicable to monatomic gases are considered. G. S.

**Kinetic Properties of a Molecule in a Substance.** RICHARD D. KLEEMAN (*Phil. Mag.*, 1912, [vi], 24, 101—118).—Since the temperature registered by a thermometer immersed in a perfect gas is unaltered when the gas expands without doing external work, it appears that the temperature indicated is independent of the number of molecules impinging per second on unit area of the surface of the bulb. Since, also, the registered temperature is independent of the

material of the bulb, it follows that this temperature is solely regulated by the velocity of the molecules when free from the action of external forces.

The effect of molecular attraction is to make the molecules approach one another on collision with a greater velocity than they would have if there were no molecular attraction. The average velocity of a molecule may thus be much larger than the minimum velocity which corresponds with its temperature.

In respect of the pressure exerted by the molecules, it is pointed out that the attraction which the walls of the containing vessel exert on a molecule will not affect the magnitude of the change of momentum during collision, and, therefore, the pressure exerted by a molecule will depend only on its minimum, that is, the velocity it possesses when free from the action of external forces. On the basis of these considerations, formulæ are obtained which give the number of molecules passing through one square cm. per sec. General formulæ are also deduced for the coefficient of viscosity, the thermal conductivity, the coefficient of diffusion, and the velocity of sound. H. M. D.

**A Convenient Stirring Thermometer.** A. SCHOLZ (*Chem. Zeit.*, 1912, 36, 541).—A glass stirring rod is attached to a thermometer by two rubber bands, the end of the rod projecting slightly beyond the bulb, or even being bent round so as to protect the bulb.

C. H. D.

**Cryoscopy and Heats of Solution, Fusion, and Vaporisation of cycloHexanol.** ROBERT DE FORCRAND (*Compt. rend.*, 1912, 154, 1767—1770).—Pure cyclohexanol melts at 22·45° (compare this vol., i, 548), but the presence of the merest trace of water is sufficient to lower the melting point. On exposure to the air, even at 10°, the crystals rapidly liquefy, owing to absorption of moisture.

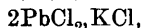
From cryoscopic measurements in which benzene, water, and ethylene dibromide were used respectively as solutes, the molecular depression of the freezing point (of cyclohexanol) is found to be 382·8°. This value is very high, and explains the effect of traces of water on the melting point; 0·1% of water would cause a depression of 2·13°. The heat of fusion is then calculated (by van't Hoff's formula) to be 0·448 Cal. per mol. This value could not be checked by direct experiment; it was determined indirectly, however, by measuring the heat of solution of the solid at 20·33° and of the liquid at 20·33°, and found to be 0·412 Cal. per mol., a sufficiently good agreement.

The boiling point at pressures varying from 555·5—821·5 mm. was also determined, and from the results the molecular heat of vaporisation was found to be 11·657 Cal. Trouton's coefficient is then 26·87, which indicates very marked association, as is the case with other alcohols. T. S. P.

**New Formulæ for Representing the Vapour Pressure of Water Vapour.** P. H. HOFBAUER (*Zeitsch. physikal. Chem.*, 1912, 80, 117—124).—A theoretical paper in which a number of formulæ

for representing the variation of the vapour pressure of water with the temperature are suggested, and are shown to afford a satisfactory representation of the experimental results. Up to  $100^{\circ}$  the following formula holds:  $\log.\log.760/p = 4.08000 + \log.(373 - \theta) - (1 + 1/6.9)(\log.373 + \log.\theta)$ ; for the vapour pressure of ice it has the form  $\log.\log.4.579/p = 1.10270 + \log.(273 - \theta) - (1 + 1/20.7)\log.\theta$ , and for temperatures between  $100^{\circ}$  and  $200^{\circ}$  the following formula is valid:  $\log.\log.p/760 = 1.13558 + \log.(\theta - 373) - (1 + 1/6.9)\log.\theta$ , where  $p$  represents in each case the saturation pressure at the absolute temperature  $\theta$ . Modifications of these formulæ are also suggested. G. S.

**Chemical Affinity. VII. Formation of Double Salts and Double Decomposition.** J. N. BRÖNSTED (*Zeitsch. physikal. Chem.*, 1912, 80, 206—234).—The principles established in a previous paper (compare Abstr., 1911, ii, 381, 856) are now applied to determine the affinity and heat of formation of the double salts,  $\text{CuCl}_2.2\text{KCl}$ ,



and  $\text{PbCl}_2.\text{KCl}.\frac{1}{3}\text{H}_2\text{O}$ . On the basis of these results the affinity and the heat change of the reactions between the chlorides, nitrates, sulphates, and chlorates of sodium and potassium have been obtained.

The complete equilibrium diagram in the system  $\text{KCl}-\text{CuCl}-\text{H}_2\text{O}$  have been established by solubility measurements at  $22^{\circ}$ . Only one double compound,  $\text{CuCl}_2.2\text{KCl}$ , exists under these conditions; it forms fairly large, colourless crystals, fairly stable in the air. The affinity of the reaction  $\text{CuCl} + 2\text{KCl} \rightarrow \text{CuCl}_2.2\text{KCl}$  (all the substances taken in crystalline form) is  $1380 - 1.4t$  cal., and the heat development between  $0^{\circ}$  and  $60^{\circ}$  is 1760 cal.

The equilibrium in the system  $\text{PbCl}_2-\text{KCl}-\text{H}_2\text{O}$  has been determined at  $20^{\circ}$ . Only two compounds,  $2\text{PbCl}_2.\text{KCl}$  and  $\text{PbCl}_2.\text{KCl}.\frac{1}{3}\text{H}_2\text{O}$ , already described by previous observers, exist under these conditions. The affinity and heat of formation of these salts have been obtained by *E.M.F.* measurements in the usual way.

In the determination of the affinity and heat changes in the reactions between alkali salts, only the double lead salts were found suitable. As an illustration of the method, the *E.M.F.* of the changes  $2\text{Pb} + 4\text{HgCl} + \text{KNO}_3 + \text{NaCl} \rightarrow 2\text{PbCl}_2.\text{KCl} + \text{NaNO}_3 + 4\text{Hg}$  and  $2\text{Pb} + 4\text{HgCl} + \text{KClO}_3 + \text{NaCl} \rightarrow 2\text{PbCl}_2.\text{KCl} + \text{NaClO}_3 + \text{Hg}$  were measured, the difference  $\text{KNO}_3 + \text{NaClO}_3 \rightarrow \text{KClO}_3 + \text{NaNO}_3$  being the reaction under investigation. The free energy is positive for the following reactions from left to right:  $\text{KCl} + \text{NaNO}_3 \rightarrow \text{KNO}_3 + \text{NaCl}$ ;  $\text{KCl} + \frac{1}{2}\text{Na}_2\text{SO}_4 \rightarrow \frac{1}{2}\text{K}_2\text{SO}_4 + \text{NaCl}$ ;  $\text{KCl} + \text{NaClO}_3 \rightarrow \text{KClO}_3 + \text{NaCl}$ ;  $\text{KNO}_3 + \frac{1}{2}\text{Na}_2\text{SO}_4 \rightarrow \frac{1}{2}\text{K}_2\text{SO}_4 + \text{NaNO}_3$ ;  $\text{KNO}_3 + \text{NaClO}_3 \rightarrow \text{KClO}_3 + \text{NaNO}_3$ ;  $\frac{1}{2}\text{K}_2\text{SO}_4 + \text{NaClO}_3 \rightarrow \frac{1}{2}\text{Na}_2\text{SO}_4 + \text{KClO}_3$ .

The affinity, temperature-coefficient of the [affinity, and heat development of these six reactions are given, and it is shown that the heat development obtained indirectly as above is, in each case, in good agreement with that determined calorimetrically. G. S.

**Space Formulæ and Heats of Combustion of Acyclic Hydrocarbons.** RUPERTO LOBO GÓMEZ (*Anal. Fis. Quim.*, 1912, 10, 158—166).—The heat of combustion of a hydrocarbon may be

calculated by means of the formulæ: paraffin series,  $157n + 55$ ; olefine series,  $157n + 28$ ; acetylene series,  $157n + 2$ ; diolefine series,  $157n - 39$ ; diacetylene series,  $157n - 91$ ,  $n$  being the number of carbon atoms.  
G. D. L.

**Heat of Solution of Potassium Nitrate at High Temperatures.** M. K. LEVALT-EZERSKY (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 665—677).—By means of a special apparatus the author has measured the integral heat of solution and the heat of dilution of potassium nitrate at  $50^\circ$ ,  $60^\circ$ , and  $70^\circ$ .

The values in cal. of the integral heats of solution for those quantities of the salt which at the given temperatures saturate 1 gram-mol. of water are:  $Q_\sigma = 779$  at  $50^\circ$ , 927 at  $60^\circ$ , and 1126 at  $70^\circ$ , so that not only does the absolute magnitude of  $Q_\sigma$  increase with rise of temperature, but  $dQ_\sigma/dt$  also increases.

The dissolution of 1 gram of the salt in  $p$  grams of water to give a solution having a certain temperature may be effected in two ways: (1) The salt at temperature  $t_1$  is dissolved in water at the same temperature, and the solution then cooled to  $t_2$ ; in this case the heat effect of the process is given by  $Q_{t_1} - \kappa(1+p)(t_1 - t_2)$ , where  $\kappa$  is the specific heat of the solution. (2) The salt and water are cooled separately to  $t_2$  and mixed at this temperature; the heat effect is then expressed by  $Q_{t_2} - (c+p)(t_1 - t_2)$ . Since, in the two instances, the initial and final states are the same, these two heat effects must be equal, and therefore  $Q_{t_1} = Q_{t_2} - [(c+p)/(1+p) - \kappa](1+p)(t_1 - t_2)$ . Here  $(c+p)/(1+p)$  represents the specific heat of the solution calculated as the arithmetic mean of the specific heats of its constituents. If  $\kappa$  is less than  $(c+p)/(1+p)$ , the heat of solution will diminish with rise of temperature;  $p$  may then be an arbitrary number, and the rule will hold for all heats of solution whether initial or integral. Stackelberg (*Abstr.*, 1896, ii, 589) showed that diminution of the integral heat of solution with rise of temperature should be a general phenomenon, and Bindel (*Abstr.*, 1890, 1042), from the results of investigations of supersaturated solutions of a number of salts, arrived at the conclusion that the specific heat is always less than the calculated value, this being also found by Personne (*Ann. Chim. Phys.*, 1856, [iii], 33) to be the case with dilute solutions. The same result is obtained at the high temperatures of the author's experiments.

Measurements of the integral heats of solution of potassium nitrate in a small and constant porportion of water at  $50^\circ$ ,  $60^\circ$ , and  $70^\circ$  show that the diminution of the integral heat of solution with rise of temperature is very slow. Thus, with 1 gram-mol. of the salt in 6.56 gram-mols. of water, the value is 5.11 at  $50^\circ$ , 5.07 at  $60^\circ$ , and 5.00 at  $70^\circ$ . The initial heat of solution, however, diminishes more rapidly with rise of temperature, the value for 1 gram-mol. of the salt in 200 gram-mols. of water being  $-9.22$  Cals. at  $0^\circ$ ,  $-8.52$  at  $18^\circ$ ,  $-7.27$  at  $50^\circ$ , and  $-6.75$  at  $70^\circ$ .

The heat effect of dilution of potassium nitrate solutions diminishes in absolute magnitude with rise of temperature. Thomsen (*Thermochemische Untersuchungen*, Vol. I.), from the results of experiments on the dilution of solutions at  $7-8^\circ$  and at  $24-25^\circ$ , drew the conclusion

that, independently of the sign of the heat effect, the change of the latter with rise of temperature is always negative. This rule is found to hold for solutions of potassium nitrate for the limits of temperature 50—70°.

The magnitude of the integral heat of solution of potassium nitrate, referred to 1 gram-mol. of solvent, increases with rise of temperature, and this may be regarded as typical of salts the solubilities of which increase rapidly as the temperature is raised. T. H. P.

**The Density of Liquids below 0°.** JEAN TIMMERMANS (*Bull. Soc. chim. Belg.*, 1912, 26, 205—215).—The coefficient of expansion below 0° is given for a dozen organic liquids with an accuracy of 1 in 3000. The law of the rectilinear diameter, namely, that the mean of the densities of a liquid and of its saturated vapour is a linear function of the temperature, does not hold absolutely, provided that the observations are extended sufficiently far from the critical temperature. For example, the rectilinear diameter for normal pentane is a straight line between the critical temperature (+197°) and 0°, but curves between 0° and the solidification point (−130°).

No liquids other than water and helium, even including substances which are known to be polymerised, exhibit the phenomenon of a maximum density.

The law of corresponding states as modified by Meyer is applicable even at very low temperatures.

The ratio of the maximum density of a fluid to the critical density is equal to the ratio of the critical density to the theoretical density.

E. F. A.

**Dilatometric Investigation of Certain Synthetic Processes.** GINO GALEOTTI (*Zeitsch. physikal. Chem.*, 1912, 80, 241—250).—In a previous paper (compare Abstr., 1911, ii, 257) it was shown that certain cases of hydrolytic decomposition were accompanied by diminution of volume. It is now shown that certain syntheses, such as the formation of ethyl acetate, ethyl butyrate, butyryn, and olein, are attended by a diminution of volume. The explanation advanced is that the water passing from the substances into the mass of solvent occupies a greater volume in the latter circumstances.

G. S.

**A New Hypothesis Relating to the Nature of Different States of Aggregation and of [Allotropic] Modifications.** LÉON SCHAMES (*Ann. Physik*, 1912, [iv], 38, 830—848).—The view is expressed that every change in the state of aggregation of a substance or in the allotropic form of an element is accompanied by a change in molecular complexity. The transition from the gaseous to the liquid and from the liquid to the solid state is supposed to be attended by a sharp increase in the degree of association. It is shown that various facts can be satisfactorily interpreted in terms of this hypothesis, and the properties of benzene and water, as representing respectively a normal and an anomalous liquid, are more particularly considered. Whereas, according to the author, both liquids consist of associated

molecules, the difference in their physical behaviour is due to the circumstance that the association of benzene is almost independent of the temperature, whereas that of water increases continuously as the temperature decreases. In accordance with this view, a modification of the ordinary molecular surface energy equation (Eötvös-Ramsay) is suggested, and this modified form represents the behaviour of both the so-called normal and associated liquids without any distinction.

Not only is a change in state of aggregation attributable to an alteration in molecular complexity, but the author shows that the change from one allotropic form to another and the development of ferromagnetic properties may also be due to the same cause.

H. M. D.

**Condensation of Metallic Vapours.** VOLKMAR KOHLSCHÜTTER and C. EHLERS (*Zeitsch. Elektrochem.*, 1912, 18, 373—380).—In order to determine how the form in which a metal condenses is influenced by the nature of the indifferent gas with which it is in contact, arsenic, selenium, cadmium, and zinc were slowly sublimed in a vacuum and also in different gases at various pressures, and the deposited metals examined microscopically. It was found that metals which sublime in compact form in a vacuum or in a gas at low pressure are obtained in a more finely divided form the greater the pressure of the gas, and for different gases at equal pressures the state of division is the finer the denser the gas. A possible explanation is that the molecular movements which cause Brownian motion in suspended particles act in opposition to the surface tension and cohesion forces which tend to increase the size of the condensed particles.

The paper is illustrated by a large number of photo-micrographs.

G. S.

**Alteration of Viscosity on Solution.** CARL SCHALL (*Zeitsch. Elektrochem.*, 1912, 18, 500—503. Compare this vol., ii, 434).—The rule enunciated in the previous paper (*loc. cit.*), that in the neighbourhood of the freezing point of the solvent the temperature-coefficient of the viscosity is proportional to the freezing-point depression, is shown to hold for certain classes of aqueous solutions of inorganic salts, more particularly the alkali halides and nitrates. The available data are tabulated in full and represented graphically.

G. S.

**Methods of Determining the Association Factors of Liquids.** DAN TYRER (*Zeitsch. physikal. Chem.*, 1912, 80, 50—66).—All the methods hitherto suggested for determining the degree of association of liquids are unsatisfactory. In particular, the methods depending on surface-tension measurements are untrustworthy, since in all probability the state of the surface layer of a liquid is very different from that of the interior. There are other objections to the well-known Ramsay-Shields method; for instance, the "true critical temperature" is not constant, as assumed, but depends on the complexity of the liquid, which alters with the temperature, the observed critical temperature being the lowest, as it corresponds with the smallest value for the molecular complexity.

The conditions which must be fulfilled by an equation which admits of a satisfactory calculation of the degree of association of a liquid are given. One condition is that all the physical constants in the equation should refer to the main bulk of liquid and not to localised properties, such as surface tension and vapour pressure; they must also be independent of the vapour phase, or refer to a condition in which the influence of the vapour phase can be neglected. The different respects in which the methods hitherto suggested (compare Batschinski, Abstr., 1911, ii, 189; Longinescu, Abstr., 1908, ii, 931; Traube, Abstr., 1896, ii, 153, 411) fail to satisfy the conditions are given. The method of Guye (Abstr., 1893, ii, 204) approximately fulfils all the conditions, but is only applicable at the critical temperature. G. S.

**Surface Tension and Coagulation of Colloidal Systems. Theory of the Action of Poisons, Drugs, and Dyes.** ISIDOR TRAUBE (*Kolloid. Chem. Beihefte*, 1912, 3, 237—336).—It is shown in a very extended series of experiments that there is a close analogy between the action of salts, acids, alkaloids, etc., in diminishing the surface tension and degree of dispersion (leading to coagulation) of solutions of dyes, and that these phenomena throw light on the nature of the action of poisons and drugs. The surface tension was measured by the drop method. No special precautions were taken to purify the dyes.

Dyes vary greatly in respect of their influence on the surface-tension of water. Rhodamine is so active that 1 part in 20,000,000 parts of solution can be detected in this way, whilst salts of sulphonic acids have a comparatively slight influence.

In the case of the basic dyes rhodamine- $\beta$  and malachite-green, the activity of the anions both with reference to coagulation and diminution of the surface tensions of the solutions is in the order:  $I > ClO_3 > NO_3 > Br > Cl$ . On the other hand, the nature of the anion has very little influence on the physical properties of solutions of the acid dyes wool-violet and benzopurpurin- $\beta$ .

Solutions of night-blue (0.2%) and wool-violet-S were very fully investigated. With the first-mentioned solution, a number of salts of the alkalis, such as potassium iodide and nitrate, produce at first increased surface tension, which reaches a maximum and then diminishes as the amount of salt is progressively increased until it reaches that of water, when a further small addition of salt causes precipitation in the previously clear solution. The maximum of surface tension is attained in different concentrations with the different salts; the order of the anions is as follows:  $I, CNS, ClO_4, ClO_3, Br, CN, Cl, OH, F, SO_4, P_2O_7$ , which is closely parallel to the cohesion pressure series, as given by the author (compare Abstr., 1911, ii, 469). As regards the action of salts of the alkaline earths and heavy metals, the cations, with the exception of mercury (the chloride and cyanide were used) have very little effect on night-blue. The order of the activity of acids towards night-blue has also been determined; the effect on the surface tension and degree of dispersion is closely parallel. Organic cations, including poisonous alkaloid salts, and

indifferent substances have very little influence on the physical properties of night-blue. It is pointed out that there is a close parallelism as regards the action of different substances on night-blue and (as regards poisoning effect) on blood and protoplasm.

Just as the basic dye night-blue is chiefly affected by anions, so the nature of the cation is of main importance as regards the acid dye wool-violet-S. Organic bases, including the poisonous alkaloids and their salts, have considerable influence on the physical properties of wool-violet, and the order of their activity is similar to their effect as blood poisons.

Experiments on the effect of different classes of chemical compounds on the surface tension and dispersion of lecithin and soap solutions, blood corpuscles, proteins, etc., are described, and it is shown that the order of activity of different substances is in all cases parallel to that observed for dyes. The poisonous effect of mercuric chloride can be neutralised to some extent by the subsequent addition of potassium iodide. Salvarsan is particular effective as a coagulating agent.

As regards the reciprocal action of different substances, it is shown that alkaloids caused coagulation in approximately the same order as they are coagulated, and for this and other reasons, the conclusion is drawn that the physical action of substances on colloidal systems is the sum of two constants, one depending on the nature of the system, the other on that of the substance.

These considerations are applied to elucidate the nature of the action of poisons and of drugs, and the nature of dyeing. In connexion with drugs, the importance of the fact that cations affect mainly anionic colloids and anions act chiefly on cationic colloids has been insufficiently appreciated.

G. S.

**The Physical Chemistry of the Lipoids. I. The Relationship of dyes to Lipoids.** SIEGFRIED LOEWE (*Biochem. Zeitsch.*, 1912, 42, 150—189)—The distribution was investigated of methylene-blue between an aqueous phase and a chloroform phase, in which various lipoids (cephalin, cerebroside, the other brain lipoids, cholesterol, linseed oil, and thymol) were dissolved. The pigment (methylene-blue) was estimated in the aqueous phase by precipitation with crystal-Ponceau, according to a method originally suggested by Pelet and Garuti. The two phases were left in contact until equilibrium was established, shaking being dispensed with owing to the formation of permanent emulsions. Several days were necessary to attain equilibrium. The concentration of the dye in water and of the lipid in chloroform was varied in the different experiments. The distribution of the dye does not obey Henry's law. In the majority of cases it appears to follow the exponential equation of an adsorption phenomenon. Nevertheless, the various lipoids behave differently in this respect, in some cases the amount of dye depending on the concentration of the lipid in chloroform, and in other cases being independent of this factor. The author suggests the division of the various lipoids into four groups according to their behaviour as regards the distribution of dyes.

S. B. S.

**The Physical Chemistry of the Lipoids. II. Relationship of Lipoids to Other Organic Substances (Narcotics, Hypnotics, etc.).** SIEGFRIED LOEWE (*Biochem. Zeitsch.*, 1912, 42, 190—204).—The author draws the conclusion, from a re-examination of Baum's numbers on the distribution of sulphonal, trional, and tetrional between olive oil and an aqueous phase, that the process is one of adsorption of the narcotic by oil, in which the exponent is greater than 1. The adsorption of chloral hydrate by cholesterol is so small that the process can play no essential part in the organism. From his own experiments, the author draws the conclusion that the attachments of chloroform by the white matter and of nicotine by both white and grey matters of the brain are adsorptive processes, as are also the combinations of tetanus toxin with brain and lipoids.

S. B. S.

**The Physical Chemistry of Lipoids. III. Diffusion into Lipoids.** SIEGFRIED LOEWE (*Biochem. Zeitsch.*, 1912, 42, 205—206).—In confirmation of the statements that lipoids do not act as true solvents, but rather as adsorbents, the author shows that nicotine does not diffuse through layers of cephalin (not dissolved in a solvent), or methylene-blue through lipoids.

S. B. S.

**The Physical Chemistry of Lipoids. IV. The Properties of Lipoid Solutions in Organic Solvents.** SIEGFRIED LOEWE (*Biochem. Zeitsch.*, 1912, 42, 207—218).—In contrast to other lipoids, cholesterol raises the surface tension of chloroform; the other lipoids depress it. The influence of solution of lipoids on the vapour pressure of organic solvents was investigated by Barger's microscopic method. From the results, the conclusion is drawn that cholesterol, of all the lipoids investigated, is the only one in true solution in all organic solvents investigated; phrenosin appears to form a true solution in alcohol, but not in chloroform. The solutions of all, even of cholesterol, are optically non-homogeneous. The author finally summarises his results, from which he draws the conclusion that the lipoids behave, generally, as colloids. Their attachment to narcotics, dyes, etc., is not a linear function of the concentration of the latter in water, but agrees rather with the exponential equation proposed by Freundlich for adsorption phenomena.

S. B. S.

**Adsorption.** KNUD ESTRUP (*Oversigt K. Danske Vidensk. Selsk. Forh.* 1912, No. 2, 127—151).—The chief adsorbent used by the author was blood charcoal, and in order to determine whether it was pure enough for use the following method, which is of general application, was used. The adsorption of iodic acid both with respect to hydron and iodate-ion was investigated; if both ions are adsorbed to the same extent, the adsorbent contains neither alkali nor acid, and can be taken as pure. Neither bone charcoal nor sugar charcoal was found to be pure enough, whilst Merck's blood charcoal gave satisfactory results.

Investigations of mixtures, the components of which do not interact chemically, confirmed already known results, that the adsorption of each component is diminished by the presence of the other. The

mixtures used were: potassium hydroxide and potassium iodate, potassium hydroxide and propyl alcohol, potassium hydroxide and amyl alcohol, cadmium iodide and acetone, iodic acid and succinic acid. In the case of mixtures containing potassium iodate, in which the components react chemically or affect each other's dissociation, the adsorption of the iodate ion is increased by successive additions of an organic acid (acetic or succinic acid). The adsorption constant  $1/n$  in the adsorption isotherm  $x/m = ac^{1/n}$ , remains practically constant, whilst  $a$  increases with the concentration of the acid. The system, potassium iodate and malonic acid, gave anomalous results, owing to chemical action taking place with evolution of carbon dioxide.

Measurements are given of the adsorption of potassium iodate by blood charcoal in the simultaneous presence of two other components, namely, (a) oxalic and succinic acids, (b) acetone and ethyl ether.

T. S. P.

**Adsorption. V. Adsorption by Starch of Substances Soluble in Water.** ADAM W. RAKOWSKI (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 586—605. Compare Abstr., 1911, ii, 470, 471; this vol., ii, 237).—Inorganic and organic acids and salts are adsorbed, either not at all or but slightly, by starch in an aqueous medium; ammonium hydroxide is adsorbed to a small extent. Starch exhibits marked adsorptive properties towards alkalis in aqueous solution, hydroxides of heavy metals in aqueous-ammoniacal solutions, and basic colouring matters. The phenomena of adsorption by starch of substances dissolved in water clearly reveal the chemical nature of the adsorption, which consists of two processes of undetermined character. Calculation of the experimental results by the ordinary adsorption formula,  $c_2 = \beta c_1^{1/p}$ , show that for lithium, sodium, potassium, and barium hydroxides the values of the coefficient  $1/p$  vary within very narrow limits, and that the value of the coefficient  $\beta$  for lithium, sodium, and potassium hydroxides is different from that for barium and strontium hydroxides. The velocity of adsorption by starch in water is very considerable during the first few seconds and minutes, but in alcohol no such stage of rapid adsorption is observed.

T. H. P. .

**Theory of the Curved Capillary Layer.** GERRIT BAKKER (*Zeitsch. physikal. Chem.*, 1912, 80, 129—147. Compare Abstr., 1905, ii, 304).—An accurate definition of the radius  $R$  of a liquid particle in contact with its own vapour is given which permits of the application of certain equations to particles of any magnitude. A sphere is imagined concentric with the drop constructed through the capillary layer, the radius  $R$  being so chosen that if the capillary layer is removed and the homogeneous phases of liquid and vapour continued up to the sphere, the total mass of material is not altered. If the capillary energy per unit of surface of the sphere is represented by  $H$ , then the expression  $\eta_s = -\partial H/\partial T$  deduced by Gibbs for the condition that the radius of the sphere is great compared with the thickness of the capillary layer, is shown to be valid for any degree of curvature. Certain equations representing the capillary energy and the thermodynamic potential of the phases are also deduced.

G. S.

**Diffusion of Alkali Salt Vapours in Flames.** HAROLD A. WILSON (*Phil. Mag.*, 1912, [vi], 24, 118—125).—A method of measuring the coefficients of diffusion of salt vapours in flames is described, in which a small bead of salt is introduced into a steady flame, and the shape of the region surrounding the bead which emits light is determined. From the dimensions of the luminous region and the velocity of the flame gases, the coefficient of diffusion of the salt vapour can be readily calculated. From such measurements it appears that caesium, rubidium, and potassium salt vapours diffuse at nearly equal rates, whilst sodium and lithium diffuse more quickly. The values obtained for the diffusion coefficients are: lithium 14.5, sodium 11.5, potassium 4.7, rubidium 4.4, and caesium 4.4.

The average values of the charges on the various metal atoms are also calculated. The numbers indicate that the average charge on lithium and sodium atoms is about equal to that on the univalent ion in solutions, whilst the average charge on potassium, rubidium, and caesium is nearly three times as large. The loss of several electrons by the strongly electro-positive atoms is probably a consequence of the high temperature of the flame. Earlier experiments at a lower temperature (1400°) showed that all the alkali metal atoms lose only a single electron at this temperature. H. M. D.

**Fused Salts as Solvents. The Ionisation of Dissolved Salts.** WILLIAM C. BRAY (*Zeitsch. physikal. Chem.*, 1912, 80, 251—253); OTTO SACKUR (*ibid.*, 254).—The first-mentioned author states that Sackur has overlooked the work of Goodwin and Kalmus (*Physical Review*, 1909, 28, 19) on the subject indicated in the title (compare this vol., ii, 233), but Sackur replies that this work was taken into account in his earlier papers on the subject. G. S.

**Eutectic Crystallisation.** RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1912, 76, 425—436).—The crystallisation of eutectics follows the same laws as that of one-component systems, and the two components crystallise simultaneously, not alternately. The fineness of grain depends on the form of the curves of spontaneous crystallisation and of linear velocity of crystallisation. If the velocity of spontaneous crystallisation increases more rapidly with falling temperature than the linear velocity, slow cooling gives a fine conglomerate, and rapid cooling a coarser one, whilst the reverse effect is obtained when the relative position of the two curves is the opposite. It is shown that the first case occurs in alloys of zinc and cadmium. The structure of the eutectic is spherulitic, made up of radial fibres, which become parallel where they grow perpendicularly to a cooling surface. The enclosure of one component by the other, frequently observed in eutectics, is due to differences in the linear velocities of crystallisation, resulting in the degree of undercooling at the boundary of crystallisation being unequal for the two components. C. H. D.

**Colloidal Chemistry and Twin Crystals.** P. NIGGLI (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 268—273).—It is pointed out that in a system of a definite degree of dispersion, twin crystals are labile with

reference to single crystals, and, further, that in the formation of twin crystals both in fused substances and in solution the state of affairs in the highly disperse system is of main importance. No new experimental results are adduced.

G. S.

**The Determination of the Concentration of Colloidal Solutions by means of the New Liquid Interferometer.** ROBERT MARC (*Chem. Zeit.*, 1912, 36, 537—540).—The Zeiss interferometer, used to determine the refractive index of liquids, serves also to determine the concentration of colloidal solutions in many cases. It is found that the instrument allows of the detection of 0.002 gram of a salt in 100 c.c. of water. Colloidal solutions can be determined with nearly the same accuracy, if not too turbid. The refractivity of such solutions does not alter much with time, although other properties change rapidly. The refraction of any one colloidal substance is very nearly proportional to the concentration, but for more exact estimations a calibration curve should be constructed. Care must be taken to choose the right bands for coincidence, colloidal solutions presenting a special difficulty in this respect.

The instrument may be used to determine the adsorption of colloids by precipitates, the refractivity of the solution being measured before and after the adsorption. The method has been applied to the determination of the quantity of colloids present in potable waters, by taking advantage of the fact that the colloid may be removed by adsorption by a suitable substance. Details of such estimations are to be published.

C. H. D.

**Periodic Autokatakinesis (Autokatakinetic Decomposition).** ALFRED J. LOTKA (*Zeitsch. physikal. Chem.*, 1912, 80, 159—164).—In a previous paper (compare Abstr., 1910, ii, 401) differential equations for autocatalysed reactions which proceed in a periodic (oscillatory) manner were deduced, and solutions of these equations are now given. The equations are applied to the case of a system composed of a number of biological species and their decomposition products, etc., and it is shown that in certain conditions growth may occur in an oscillatory manner, with alternating periods of increase and diminution.

G. S.

**Precipitation from Salt Solutions by Alkali Hydroxides and Carbonates.** EDUARD JORDIS (*Zeitsch. Elektrochem.*, 1912, 18, 553—561).—In the first series of experiments the proportion of certain alkalis and alkali carbonates required to cause complete precipitation of the iron from solutions of ferric chloride and sulphate in different dilutions has been determined, and the results are represented graphically. In concentrated solution, from 90—95% of the theoretical amount (depending on the nature of the alkali) is required to bring about complete precipitation; the proportion increases with the dilution, and ultimately, in the case of ammonium and potassium carbonates, exceeds 100%.

In order to elucidate the nature of the phenomena, the precipitates obtained in different dilutions have been analysed, and the results are

shown graphically, the abscissæ representing dilutions and the ordinates the proportions of the different components. The interpretation of the results is rendered difficult, as no precipitate occurs until a considerable proportion of alkali has been added, and therefore similar experiments have been made with copper sulphate solutions, in which a precipitate forms almost at once. Sodium and potassium hydroxide give almost identical curves. Up to 0.75 equivalent the precipitate is greenish-blue and is a basic salt, containing a large proportion of  $\text{SO}_4$  and very little alkali; with further addition of alkali the precipitate becomes darker blue and unstable, tending to form a brown precipitate. Contrary to the accepted opinion, the bluish-white precipitate obtained on adding alkali to a solution of copper sulphate is a basic salt; the dark blue and brownish-black precipitates both represent the hydroxide and not the oxide. For the results with other alkaline precipitants, the original paper must be consulted. G. S.

**The Velocity of Absorption of Water by the Alkali Chlorides.** M. C. SCHUYTEN (*Bull. Soc. chim. Belg.*, 1912, 26, 262—265).—The chlorides were dried in a desiccator until of constant weight; this took two or three days only with sodium and potassium chlorides, eighty days with ammonium chloride, and was not complete after ninety-eight days with lithium chloride. They were then exposed to the atmosphere under identical conditions.

The results quoted indicate that lithium and sodium chlorides absorb water more rapidly and in larger quantities than ammonium or potassium chlorides.

The experiments were broken off for some months; on resumption, the sodium and lithium chloride curves increased regularly, but those of the ammonium and potassium salts show a bend becoming flatter. The conclusion is drawn that the water diffuses less rapidly into the interior of the mass in the case of these two salts. E. F. A.

**Velocity of Gas Reactions.** MAX TRAUTZ (*Zeitsch. Elektrochem.*, 1912, 18, 513—520).—In the first part of the paper the velocity coefficients of a number of gas reactions, including the formation of hydrogen iodide, hydrogen bromide, hydrogen sulphide, and water from the respective elements, are calculated on the principles described in previous papers (Abstr., 1908, ii, 824; 1909, ii, 557, 651; 1910, ii, 24, 114, 1051; 1911, ii, 381). The dissociation and thermal constants of the free halogens are also discussed, and it is shown that the heat of dissociation of bromine is 65,774 cal.

In connexion with these calculations the specific heat of chlorine at constant pressure has been measured, and the ratio of the specific heats at constant volume,  $C_v$ , and at constant pressure,  $C_p$ , determined by Kundt's method. The mean values of  $C_v$  at one atmosphere pressure are as follows: 5.22 in the interval 25—100°; 5.35 at 25—150°, and 5.47 at 25—200°. It is shown by two different methods that the value of  $C_v$  diminishes to some extent when the gas is exposed to the light of a quartz lamp. According to the first method, it is found that the wave-length in the Kundt's tube alters

on exposing the gas to light, whilst according to the alternative method, the expansion is not the same when the same amount of heat is supplied to the illuminated and non-illuminated gas under conditions otherwise similar. G. S.

**Rate of Decomposition of Hydrogen Peroxide under the Influence of Heat.** GEORGES LEMOINE (*Compt. rend.*, 1912, 155, 9—16).—The decomposition of hydrogen peroxide under the influence of heat is regulated principally by the amount of water existing at each instant in the liquid, and follows a mathematical law resulting from this; thus the water acts as a catalyst. In the first part of the paper the author gives a mathematical discussion of the question, whilst in the latter part experimental results and curves are given, which agree closely with those calculated by him from his equations. The catalytic effect of the water is in accord with the already observed slow decomposition of very concentrated hydrogen peroxide. The physical state of the walls of the containing vessels has a marked influence on the results. W. G.

**Decomposition of Sulphur Trioxide in Quartz Tubes.** MAX BODENSTEIN and FRANZ KRANENDIECK (*Zeitsch. physikal. Chem.*, 1912, 80, 148—158).—The rate of decomposition of sulphur trioxide in a quartz tube at 809° and 859° has been determined by observing the rate of change of pressure on a manometer. In the course of an experiment the reaction appears to be of the third order, but when the initial concentration is varied, it is approximately of the first order, so that the diminution of speed in the course of a reaction must be due to retardation by the products of reaction. It is noteworthy, however, that when sulphur dioxide or oxygen are added at the commencement of a reaction they have no influence on the rate of decomposition. In order to elucidate this behaviour, after partial decomposition had taken place and reaction products had accumulated, a fresh quantity of sulphur trioxide was added. In this case a period of induction occurred which lasted four minutes at 859° and seventeen minutes at 809°; the reaction then started slowly, and rapidly increased in speed, so that the amount decomposed after a given time was greater than in the simple reaction, where no induction period occurs. No explanation of these remarkable observations has been discovered. The temperature-coefficient for 10° between 809° and 859° is 1·57. G. S.

**Velocity of Decomposition of Ammonium Tetrathionate at Different Temperatures.** DÉSIRÉ DE PAEPE (*Bull. Soc. chim. Belg.*, 1912, 26, 244—249).—Ammonium tetrathionate decomposes very slowly at the ordinary temperature and more quickly when warmed into ammonium sulphate, sulphur dioxide, and sulphur. In presence of ammonium thiosulphate, ammonium tetrathionate is re-formed:  $2(\text{NH}_4)_2\text{S}_2\text{O}_3 + 3\text{SO}_2 + \text{S} = 2(\text{NH}_4)_2\text{S}_4\text{O}_6$ .

Above 60° the velocity of the latter reaction becomes small. When the concentration of thiosulphate is within certain limits, the final result is that for every three molecules of tetrathionate decomposed two are re-formed at the expense of two molecules of thiosulphate.

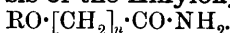
Provided the total concentration of the ammonium salts remains the same, the velocity constant  $K$  is a constant whatever be the initial proportions of the three salts considered.

The value of  $K$  is determined at different temperatures; the ratio  $K_{45}/K_{20}=40$  is the same whatever the total concentration of the ammonium salts; similarly, the ratio  $K_{60}/K_{20}=160$  remains unaltered by changes in the concentration.

Using these values in van't Hoff's formula,  $d \log k/dT = -U/RT^2$ , values of  $-74,300$  and  $-82,500$  calories are obtained for  $U$ , whereas the value of  $U$  determined from thermochemical data is  $-81,700$  calories.

E. F. A.

### Velocity of Hydrolysis of the Alkyl-oxy-amides:



SULO KILPI (*Zeitsch. physikal. Chem.*, 1912, 80, 165—191. Compare Crocker, *Trans.*, 1907, 91, 593).—The rate of hydrolysis of the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -alkyloxyamides in the presence of  $N/2$ -hydrochloric acid has been measured at  $42^\circ$ . The rate of reaction was determined by titrating the ammonium salt with sodium hydroxide in a mixture of ethyl alcohol and water, phenolphthalein being used as indicator. The method depends on the fact that the indicator is not affected by free ammonia in alcoholic solution. The change of colour of the indicator was sharper in the presence of a uranium salt. The titration results were corrected by a complicated method, which is fully described. The velocity constants for the  $\alpha$ -,  $\beta$ -, and  $\gamma$ -compounds are in the ratio 3:1:2. The substitution of an alkoxyl group for hydrogen in the  $\alpha$ - or  $\gamma$ -position accelerates, in the  $\beta$ -position retards, the hydrolysis of amides.

The results are discussed in connexion with Michael's theory of the reactivity of carbon compounds, and it is shown that the rate of hydrolysis increases with increasing negativity of the carbonyl carbon atom.

G. S.

### Catalytic Action of Hydrogen Ions in Alcoholic Solutions.

GEORG BREDIG [with W. S. MILLAR and H. BRAUNE] (*Zeitsch. Elektrochem.*, 1912, 18, 535—539. Compare Bredig and Fraenkel, *Abstr.*, 1906, ii, 426).—The effect of small quantities of water on the rate of decomposition of ethyl diazoacetate in the presence of acids, according to the equation:  $\text{N}_2 \cdot \text{CH} \cdot \text{CO}_2\text{Et} + \text{Et} \cdot \text{OH} = \text{OEt} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} + \text{N}_2$  (Bredig and Fraenkel, *loc. cit.*), has been investigated, and it is shown that the phenomena correspond closely with those observed by Goldschmidt and his co-workers in ester formation (compare *Abstr.*, 1910, ii, 283). As in the latter case, water retards the action to a greater extent in isobutyl alcohol than in ethyl alcohol, and in the latter solvent more than in methyl alcohol. The results did not at first sight appear to correspond with Goldschmidt's formula,  $n = k'C - r$ , where  $n$  represents the amount of water added,  $k'$  is the reciprocal of the catalytic velocity constant,  $r$  the hydrolytic equilibrium constant of the complex ion, and  $C$  a constant dependent on the nature and concentration of the acid. When, however, the effect of water on the electrical conductivity is taken into account on the assumption that the alteration of the

electrical conductivity corresponds with the alteration in the ionic concentration of the catalysing acid, the equation represents the experimental results with a fair degree of accuracy. Further investigation of the deviations by Snethlage (compare next abstract) leads to the conclusion that the catalytic action of acids in alcoholic solution does not depend on the  $H^+$  ion concentration alone, but also, and in some cases to a considerable extent, on the non-ionised portion of the acid.

G. S.

**Catalytic Action of Undissociated Acids.** H. C. H. SNETHLAGE (*Zeitsch. Elektrochem.*, 1912, 18, 539—545. Compare Bredig, previous abstract).—The relative catalytic activity of hydrogen ions and the non-ionised part of an acid can be determined by comparison of the catalytic effect in the presence and absence of a neutral salt of the acid. When ethyl diazoacetate is decomposed under the catalytic influence of picric acid, a certain limiting speed is reached by increasing the salt concentration until the acid is practically non-ionised; this is ascribed to the effect of the non-ionised acid. It is calculated that the ratio of the velocity constant,  $k_m$ , for the non-ionised acid to that for hydrogen ions,  $k_H$ , is 0.06, whilst Goldschmidt found in esterification experiments with the same acid,  $k_m:k_H=0.04$ . The ratio for trichloroacetic acid is 0.0018, and for trinitrobenzoic acid, 0.0012. From a comparison of these numbers with the dissociation constants of the acids, it is shown that the two run parallel; the stronger the acid the greater the catalytic action of the non-ionised molecule.

Of the strong acids, only sulphosalicylic acid and hydrochloric acid have been investigated in aqueous solution, but there is evidence that the non-ionised acid at least is as active as the ionised part in this solvent. The same conclusion can be drawn from the results of Goldschmidt's experiments on esterification (*loc. cit.*). From the data of Arrhenius on the catalytic decomposition of sucrose under the influence of a mixture of a strong acid (nitric acid) and a weak organic acid in aqueous solution, it is shown that the ratio  $k_m:k_H$  increases regularly with increasing affinity constant, and, from comparison with the results in alcoholic solution, that the ratio is nearly independent of the solvent.

The phenomenon of neutral salt action is also ascribed to the catalytic activity of the non-ionised portion of the acid, and it is shown that, in aqueous solution,  $k_m:k_H$  for hydrochloric acid is about 2. Neutral salts with a common ion increase the non-ionised portion of the acid, and therefore increase its catalytic activity.

G. S.

**Atoms, Molecules, Ions, Electrons.** ALEXANDRE DE HEMPTINNE (*Bull. Soc. chim. Belg.*, 1912, 26, 294—304).—An historical résumé. The conclusion is arrived at that the ions and electrons of the physicist have only a distant relationship to the atoms and molecules of the chemist. Even in cases where the ions and electrons in gases seem to play a chemical rôle, this is in reality only of secondary nature. The ions and electrons only serve to modify the behaviour of the atoms without themselves having a well characterised chemical individuality.

E. F. A.

**Interpretation of the Periodic System of the Elements.** S. VOINICH-SJANOSCHENTZKY (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 532—564).—The author interprets the periodic system according to the frequencies of atomic vibration of the elements. The paper does not lend itself to abstraction. T. H. P.

**Molecular or Atomic Percentages, and Percentages by Weight in Binary and Ternary Systems.** ERNST JÄNECKE (*Metallurgie*, 1912, 9, 320—324).—A mathematical proof of the geometrical construction proposed by Hoffmann (this vol., ii, 340), together with a modified construction. C. H. D.

**Two Laboratory Condensers with Internal Cooling.** ERIK SCHIRM (*Zeitsch. angew. Chem.*, 1912, 25, 1225—1226).—Two simple vertical condensers with internal cooling are described. The annular condensing space is provided with a side-arm for distillation, and with a neck at the lower end. In one form the mantle is fitted to the inner vessel by means of cork or rubber, in the second a ground joint is used. C. H. D.

**Partition-coefficients.** JOSE RODRIGUEZ CARRACIDO (*Anal. Fis. Quim.*, 1912, 10, 190—191).—A lecture demonstration on partition is afforded by shaking iodine water with carbon disulphide, and showing that the water still contains iodine by means of starch paper. On now adding a crystal of potassium iodide, it may be shown that the carbon disulphide remains faintly pink even after prolonged agitation. G. D. L.

**Photochemical Lecture Experiments of Plant Physiological Interest.** OSKAR BAUDISCH and ERWIN MAYER (*Ber.*, 1912, 45, 1771—1775. Compare Baudisch, Abstr., 1911, ii, 523).—When aqueous solutions of potassium nitrate are exposed in a flat dish to the rays of a mercury lamp, oxygen is very soon liberated. This is made visible by the addition of a little starch and potassium iodide: a blue coloration is produced in five to ten seconds. The interposition of a glass plate delays change for twenty minutes. The same change also takes place in sunlight. By interposing various solutions, the influence of light of different wave-lengths on the rate of elimination of oxygen can be measured.

Aloin, which becomes red, may also be used to detect the liberation of oxygen; this reagent is also applicable to show the elimination of oxygen from nitrites, and also from aliphatic and aromatic nitro-compounds, a process which takes from two minutes' exposure with nitromethane to some seventeen minutes with nitrobenzene.

The aliphatic nitro-compounds when exposed to light with *o*-, *m*-, and *p*-phenylenediamine give the same colour reactions as the aliphatic aldoximes, from which it is assumed that the nitro-compounds are partly converted into these.

The colour reactions given by the aldoximes are due to labile intermediate compounds formed during the Beckmann rearrangement into the corresponding acid amides. E. F. A.

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## Inorganic Chemistry.

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**Apparatus for the Electrolytic Production of Oxygen and Hydrogen.** GEBR. RUHSTRAT (*Zeitsch. angew. Chem.*, 1912, 25, 1277—1278).—The apparatus consists of a glass cylinder with wooden lid, supporting an inner glass cylinder open below. A sheet nickel electrode is inside this cylinder, the other electrode, also of nickel, being in the annular space. The electrolyte is 30% sodium hydroxide. The inner electrode is made the cathode or the anode, according as hydrogen or oxygen is required. The apparatus regulates itself automatically, like a Kipp apparatus, the liquid in the inner space only rising high enough to maintain the pressure at which the gas is being delivered. With a current of 3 amperes, 20 c.c. of hydrogen are evolved per minute. A layer of paraffin is used to cover the electrolyte, and the air is removed before beginning to collect the gas.

C. H. D.

**Ultramicroscopy of Iodine Solutions.** J. AMANN (*Kolloid. Chem. Beihefte*, 1912, 3, 337—360. Compare Abstr., 1910, ii, 496, 844).—Some of the observations described in the paper have already been published (*loc. cit.*). The results are summarised as follows: Iodine can exist in solution in seven different forms: (1) as  $I^-$  and  $I_3^-$  ions; (2) as free iodine,  $I_2$ , in true solution; (3) as polymerides of free iodine in ultramicroscopic and amicroscopic particles; (4) free iodine as microscopic particles suspended in the liquid; (5) combined iodine in true solution, forming definite additive compounds,  $I_2Solv_n$ , with the solvent; (6) combined iodine in the polymerised molecule of a true additive compound in the colloidal state; (7) as a micellar adsorption compound of indefinite composition, varying with the conditions.

Any alteration of the free energy must affect the complicated equilibrium in such systems, and alterations of colour, for instance, are probably not due solely to the formation of compounds with the solvent, but also to the occurrence of free iodine in the colloidal phase. The latter may be composed of free iodine or of additive compounds with the solvent.

The alteration in the colour of the solutions due to light probably consists mainly in a reduction of the additive compounds under definite conditions of temperature and pressure, free iodine acting as catalyst.

G. S.

**Stability of the Hypiodites.** VICTOR AUGER (*Compt. rend.*, 1912, 154, 1806—1807 \*).—Förster and Gyr (Abstr., 1903, ii, 209) state that the reaction represented by the equation:  $MOI + MI + 2MHCO_3 = I_2 + 2M_2CO_3 + H_2O$  is far from complete, even in the presence of a large excess of a saturated solution of the alkali hydrogen carbonate. The author finds that this is probably due to the action of the normal carbonate, which is present, on the iodine, with the consequent re-formation of hypiodites. If the hydrogen carbonate used is saturated with carbon dioxide or diluted with water saturated with carbon dioxide,

\* and *Bull. Soc. chim.*, 1912, [iv], 11, 728—731.

the reaction is complete in the sense of the above equation. Hypoiodite is not formed from iodine and an alkali hydrogen carbonate in the presence of carbon dioxide, even after several days.

The observation of Lunge and Schoch (Abstr., 1883, 17), that calcium hypoiodite is not readily destroyed by boiling its solution, is incorrect. These authors based their conclusions on the results of the decolorisation of indigo-carmin by the solution examined. This solution contained calcium hydroxide, however, which of itself rapidly destroys indigo-carmin.

T. S. P.

**Colloidal Sulphur and Iodic Acid.** M. RAFFO and G. ROSSI (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 278—280).—When colloidal sulphur and iodic acid are mixed, a deep red colour due to free iodine is immediately developed, and subsequently a voluminous, dark red precipitate composed of a mixture of iodine and sulphur separates. There is evidence that the sulphur is oxidised to sulphur dioxide by the iodic acid, the resulting hydriodic acid is oxidised to free iodine by part of the iodic acid, and the latter also oxidises the sulphur dioxide to sulphuric acid. Quantitative investigation shows that under certain conditions the reaction increases at first with the iodic acid concentration, attains a maximum, and beyond that point diminishes with further increase in concentration. According to the conditions the reaction proceeds until the iodic acid or the sulphur is used up, or until the sulphur separates in gelatinous form.

G. S.

**Colours Due to Sulphur.** JOSEF HOFFMANN (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 275—278).—It is shown that the colour of ultramarine is due to the presence of sulphur in colloidal solution, and that a number of compounds act as suitable solvents for colloidal sulphur.

The silicon dioxide in ultramarine can be completely displaced by boron trioxide without the disappearance of the blue colour. Further, the colour does not greatly alter for variation in the composition of the solvent from  $\text{Na}_2\text{B}_6\text{O}_{10}$  to  $\text{Na}_2\text{B}_{10}\text{O}_{16}$ , which speaks in favour of the solution theory. Further, when potassium thiocyanate is dehydrated and heated to redness, it becomes blue, and sulphur can be extracted from the cooled mass, which shows that potassium cyanide and thiocyanate are suitable solvents for colloidal sulphur. Finally, phosphoric oxide also gives a deep blue colour on fusing with sodium sulphide at  $900^\circ$ , but the colour disappears on cooling.

It is suggested that the blue colour of the solution obtained by dissolving disulphur trioxide in concentrated sulphuric acid is due to the presence of a trace of colloidal sulphur.

G. S.

**Pyrosulphuryl Chloride and Chlorosulphonic Acid.** CHARLES ROBERT SANGER and EMILE RAYMOND RIEGEL (*Zeitsch. anorg. Chem.*, 1912, 76, 79—128).—After a review of the known methods of preparing pyrosulphuryl chloride and chlorosulphonic acid, experiments to determine the best methods are described.

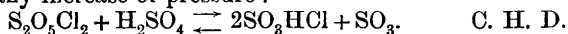
A mixture of fuming sulphuric acid and sulphur trioxide is added gradually to an excess of dry carbon tetrachloride in a heated flask. The reaction occurring is  $2\text{SO}_3 + \text{CCl}_4 = \text{COCl}_2 + \text{S}_2\text{O}_5\text{Cl}_2$ , but chloro-

sulphonic acid is also formed. After gas ceases to be evolved, the product is distilled and fractionated. The first fraction, b. p. 125—130°, contains carbonyl chloride and carbon tetrachloride; the second, up to 160°, is again distilled, and that boiling above 130° is taken. This is then mixed at 0° with sodium chloride, previously dried at 150°:  $\text{SO}_3\text{HCl} + \text{NaCl} = \text{SO}_3\text{NaCl} + \text{HCl}$ . When the evolution of hydrogen chloride has ceased, the mixture is distilled under 20—30 mm. pressure. The product is purified by a final distillation from sodium chloride under reduced pressure.

Pyrosulphuryl chloride has b. p. 152.5—153°/766 mm. and 56—57°/19 mm., without appreciable decomposition in the absence of moisture. It has  $D_4^{20}$  1.837 and  $D_4^0$  1.872, and m. p. -37.5 to -37°.

Chlorosulphonic acid is prepared by passing dry hydrogen chloride into sulphuric acid containing sulphur trioxide and distilling in hydrogen chloride, collecting the fraction between 145° and 160°. It is best purified by fractional crystallisation at a low temperature, and then has b. p. 151—152°/765 mm. and 74—75°/19 mm., but dissociates considerably under low pressures. The crystalline solid has m. p. -81 to -80°, but when impure a glass is readily formed. Chlorosulphonic acid has  $D_4^{20}$  1.753,  $D_4^0$  1.784.

The two compounds may be distinguished by their behaviour towards powdered selenium or tellurium, which gives colorations with chlorosulphonic acid, but not with pyrosulphuryl chloride. The latter compound is much less readily attacked by water than chlorosulphonic acid. When pyrosulphuryl chloride and sulphuric acid are sealed together in a glass tube, the originally immiscible liquids become homogeneous in the course of a month, and chlorosulphonic acid is formed without any increase of pressure:



**The Molecular Weight of Selenium in Solution.** F. OLIVARI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 718—726).—The examination of mixtures of selenium and iodine indicates the molecular weight  $\text{Se}_2$  (Abstr., 1909, ii, 39, 568, 996), differing widely from the values  $\text{Se}_3$  and  $\text{Se}_{10}$  obtained by Beckmann with phosphorus and methylene iodide (Abstr., 1904, ii, 235). Determinations of the freezing point of solutions of selenium in fused mercuric chloride (Abstr., 1909, ii, 805) show that the molecular weight diminishes with increasing dilution.

The freezing-point curve of mixtures of mercuric bromide and selenium shows that a compound does not exist, and that there is a region of immiscibility in the liquid state from 16 to 53% Se. The eutectic point is at 210° and about 81% Se. The molecular lowering, determined by means of anthraquinone, phenanthraquinone and sulphur, is 405 (403: Guinchant, Abstr., 1909, ii, 790). The molecular weight of selenium ranges from  $\text{Se}_3$  or  $\text{Se}_4$  in dilute solutions to  $\text{Se}_3$  in concentrated solutions. C. H. D.

**The Formation of Nitrogen Oxides by the Electric Spark Discharge in Liquid Air.** ERNST MÜLLER (*Zeitsch. anorg. Chem.*, 1912, 76, 324—346).—An electric discharge in liquid air leads to the

formation of green flocks, described as nitrogen trioxide (Helbig, Abstr., 1903, ii, 361). The green substance rapidly becomes blue in light, and the author (*Zeitsch. angew. Chem.*, 1911, 24, 1179) suggested the formula  $\text{NO}_3$  for it, decomposing according to the equation  $2\text{NO}_3 = \text{N}_2\text{O}_3 + \text{O}_2$ . Raschig (this vol., ii, 346) has proposed the same formula for a product obtained by passing nitric oxide into liquid air or oxygen. It is now found that ozone is not formed in the decomposition, that originally observed being of separate origin. When a discharge of high frequency is employed, ozone is obtained, unaccompanied by the green compound.

The analysis is difficult on account of the adherence of liquid oxygen to the solid. The ratio  $\text{N}:\text{O} = 1:1.5$  is obtained, whether the oxygen is removed by evacuating at a low temperature or by warming to  $-118^\circ$ , or by washing with liquid nitrogen and removing this at  $-140^\circ$ . The melting point, determined by means of a platinum resistance thermometer, is  $-102^\circ$ , and this is the same for the product obtained by Raschig's method. Raschig's result (1:3) is probably due to adherence of oxygen. It is shown that silica retains much oxygen, even above  $-158^\circ$ . It is possible that a higher oxide exists at low temperatures and in presence of an excess of oxygen, but the compound isolated is in all cases nitrogen trioxide. C. H. D.

**The Catalytic Oxidation of Aqueous Solutions of Hypophosphites.** ADOLF SIEVERTS and F. LOESSNER (*Zeitsch. anorg. Chem.*, 1912, 76, 1—29. Compare Abstr., 1909, ii, 883).—Palladium catalyses the oxidation of hypophosphorous acid, whilst the similar action of copper and silver precipitates has been attributed to the presence of hydrides (Bartlett and Merrill, Abstr., 1895, ii, 268; Bartlett and Rice, *ibid.*, 1897, ii, 212). It is now shown that the active substances are the metals, and not the hydrides.

The reduction of copper sulphate with sodium hypophosphite yields a red, spongy mass, which does not contain hydrogen, but consists of copper with small quantities of oxygen and phosphorus, the oxygen being absorbed during washing and drying. It is active towards hypophosphites.

Silver nitrate and hypophosphorous acid, free from chlorine, yield a precipitate which is also free from hydrogen.

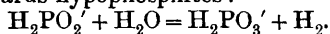
On addition of sodium hypophosphite to an excess of palladium sulphate, leaflets of metallic palladium are precipitated without evolution of hydrogen. When the hypophosphite is in excess, the quantitative results do not prove whether the metal or a hydride is the active substance, as palladium saturated with hydrogen precipitates palladium from its salts. Palladium precipitated by means of carbon monoxide, which cannot contain hydrogen, also decomposes hypophosphites, indicating that the metal is, as in other cases, itself active.

Platinum black is not a catalyst for the decomposition of hypophosphites. The oxidation which takes place is proportional to the weight of the platinum black used, and is due to the oxygen retained by it.

Bach's results for the kinetics of the decomposition by palladium

(Abstr., 1910, ii, 31) are confirmed and extended. Instead of measuring the hydrogen evolved, the solution is agitated by means of a stream of hydrogen, and the reaction is followed iodometrically. The palladium shows "fatigue," but its properties are restored by washing and drying at 100°.

Sodium and potassium hydroxides are equally active as catalytic oxidising agents towards hypophosphites:



A special apparatus for the experiments is described. The reaction is of the first order, and its temperature-coefficient, determined by experiments at 91° and 100°, is normal. The velocity at 100° is much less than that found with palladium black at the ordinary temperature. C. H. D.

**Ultraphosphates. I. Some Salts of the Least Hydrrous Phosphoric Acid.** ADOLF V. KROLL (*Zeitsch. anorg. Chem.*, 1912, 76, 387—418).—This investigation was begun with the "tetrabasic" calcium phosphate,  $4\text{CaO}, 3\text{P}_2\text{O}_5$ , of Thomas slag. The readily volatile modification of phosphoric oxide, obtained by the direct combustion of phosphorus, is sublimed in oxygen through platinum black and passed over heated lime. Heat is developed, and a fused mass is obtained, having the composition  $5\text{CaO}, 3\text{P}_2\text{O}_5$ . When, however, the temperature is kept at 350°, the glassy product has the composition  $2\text{CaO}, 3\text{P}_2\text{O}_5$ , but passes into the more basic compound when fused. Small quantities of a platinum phosphate are always formed from the platinum boat used.

Phosphoric oxide reacts with silver at a high temperature, forming a yellow glass,  $\text{Ag}_2\text{O}, 3\text{P}_2\text{O}_5$ , which dissolves in water to a ruby-red solution, containing colloidal silver. If the glass is somewhat overheated, a silver ruby glass is obtained. This has not yet been found to occur with silicates or phosphates. The fused product is almost colourless, but yields the red colloidal solution with water. The aqueous solution contains an acid silver metaphosphate. It yields a brown precipitate with sodium orthophosphate.

Lead or lead oxide, when heated in phosphoric oxide vapour, yields a clear liquid, from which the stable salt,  $5\text{PbO}, 3\text{P}_2\text{O}_5$ , crystallises. The ultraphosphate,  $\text{PbO}, 3\text{P}_2\text{O}_5$ , has also been obtained. Similar salts of nickel and magnesium appear to exist. Alkali hydroxides and carbonates yield products approaching the composition  $2\text{Na}_2\text{O}, 3\text{P}_2\text{O}_5$ ,  $2\text{Li}_2\text{O}, 3\text{P}_2\text{O}_5$ , and  $\text{K}_2\text{O}, 3\text{P}_2\text{O}_5$ .

The dehydration of metaphosphoric acid by heat does not give any definite ultraphosphoric acid, the results being complicated by the volatility of the acids. Rough experiments with lead oxide and metaphosphoric acid suggest that hydrates of the ultra-acids may exist. C. H. D.

**The Oxidation of Arsenious Acid by the Oxygen of the Air.** F. REINTHALER (*Chem. Zeit.*, 1912, 36, 713).—A solution containing sodium dihydrogen arsenite and sodium hydrogen carbonate undergoes slow oxidation on warming in contact with the air, in contradiction to a statement by Mohr that it remains unaltered. At

ordinary temperatures no oxidation could be detected after four months.  
T. S. P.

**The Chemical Behaviour of the Different Modifications of Silica.** ROBERT SCHWARZ (*Zeitsch. anorg. Chem.*, 1912, 76, 422—424).—Tridymite is conveniently prepared artificially by fusing sodium silicate with three times its weight of sodium phosphate for six hours at 1000°, extracting with water, filtering, and washing until free from phosphate. The residue has D 2·310, and forms microscopic, hexagonal tablets.

Cristobalite is obtained by heating powdered transparent silica glass in a porcelain furnace. It has D 2·319, and becomes isotropic after a short heating at 250°, whilst tridymite remains doubly refracting after the same treatment.

The different modifications of silica, reduced to a uniform fineness of 0·04 mm. by elutriation, show little difference in their behaviour towards boiling 5% sodium carbonate solution, but the solubility in hydrofluoric acid varies considerably. Thus, heating for an hour with 1% hydrofluoric acid, renewing the evaporated water every twenty minutes, dissolves 5·2% of quartz, 20·3% of tridymite, 25·8% of cristobalite, and 52·9% of amorphous silica. The modification stable at the ordinary temperature, quartz, is therefore the least reactive.  
C. H. D.

**Growth of Silicic Acid Gels.** RAPHAEL E. LIESEGANG (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 273—275).—When a non-dialysed silicic acid sol, prepared in the usual way, is poured into a flask in the bottom of which are crystals of sodium carbonate, the gel formation (due to the removal of hydrochloric acid) begins at the surface of the crystals and spreads outwards. That the effect is not due to diffusion of the sodium salt is shown by the fact that a non-diffusible substance, such as calcium carbonate, has the same effect as the former salt; the phenomenon is therefore connected with the diffusion of the hydrochloric acid into the carbonate. These results offer a possible explanation of the change of mussel shells to a silicious material, and of the occurrence of opals in cracks in limestone rocks.

Experiments were made with silicic acid sols which contained calcium nitrate, ferrous sulphate, or ferric chloride, and were poured on to sodium carbonate crystals with the object of throwing light on the origin of banded structures, such as oolites, but the results were not conclusive.  
G. S.

**The Reduction of Silicates by means of Metallic Calcium.** EDGAR WEDEKIND and LUCIEN DÜRR (*Zeitsch. angew. Chem.*, 1912, 25, 1265—1268).—The powdered silicates are mixed with calcium turnings and heated in an exhausted iron tube. The product is powdered, and washed successively with water, acetic or hydrochloric acid, water, and acetone. It has not been found possible to prepare definite silicides in this way. Aluminium silicate is hardly attacked, but other silicates undergo reduction, the silicides being probably

formed as intermediate products. Wollastonite yields an insoluble residue of unknown composition, whilst zircon yields impure zirconium, rhodonite is converted into products soluble in dilute acids, and garnierite yields an impure nickel calcium silicide. Glucinum silicide is obtained, but not in a completely pure form, by the reduction of beryl. C. H. D.

**Periodates of the Alkali Metals.** VICTOR AUGER (*Compt. rend.*, 1912, 154, 1699—1700\*).—The author has not been able to confirm the observation of Garzarolli-Thurnlackh (Abstr., 1902, ii, 67) that periodate is formed when ozone acts on a solution of potassium iodide. The latter observer tested for periodate by passing a current of carbon dioxide through the solution containing the products of oxidation and unaltered iodide, assuming that iodine is not liberated from a mixture of iodide and iodate under such conditions, whereas it is from periodate and iodide. The author shows, however, that iodine is liberated from iodide and iodate by carbon dioxide unless a large excess of sodium hydrogen carbonate is present.

The observations of both Garzarolli-Thurnlackh (*loc. cit.*) and of Péchard (Abstr., 1900, ii, 536) on the interaction between iodide and periodate are incorrect, being vitiated by taking no precautions to exclude carbon dioxide. The first reaction which takes place is given by the equation:  $3\text{NaIO}_4 + 2\text{NaI} + 3\text{H}_2\text{O} = 2\text{Na}_2\text{H}_3\text{IO}_6 + \text{NaIO}_3 + \text{I}_2$ , which is then followed by the reaction:  $2\text{Na}_2\text{H}_3\text{IO}_6 + \text{I}_2 = 3\text{NaIO}_3 + \text{NaI} + 3\text{H}_2\text{O}$ . In the presence of carbon dioxide, the periodate,  $\text{Na}_2\text{H}_3\text{IO}_6$ , first gives the periodate,  $\text{NaIO}_4$ , and this then interacts with the iodide in the presence of carbon dioxide, giving iodate and iodine. T. S. P.

**Reciprocal Behaviour of Alkali Sulphates, Chromates, Molybdates, and Tungstates at Low and at High Temperatures.** I. MARIO AMADORI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 667—673. Compare this vol., ii, 48, 154).—One hundred grams of water at 25° dissolve 12.10 grams of potassium sulphate, 64.62 grams of potassium chromate, and 184.6 grams of potassium molybdate. The last salt crystallises anhydrous from water at 25°, and in contact with water at this temperature remains anhydrous.

In agreement with the results of Fock (Abstr., 1897, ii, 479), and in contradiction to those of Hertz (*Diss.*, Berlin, 1895), the solubility curve of potassium sulphate and chromate is of Roozeboom's type I. The mutual solubility of the two salts in the solid state is complete, and the more soluble of the salts (the chromate) is always in greater proportion in the solution than in the crystals.

Potassium chromate and molybdate give a solubility isotherm similar to that of the preceding case, and the relation between the two salts in the solution and in the crystals varies in a similar manner. The same holds for the sulphate and molybdate.

It cannot be asserted definitely that, in these cases, the solubility isotherms and the curves representing the relation between the concentrations of the two salts in the crystals and in the solutions are

\* and *Bull. Soc. chim.*, 1912, [iv], 11, 731—737.

continuous, but the general characters of the curve indicate such to be the case.

T. H. P.

**Capacity of Sodium Halides for Forming Solid Solutions at High Temperatures.** MARIO AMADORI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 467—472. Compare this vol., ii, 48).—These investigations were made at high temperatures, because, unlike the potassium salts, sodium bromide and iodide crystallise from water with  $2\text{H}_2\text{O}$ . The melting points of the pure sodium salts are: chloride,  $808^\circ$ ; bromide,  $748^\circ$ ; iodide,  $662^\circ$ .

The solidifying point of the bromide is slightly lowered (to  $744^\circ$ ) by addition of chloride. The cooling curves of the separate mixtures show merely a retardation over at most  $10\text{--}12^\circ$ . These curves and the diagram of state demonstrate the complete solubility of the chloride and bromide at high temperatures (compare Ruff and Plato, *Abstr.*, 1903, ii, 588).

The system  $\text{NaBr--NaI}$  exhibits behaviour similar to that of the preceding pair, the minimum temperature of crystallisation being  $645^\circ$ , and the two salts being miscible in all proportions in the solid state. The cooling shows no anomaly which can be attributed to the decomposition of mixed crystals.

In the system  $\text{NaCl--NaI}$ , mixtures containing from 0 to 26 mols. % of the chloride crystallise over a wide interval, solid solutions of chloride in iodide being deposited. Mixtures containing 25—96 mols. % of the chloride deposit firstly mixed crystals more or less rich in chloride, and later, at  $578^\circ$ , a eutectic mixture of limiting mixed crystals. When the proportion of chloride exceeds 96 mols. %, the cooling curves show no eutectic arrest, homogeneous mixed crystals being formed on solidification. The curve of primary crystallisation consists of two branches meeting in the eutectic point  $578^\circ$ , which corresponds with 37 mols. %  $\text{NaCl}$  (compare Ruff and Plato, *loc. cit.*).

The crystallisation curves determined by Vrschesnevsky (this vol., ii, 137) for  $\text{KCl--KBr}$ ,  $\text{KBr--KI}$ , and  $\text{KCl--KI}$  differ considerably from those obtained by the author and Pampanini (this vol., ii, 48). For the third pair the difference between the temperatures of primary crystallisation are not so great as with the other pairs, but whilst the author's results indicate restricted solubility in the solid state, those of Vrschesnevsky point to complete solubility.

T. H. P.

**The Binary Systems  $\text{Li}_2\text{SiO}_3\text{--Al}_2(\text{SiO}_3)_3$ ,  $\text{Li}_4\text{SiO}_4\text{--Al}_4(\text{SiO}_4)_3$ ,  $\text{LiAlO}_2\text{--SiO}_2$ , and the Lithium Aluminosilicate Minerals.** R. BALLÓ and EMIL DITTLER (*Zeitsch. anorg. Chem.*, 1912, 76, 39—69).—The above systems have been investigated as a part of the ternary system  $\text{Li}_2\text{O--Al}_2\text{O}_3\text{--SiO}_2$ . Two lithium silicates are known to be stable,  $\text{Li}_2\text{SiO}_3$ , m. p.  $1180^\circ$ , and  $\text{Li}_4\text{SiO}_4$ , m. p.  $1217^\circ$ , whilst only a single aluminium silicate,  $\text{Al}_2\text{SiO}_5$ , is stable in contact with the liquid phase.

Mixtures of lithium and aluminium metasilicates, prepared from their pure constituents, give a freezing-point curve which indicates that, starting from the lithium end, solid solutions are formed as far as 30 mol. %  $\text{Al}_2(\text{SiO}_3)_3$ , and that beyond the eutectic point a maximum

occurs at  $965^{\circ}$ , corresponding with the compound  $2\text{Li}_2\text{SiO}_3 \cdot \text{Al}_2(\text{SiO}_3)_3$ . There is then a second eutectic point at  $920^{\circ}$ , and the curve rises steeply to a maximum at  $1275^{\circ}$ , corresponding with  $\text{Li}_2\text{SiO}_3 \cdot \text{Al}_2(\text{SiO}_3)_3$ . The third eutectic point is at  $1200^{\circ}$ . The conclusions drawn from the curve are confirmed by determinations of the density and by the examination of micro-sections. The second compound differs widely from natural spodumene and kunzite, which have the same composition and yield a product identical with the synthetic compound when fused and slowly cooled. The refractive index of natural spodumene is 1.665, and that of the artificial compound ( $\gamma$ -spodumene) 1.525. The velocity of transformation of spodumene has been studied at different temperatures (compare Endell and Rieke, this vol., ii, 266). The violet colour characteristic of kunzite is obtained by rapid cooling of the molten mass.  $\beta$ -Spodumene is formed on heating to about  $1000^{\circ}$ , and has D 2.41, against 3.17 for  $\alpha$ - and 2.313 for  $\gamma$ -spodumene. The glass has D 2.36.

Mixtures corresponding with the orthosilicates give a freezing-point curve on which the compound  $3\text{Li}_4\text{SiO}_4 \cdot \text{Al}_4(\text{SiO}_4)_3$  does not appear as a maximum, but indicates decomposition, at  $1079^{\circ}$ , below the melting point. There are eutectic points at  $1020^{\circ}$  and  $1170^{\circ}$ , with an intervening maximum at  $1330^{\circ}$ , corresponding with the compound  $\text{Li}_4\text{SiO}_4 \cdot \text{Al}_4(\text{SiO}_4)_3$ , identical in composition with eucryptite, which does not occur in sufficiently distinct crystals to establish the complete identity. Eutectic structures are well developed. All these silicates crystallise well.

Lithium aluminates are only formed at high temperatures. The mixture having the composition  $\text{LiAlO}_2$  melts at  $1900$ – $2000^{\circ}$ , and is homogeneous on cooling. It can retain up to 12.5 mol. %  $\text{Al}_2\text{O}_3$  in solid solution, beyond which point corundum also crystallises.

In the system  $\text{LiAlO}_2$ – $\text{SiO}_2$  the two double silicates, and also two complex silicates,  $\text{LiAlSi}_3\text{O}_8$ , m. p. about  $1250^{\circ}$ , and  $\text{LiAlSi}_4\text{O}_{10}$ , m. p. about  $1200^{\circ}$ , have been detected, but neither has been completely identified with petalite. Natural petalite undergoes a change at  $1200^{\circ}$ , becoming isotropic without assuming all the properties of the glass.

C. H. D.

**The Ternary System Silver-Tin-Lead.** NICOLA PARRAVANO (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 575–581).—A theoretical discussion, in which the conclusions previously arrived at as to the constitution of ternary systems (Abstr., 1911, ii, 704, 705; compare Sahmen, this vol., ii, 438) are applied to the system silver-tin-lead (Abstr., 1911, ii, 281).

C. H. D.

**Thermal Analysis of the System  $\text{AgCl}$ – $\text{Ag}_2\text{S}$ .** CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 479–482).—The solidification curve of the system  $\text{AgCl}$ – $\text{Ag}_2\text{S}$  consists of two branches meeting in the eutectic point  $380^{\circ}$ , which correspond with 35 mol. % of the sulphide. The latter solidifies with slight development of heat, so that it is difficult to fix exactly the commencement of crystallisation with the mixtures rich in sulphide.

The results of the thermal analysis and those obtained by etching the various mixtures with dilute nitric acid (1 : 1) indicate that silver

sulphide in the solid state dissolves about 10 mol. % of the chloride. It cannot, however, be decided if, or to what extent, the sulphide dissolves in the chloride.

The transformation point of silver sulphide shown in the cooling curve of the pure salt as a slight retardation cannot be detected with certainty with mixtures rich in the sulphide; it is probably rapidly lowered by addition of chloride.

T. H. P.

[Oxy-salts of the Alkaline-earth Metal Halides.] FRANS A. H. SCHREINEMAKERS and J. MILIKAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 52—54. Compare Abstr., 1911, ii, 983).—The ternary systems belonging to the series water, alkaline-earth metal halide, alkaline-earth metal oxide have been investigated at definite temperatures, and the nature of the solid phases has been deduced by application of the residue method. In this way the following oxy-halogen salts have been shown to exist in contact with solution. At 10° and 25°,  $\text{CaCl}_2, 3\text{CaO}, 16\text{H}_2\text{O}$  and  $\text{CaCl}_2, \text{CaO}, 2\text{H}_2\text{O}$ ; at 50°,  $\text{CaCl}_2, \text{CaO}, 2\text{H}_2\text{O}$  and  $\text{CaCl}_2, \text{CaO}, 3\text{H}_2\text{O}$ ; at 25°,  $\text{CaBr}_2, 3\text{CaO}, 16\text{H}_2\text{O}$  and  $3\text{CaBr}_2, 4\text{CaO}, 16\text{H}_2\text{O}$ ; at 30°,  $\text{BaCl}_2, \text{BaO}, 5\text{H}_2\text{O}$ ; at 25°,  $\text{BaBr}_2, \text{BaO}, 5\text{H}_2\text{O}$ ; at 25°,  $\text{BaI}_2, \text{BaO}, 9\text{H}_2\text{O}$ .

H. M. D.

Fusion and Inversion of Calcium Carbonate. HENDRIK E. BOEKE (*Jahrb. Min.*, 1912, i, 91—121).—A special apparatus is described for equilibrium experiments at temperatures up to 1600°, and under a gas pressure of 150 atmospheres; and also an apparatus with windows of silica glass for microscopical observations under similar conditions. Calcium carbonate in its purest form of Iceland-spar fuses without decomposition at 1289° in carbon dioxide of 110 atmospheres pressure. Fusions of mixed calcium carbonate and calcium oxide form a eutectic, 91%  $\text{CaCO}_3$ , 9%  $\text{CaO}$ , at 1218°, but no mixed crystals or intermediate compound. The heating curves indicate an inversion of calcium carbonate at 970° from calcite into  $\alpha$ -calcium carbonate, but no variation in the optical character could be detected.

L. J. S.

The Distinction between Aragonite and Calcite. NIEDERSTADT (*Zeitsch. angew. Chem.*, 1912, 25, 1219—1220).—Cobalt salts are used to distinguish aragonite from calcite, the first being rapidly coloured lilac, whilst the second only assumes a bright blue colour after continued boiling. Also, aragonite precipitates ferrous carbonate, whilst calcite is only capable of precipitating iron in the ferric state. Quantitative experiments show that similar differences exist between the behaviour of calcite and of aragonite towards other metallic salts. Aragonite is the more active towards manganese, zinc, and iron, whilst copper, lead, and silver are more readily precipitated by calcite. If one gram of the powdered mineral is added to 100 c.c. of a boiling solution of manganous sulphate, and the solution is rapidly cooled after five minutes, 1% of the manganese is found to have been precipitated by the calcite, and 73.6% by the aragonite.

C. H. D.

**The Compound  $8\text{CaO}, 2\text{SiO}_2, \text{Al}_2\text{O}_3$ .** ERNST JÄNECKE (*Zeitsch. anorg. Chem.*, 1912, 76, 357—360. Compare this vol., ii, 159, 450).—In reply to the criticisms of Rankin and Wright (this vol., ii, 554), it is stated that mixtures with the composition  $8\text{CaO}, 2\text{SiO}_2, \text{Al}_2\text{O}_3$  show a very sharp arrest on the cooling curve, and that the microscopical examination of thin sections shows perfectly uniform crystals with only small enclosures of glass. The differences between the two series of observations are attributed in part to the low velocity of formation of the compound, and in part to the higher temperature used by the author in melting the mixtures. C. H. D.

**Anhydrous Sulphates. II.** G. CALCAGNI (*Atti R. Accad. Lincei*, 1912, [iv], 21, i, 483—488. Compare Abstr., 1910, ii, 1064).—The addition of barium sulphate to sodium sulphate raises the melting point of the latter from  $887^\circ$  to  $921^\circ$  for an addition of 21.6%. Further proportions of barium sulphate cause very gradual lowering of the freezing point to  $913^\circ$  for a mixture containing 29%  $\text{BaSO}_4$ . From this point the curve rises continuously to the melting point of barium sulphate, which extrapolation gives as  $1345^\circ$ . The very flat and scarcely appreciable maximum shown by the curve would correspond with the compound  $\text{BaSO}_4, 6\text{Na}_2\text{SO}_4$ , but double sulphates of this type are apparently unknown. Between 71%  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_2\text{SO}_4$  the curve shows a point corresponding with the initial crystallisation, a second with the temperature of decomposition of the solid solutions, and a third with the temperature of transformation of sodium sulphate. The following regions are distinguished: (1) existence of the homogeneous liquid phase; (2) equilibrium between  $\text{BaSO}_4$  and liquid phase; (3) existence of solid solutions; (4) equilibrium between solid solutions (3) and  $\alpha\text{-Na}_2\text{SO}_4\text{-BaSO}_4$ ; (5) existence of  $\beta\text{-Na}_2\text{SO}_4\text{-BaSO}_4$ ; (6) equilibrium between solid solutions (3) and  $\beta\text{-Na}_2\text{SO}_4\text{-BaSO}_4$ .

The addition of barium sulphate to potassium sulphate raises the melting point to a maximum of  $1080^\circ$  for a concentration of 90%  $\text{K}_2\text{SO}_4$ . As this composition would correspond with 14 mols. of  $\text{K}_2\text{SO}_4$  per mol. of  $\text{BaSO}_4$ , this maximum cannot represent a compound of the two salts. Beyond this concentration of  $\text{BaSO}_4$ , the melting point falls to  $1015^\circ$  for 60%  $\text{K}_2\text{SO}_4$ , this being the eutectic temperature. Further increase in the concentration of  $\text{BaSO}_4$  is accompanied by rise of the temperature to the melting point of the barium salt. The cooling curves of this system show, in general, three changes of direction; exceptions are that corresponding with 95%  $\text{K}_2\text{SO}_4$ , which represents the eutectic of the decomposition curve of the solid solutions, and that corresponding with 60%  $\text{K}_2\text{SO}_4$ , which is the eutectic mixture of the melting curve. Curves up to 70%  $\text{K}_2\text{SO}_4$  exhibit a point corresponding with the crystallisation of mixed crystals, another with the decomposition of the solid solutions, and a third with transformation of the potassium sulphate. The curves from 60%  $\text{K}_2\text{SO}_4$  to  $\text{BaSO}_4$  show a temperature of primary separation of barium sulphate, a eutectic temperature, and a temperature of transformation of the potassium salt.

T. H. P.

**Reciprocal Salt Pairs. II. The Salt Pair  $K_2Cl_2$ - $MgSO_4$ ,  $MgCl_2$ - $K_2SO_4$ .** ERNST JÄNECKE (*Zeitsch. physikal. Chem.*, 1912, 80, 1—12. Compare Abstr., 1908, ii, 841).—Of the four binary systems which can be formed by the salt pairs  $K_2Cl_2$ - $MgSO_4$ ,  $MgCl_2$ - $K_2SO_4$ , three have already been investigated. One of these has recently been examined by Menge (compare Abstr., 1911, ii, 982), who drew the conclusion that besides the double salt,  $KMgCl_3$ , the compound  $K_2MgCl_4$  exists within narrow limits. The author shows from a graphic representation of Menge's results, that there is no evidence of the existence of the last-mentioned compound.

The remaining binary system,  $MgCl_2$ - $MgSO_4$ , has been investigated by the thermal method. No compounds are formed; the eutectic contains about 20 mol. % of magnesium sulphate. The latter salt melts about  $1185^\circ$  with slight decomposition.

Further, a new salt,  $KMgClSO_4$ , has been prepared; it has a congruent melting point about  $920^\circ$ . It is best obtained by mixing finely powdered potassium chloride and magnesium sulphate in a covered crucible, and heating before the blowpipe until the mass fuses; on cooling, the new compound separates in tetrahedral crystals. It has not been obtained quite pure.

The limits of the different fields have been determined in a series of mixtures by the thermal method, the positions of breaks in the cooling curves being noted. The complete system is represented in a square and also on a projected space diagram. G. S.

**Glucinum Chromates.** BENNO BLEYER and A. MOORMANN (*Zeitsch. anorg. Chem.*, 1912, 76, 70—78).—The authors have failed to obtain the two crystalline salts,  $GlCrO_4 \cdot H_2O$ , and  $GlCrO_4 \cdot 6Gl(OH)_2$ , prepared by Glasmann (Abstr., 1907, ii, 545). Precipitation of glucinum sulphate by potassium chromate yields impure, amorphous products of varying composition, whilst the precipitate from the chloride has the composition  $15GlO \cdot CrO_3 \cdot 12H_2O$ , independently of the proportions of the reacting substances. Glucinum hydroxide and chromic acid yield only resinous masses, but the clear solution contains glucinum and chromium in the ratio 1:1. C. H. D.

**The Influence of Tin and Lead on the Micro-structure of Brass.** FREDERICK JOHNSON (*J. Inst. Metals*, 1912, 7, 201—217).—Tin is only very slightly soluble in the  $\alpha$ -solid solution of brass containing 30% of zinc. It dissolves readily in the  $\beta$ -solid solution of alloys containing more zinc. When lead and tin are both present, any excess of tin separates as the compound  $Cu_4Sn$ , and not as an alloy with lead. C. H. D.

**Power of Potable Water to Dissolve Lead.** PIETER A. MEERBURG (*Chem. Weekblad*, 1912, 9, 494—497. Compare Woudstra and Snuif, *ibid.*, 447).—The author is of opinion that the solubility of lead in water depends on the influence of all the constituents of the water and not on that of one constituent. It also depends on the proportions of the various constituents present. The solubility of lead

in a given water cannot be predicted from a chemical examination of either the water or the material of the service pipes.

A. J. W.

**The Behaviour of Lead, Cuprous and Silver Sulphides, and of Cuprous Oxide in the Corresponding Fused Chlorides.** WILHELM TRUTHE (*Zeitsch. anorg. Chem.*, 1912, 76, 161—173).—Lead sulphide and lead chloride mix in the fused state. Solid solutions are not formed, and the eutectic point lies at  $441^{\circ}$  and 22% PbS. Microscopical examination of the eutectic mixture shows that the sulphide determines the crystalline arrangement.

The eutectic point of mixtures of cuprous sulphide and cuprous chloride lies at  $392^{\circ}$  and 16%  $\text{Cu}_2\text{S}$ . Solid solutions are not formed. The sulphide crystals show great power of orientation.

Silver sulphide is capable of retaining about 5% of silver chloride in solid solution on crystallising, but deposits it before reaching the transformation point at  $175^{\circ}$ . The eutectic point lies at  $375^{\circ}$  and 54%  $\text{Ag}_2\text{S}$ . Both components form well-developed primary crystallites.

Cuprous oxide separates as primary crystals from all its mixtures with cuprous chloride, the latter taking the place of a eutectic, and solidifying at its usual freezing point of  $423^{\circ}$ .

C. H. D.

**The System Lead Sulphide-Tin Sulphide.** W. HEIKE (*Metallurgie*, 1912, 9, 313—319).—Mixtures of lead sulphide and stannous sulphide are melted in an atmosphere of nitrogen. Two series of solid solutions are formed, extending from 0 to 8% and from 38.7 to 100% SnS. The end concentration of this second series corresponds with the formula  $\text{PbS}, \text{SnS}$ , but it uncertain whether a compound actually exists. The slope of the last branch of the curve is very slight. Optical examination confirms the thermal results.

C. H. D.

**The Analogy between Copper and Silver.** GIUSEPPE A. BARBIERI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 560—563).—A salt of bivalent silver may be prepared by adding a solution of silver nitrate (1 mol.) in pyridine (6 mols.) to a cold solution of potassium persulphate (8 mols.). The yellow precipitate obtained has the composition  $\text{Ag}_2\text{S}_2\text{O}_8 \cdot 4\text{C}_5\text{NH}_4$ , resembling the corresponding cupric salt (Abstr., 1911, ii, 889). If very dilute solutions are used, the silver and copper compounds may be precipitated simultaneously, and by varying the proportions of the two metals, mixed crystals are obtained showing gradations of colour between the orange silver and the violet copper salts, proving the isomorphism of the two compounds.

C. H. D.

**The Properties of Alloys at High Temperatures.** GUY D. BENGOUGH (*J. Inst. Metals*, 1912, 7, 123—190).—The curves showing the variation of the breaking stress and elongation of metals with temperature have abrupt changes of direction, which occur at  $650^{\circ}$  in copper and at  $395^{\circ}$  in aluminium. These points are termed

"mechanical critical points." Above these temperatures, the mechanical properties of worked and unworked metals become identical, and the metal emits a "cry" like that of tin when strained. It is considered that this temperature represents the point at which the last traces of amorphous material disappear, and the metal becomes wholly crystalline. C. H. D.

**The Critical Point at 470° in Copper-Zinc Alloys.** HENRY C. H. CARPENTER (*J. Inst. Metals*, 1912, 7, 70—104).—Alloys of copper and zinc consisting mainly of the  $\beta$ -solid solution show a development of heat at 470° on cooling. It has not been found possible to detect any change in microscopic structure in pure  $\beta$ -alloys on cooling through this range, but if alloys containing respectively 45.77 and 49.61% of zinc ( $\beta$  with traces of the  $\alpha$  and  $\gamma$  constituents respectively) are heated for several weeks in a bath of sulphur vapour at 444.7°, resolution into the  $\alpha$  and  $\gamma$  solid solutions takes place. It is considered that 470° is a eutectoid point, and that the  $\beta$ -constituent is only stable above that temperature, the conditions thus being exactly similar to those prevailing in the copper-tin and copper-aluminium alloys.

The resolution of  $\beta$  into  $\alpha$  and  $\gamma$  is accelerated by the presence of aluminium. C. H. D.

**Thermal Analysis of Binary Mixtures of Chlorides of Univalent Elements.** CARLO SANDONNINI and P. C. AUREGGI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 493—498. Compare Abstr., 1911, ii, 606, 800; this vol., ii, 162).—Rubidium and cuprous chlorides give a somewhat complicated solidification diagram, falling from the m. p. of the rubidium salt (716°) to about 252° (51 mol. % CuCl), then to about 190° (60 mol. % CuCl), and finally to the eutectic point, 150° (68 mol. % CuCl); subsequent rise to the m. p. of cuprous chloride (422°) occurs.

The cooling curves of mixtures containing 0—51 mol. % CuCl show a point of arrest at 232—260°, the maximum duration being at 30—35 mol. % CuCl. With 20—60 mol. % CuCl, the curves show also arrests at 180—190°, the maximum duration being at 35—60 mol. %.

Crystallisation of the two salts together, under various conditions, leads to the formation of the compounds  $2\text{RbCl}, \text{CuCl}$  and  $2\text{RbCl}, 3\text{CuCl}$ , the existence of which probably explains the arrests in the cooling curves. T. H. P.

**Some Ammonio-Copper Mercuric Iodides and an Ammonio-Copper Iodide.** FRANCESCO ANDERLINI (*Gazzetta*, 1912, 42, i, 321—332).—Two ammonio-copper mercuric iodides are already known,  $\text{CuI}_2, \text{HgI}_2, 4\text{NH}_3$  and  $\text{CuI}_2, 2\text{HgI}_2, 4\text{NH}_3$ . Both of these are stable in closed vessels, but lose ammonia and iodine in contact with air.

The compound,  $\text{CuHgI}_3, 2\text{NH}_3$ , is obtained by adding ammonium sulphite to a solution of a copper salt, heating nearly to boiling, and adding a solution of potassium mercuric iodide. Mercury separates, and the solution is maintained at about 50° until clear. It is then filtered, and the brownish-yellow crystals which separate from the

filtrate on cooling are washed with aqueous alcohol and dried. Ammonia in the presence of air converts it into the corresponding blue cupric salt with  $4\text{NH}_3$ .

The compound,  $\text{CuHg}_2\text{I}_5 \cdot 3\text{NH}_3$ , is obtained by dissolving the product of the action of ammonia on mercuric iodide in ammonium sulphite, heating, and adding an ammoniacal solution of copper iodide. The blue liquid, if kept at  $60-70^\circ$ , gradually becomes yellow, and yellow crystals are deposited on cooling. Bright greenish-yellow crystals of a compound,  $\text{CuHg}_2\text{I}_5 \cdot 4\text{NH}_3$ , are obtained if the solutions are mixed cold and then warmed at  $50^\circ$  until the precipitate has redissolved.

The blue compound,  $\text{CuI}_2 \cdot \text{HgI}_2 \cdot 4\text{NH}_3$ , is converted into the green compound,  $\text{CuI}_2 \cdot 2\text{HgI}_2 \cdot 4\text{NH}_3$ , by dissolving in concentrated neutral solutions of ammonium salts, ammonia being lost:  $2[\text{CuI}_2 \cdot \text{HgI}_2 \cdot 4\text{NH}_3] = \text{CuI}_2 \cdot 2\text{HgI}_2 \cdot 4\text{NH}_3 + \text{CuI}_2 \cdot 4\text{NH}_3$ . The original compound is recovered on the addition of ammonia.

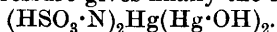
A compound,  $\text{CuHg}_3\text{I}_5 \cdot 5$  or  $6\text{NH}_3$ , has also been obtained.

*Ammonio-cuprous iodide*,  $\text{Cu}_2\text{I}_2 \cdot \text{NH}_3$ , prepared by adding an excess of ammonia to the solution containing the first ammonio-copper mercury compound, forms pale yellow scales, becoming blue in moist air.

C. H. D.

**Sulphonated Metal-amides of Mercury, Silver, and Gold, Obtained from Amido-sulphonic Acid.** KARL A. HOFMANN, ERNST BIESALSKI and ELLA SÖDERLUND (*Ber.*, 1912, 45, 1731—1736. Compare Divers and Haga, *Trans.*, 1896, 69, 1634; Kirmreuther, *Abstr.*, 1911, ii, 1098).—*Potassium mercuriamido-sulphonate*,  $\text{NHg} \cdot \text{SO}_3\text{K}$ , is obtained by neutralising 40 grams of amido-sulphonic acid with 10% potassium hydroxide, adding a further 40 c.c. of the alkali, and then digesting on the water-bath with the freshly precipitated mercuric oxide prepared from 100 grams of mercuric chloride. On concentrating the solution, the required salt separates, after cooling, in the form of thin, lancet-shaped flakes, which are strongly doubly-refracting. The salt crystallises only very slowly from solution, even when inoculated with a crystal, the various phenomena observed indicating that the crystals are probably polymerides of the molecules in solution; the same holds for the other salts to be described. The interaction of the salt with a number of reagents is described, the results all pointing to the fact that it is a true derivative of amido-sulphonic acid.

If carbon dioxide is passed for some time through the mother liquors obtained in the preparation of the above salt, an amorphous white precipitate of *potassium hydrogen trismercuri-bis-amido-sulphonate*,  $\text{KH}(\text{SO}_3\text{N})_2\text{Hg}(\text{Hg} \cdot \text{OH})_2 \cdot \text{H}_2\text{O}$ , is obtained. Complete saturation with carbon dioxide under pressure gives finally the free acid,



*Sodium mercuri-amido-sulphonate*,  $\text{NHg} \cdot \text{SO}_3\text{Na}$ , is prepared similarly to the potassium salt; it forms radiating clusters, or often felted masses, of slender, colourless needles. It differs from the potassium salt in that it is soluble in almost neutral water on heating, whereas the addition of alkali is necessary to dissolve readily the former salt.

*Potassium silver-amido-sulphonate*,  $\text{NHAg}\cdot\text{SO}_3\text{K}\cdot\text{H}_2\text{O}$ , is obtained by the action of silver nitrate on an alkaline solution of potassium amido-sulphonate in the form of silky, colourless, flat needles, which are strongly double-refracting, with parallel extinction. The stability of the combination of silver with the amide-nitrogen is of the same order as in the silver ammonias. The salt is soluble in ammonia, the solution giving a precipitate of silver with formaldehyde, and a beautiful silver mirror with tetraformaltrisazine.

*Potassium bis-auri-tris-amido-sulphonate*,  $\text{Au}_2(\text{N}\cdot\text{SO}_3\text{K})_3$ , is prepared from gold chloride and an alkaline solution of potassium amido-sulphonate; it forms small, yellow, transparent, granular crystals, and detonates on heating. The ammoniacal solution gives a gold mirror with formaldehyde or tetraformaltrisazine. The aqueous solution catalyses hydrogen peroxide, colloidal gold being formed.

The above salts, especially the mercury salts, may possibly have medicinal applications. T. S. P.

**Mercurous Chromate.** FRITZ FICHTER and G. OESTERHELD (*Zeitsch. anorg. Chem.*, 1912, 76, 347—356).—The statement is usually made that the brown precipitate obtained from mercurous salts and chromates is a basic salt, passing into the red normal salt on boiling with water. It is now shown that the brown, amorphous precipitate is mercurous chromate,  $\text{Hg}_2\text{CrO}_4$ , which is only stable in the moist condition and at low temperatures. It passes spontaneously, especially on shaking, into the red, crystalline modification, the change beginning at isolated points and spreading through the mass. When an excess of chromate is used, the initial precipitate and also the transformation product are lighter in colour, owing to finer division. Prolonged washing with water on the filter converts the amorphous modification into the basic salt,  $\text{Hg}_2\text{O}\cdot 3\text{Hg}_2\text{CrO}_4$ . If a precipitate, obtained by using an excess of mercurous nitrate, is allowed to remain in contact with the solution, it is converted in the course of several days, or by boiling in a few hours, into small, dull red needles of a salt,  $\text{Hg}_2\text{O}\cdot 2\text{Hg}_2\text{CrO}_4$ . An intermediate formation of a double salt with the nitrate does not occur. Boiling with hydrochloric acid and titration of the chlorine shows that the mercury is not present in the mercuric form. The same salt is obtained by precipitating a hot solution with an excess of chromate. C. H. D.

**The Chemistry of Thorium and the Rare Earths.** The Solubility of the Oxalates and of the Sulphates in Sulphuric Acid. FRITZ WIRTH (*Zeitsch. anorg. Chem.*, 1912, 76, 174—200. Compare Hauser and Wirth, *Abstr.*, 1909, ii, 352).—In order to separate thorium from the rare earths by precipitation as oxalate, the supernatant solution should be about 5*N*-sulphuric acid. Thorium oxalate is, however, appreciably soluble in such acid, and if it is not necessary to separate from other rare earths, it is better to precipitate from a less acid solution. If the sulphuric acid is more than 10*N*, thorium oxalate dissolves, and thorium sulphate is slowly precipitated. Yttrium oxalate is converted into sulphate by 6.1*N*-acid, whilst the oxalates of erbium, gadolinium, and samarium

dissolve without decomposition. Erbium sulphate is five times as soluble in water as lanthanum sulphate, but the solubility of the two oxalates in sulphuric acid differs very little.

The solubility curves of thorium, cerium, and lanthanum sulphates in sulphuric acid have been determined, and photographs of the hydrated sulphates are given. Thorium sulphate nonahydrate crystallises better than the other hydrates, and it is desirable that it alone should be produced in the purification of thorium. Lanthanum sulphate nonahydrate is the stable salt under the usual conditions of separation. Cerous sulphate separates as the octahydrate.

The ascending order of solubility of the sulphates in water at the ordinary temperature is La, Y, Gd, Sa, Nd, Ce, Pr, Er, Yb, but the order is completely altered in the presence of sulphuric acid. The sulphates of the yttrium group suffer a much greater diminution of solubility than those of cerium and lanthanum. Gadolinium sulphate is the most sparingly soluble in 12*N*-sulphuric acid.

C. H. D.

**The Double Nitrates of the Rare Earths. II.** GUSTAV JANTSCH (*Zeitsch. anorg. Chem.*, 1912, **76**, 303—323. Compare Jantsch and Wigdorow, *Abstr.*, 1911, ii, 114).—Double nitrates of the composition  $[M'''(\text{NO}_3)_6]M''_3 \cdot 24\text{H}_2\text{O}$ , have been prepared, in which  $M'''$  represents lanthanum, cerium, praseodymium, neodymium, samarium, or gadolinium, and  $M''$  is magnesium, zinc, nickel, cobalt, or manganese, the only exception being gadolinium manganese nitrate, which is too soluble to be obtained in a crystalline form. All these double nitrates are isomorphous, and crystallise well. All of them melt in their water of crystallisation at a definite temperature, as shown in the table :

	Mg.	Ni.	Co.	Zn.	Mn.
La .....	113·5°	110·5°	101·8°	98·0°	87·2°
Ce .....	111·5	108·5	98·5	92·8	83·7
Pr .....	111·2	108·0	97·0	91·5	81·0
Nd .....	109·0	105·6	95·5	88·5	77·0
Sm .....	96·2	92·2	83·2	76·5	70·2
Gd .....	77·5	72·5	63·2	56·5	—

the order of fusibility being the same in each series. The solubility in water follows the same order as the fusibility, the magnesium salts being the least soluble. The cerium double nitrates are, however, less soluble than those of lanthanum, although this is contrary to what is observed in the fractional crystallisation of mixtures of the double nitrates. The isomorphous bismuth salts are found to be more soluble than those of gadolinium.

The molecular volume curves show a close parallelism for the magnesium, manganese, nickel, cobalt, and zinc salts. The cobalt salts have a greater molecular volume than the nickel salts, and the neodymium salts a greater molecular volume than those of praseodymium, so that in both these cases the order is the reverse of that to be expected from the periodic arrangement. This is in accordance with previous observations in this series.

C. H. D.

**Scandium.** RICHARD J. MEYER and H. GOLDENBERG (*Chem. News*, 1912, 106, 13—14).—It having been found that iodic acid is an excellent reagent for separating thorium from mixtures with other earths (Abstr., 1910, ii, 853; 1911, ii, 825), the authors have applied it to the separation of scandium and thorium. By means of an excess of potassium iodate, thorium iodate is precipitated from a nitric acid solution as a flocculent, amorphous precipitate. Sufficient potassium iodate is used to precipitate simultaneously some scandium iodate, otherwise a complete separation of the thorium cannot be ensured.

Different specimens of scandium oxide, which had been freed from thorium by the above method, gave 44.11—44.20 as the atomic weight of scandium, in agreement with the results obtained by Nilson. Speter (Abstr., 1910, ii, 854), using the sodium carbonate method to separate scandium from thorium, obtained a scandium oxide which spectrographic and electrometric methods showed to be free from thorium, but which gave an atomic weight of 45 for scandium. The authors find that the oxide of atomic weight 45 gives an arc spectrum identical in every respect with that of the oxide of atomic weight 44.1, and draw the conclusion that the spectrographic and electrometric methods are not sensitive enough to detect 0.5% of thorium oxide in scandium oxide. The determination of the coefficient of magnetisation afforded, however, a delicate method of discriminating between the two oxides, the coefficient of magnetisation of the oxide of atomic weight 45 being  $+0.04 \times 10^{-6}$ , that of the other oxide being  $-0.12 \times 10^{-6}$ . This scandium is diamagnetic, as also are its homologues lanthanum and yttrium in the third group of the periodic system.

The regeneration of the scandium from the solution containing iodic acid is very troublesome, and the yields are unsatisfactory. The following method for separating scandium and thorium is to be preferred. The neutral solution of scandium containing thorium is dropped slowly into a concentrated solution of ammonium tartrate, which is kept well stirred, and the clear solution thus obtained is precipitated with ammonia while boiling. The scandium separates as scandium ammonium tartrate; after being collected, it is washed with a dilute solution of ammonium tartrate. The oxide obtained from the double tartrate gave an atomic weight of 43.90 for scandium.

Further experiments are necessary to determine the accurate atomic weight of scandium.

T. S. P.

**Action of Water on Aluminium "Activated" by Mercury.** ÉMILE KOHN-ABREST (*Bull. Soc. chim.*, 1912, [iv], 11, 570—576. Compare Abstr., 1910, ii, 506; this vol., ii, 648).—Aluminium foil containing 0.4 to 0.5% of copper is not activated by immersion in a 1% solution of mercuric chloride. Neither are alloys of aluminium with silicon, obtained by heating it to 1100° in silicon vapour (compare Abstr., 1910, ii, 212).

The oxide which is first formed, when activated aluminium acts on water, is obtained as black, very dense flocks. Towards the end of the reaction, a lighter layer is formed, which gradually becomes white. If this mixture of oxides is heated in boiling water, the whole instantly

becomes white. The black oxide, when dried, is pearl-grey in colour, and neither oxidises in air nor takes up water. Its colour is probably due to impurities in the aluminium used, no mercury being detected in it. The author draws the conclusion that by the oxidation of aluminium in cold water, a mixture of hydroxides is formed, varying in composition according to the conditions, such as the duration of oxidation, etc.

W. G.

**The Light Alloys of Aluminium, Zinc, and Copper.** MARIO LEVI-MALVANO and M. MARANTONIO (*Gazzetta*, 1912, 42, i, 353—360).—The part of the ternary system now studied is limited to alloys rich in aluminium, and is bounded by (a) a curve representing the composition of the saturated solid solutions of aluminium, zinc, and  $\text{Cu}_3\text{Al}$ ; (b) the eutectic curve, connecting the eutectic of the system  $\text{Cu}_3\text{Al}$ —Al with that of the system Al—Zn; (c) two curves starting from the transformation points of the system  $\text{Cu}_3\text{Al}$ —Al and intersecting the eutectic curve in two invariant points, one of which has been fixed at  $400^\circ$ . Alloys with 2% Cu and 10 or 20% Zn are completely homogeneous, while those with 6 or 10% Cu and 10 or 4% Zn contain two constituents.

C. H. D.

**The System Iron—Carbon.** ANDREAS SMITS (*Zeitsch. Elektrochem.*, 1912, 18, 362—368. Compare Ruff, this vol., ii, 353).—It is shown that the views of Ruff (*loc. cit.*) on the interpretation of his experiments on the iron—carbon equilibrium are erroneous; his results indicate the existence of hitherto unknown stable carbides or of two new modifications of graphite. The former alternative is the more probable, and a theoretical discussion of the system is given on the provisional assumption that the new carbides are represented by the formulæ  $\text{FeC}$  and  $\text{FeC}_2$  respectively. The pressure-temperature projection and two sections of the equilibrium diagram are given, and it is shown that the three-phase line carbon— $\text{FeC}$ —graphite falls with rise of temperature. The conditions under which this takes place are discussed.

G. S.

**The Formation of Osmondite in Hypo-eutectoid Steels.** J. CALIAN (*Metallurgie*, 1912, 9, 392—396).—Steels containing less than 0.9% of carbon, like those of eutectoid composition, pass through a condition corresponding with that of osmondite during cooling, but this condition may be produced at temperatures between  $300^\circ$  and  $500^\circ$ . In this state, the rate of solution in dilute sulphuric acid is a maximum. At any one temperature, the proportion of carbon present as carbide increases with diminishing carbon content.

C. H. D.

**Iron Dicarbide.** NICOLAI N. LJUBAVIN [with ZORIN and BUNZEN] (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 609—613).—The existence of the compound  $\text{FeC}_2$ , rendered probable by the results obtained by von Wittorf (this vol., ii, 259), is confirmed by the author's experiments. When heated, ammonium ferrocyanide or its double compound with ammonium chloride,  $(\text{NH}_4)_4\text{Fe}(\text{CN})_6 \cdot 2\text{NH}_4\text{Cl} \cdot 3\text{H}_2\text{O}$  yields a black

powder, which is attracted by a magnet and is sometimes accompanied by a non-magnetic brown substance. When ignited in the air, the black compound is converted into ferric oxide without change of weight, its composition being hence  $\text{FeC}_2$ ; the ferric oxide obtained in this way seems to be magnetic.

T. H. P.

**Nickel as a Catalyst.** JEAN B. SENDERENS and J. ABOULENC (*Bull. Soc. chim.*, 1912, [iv], 11, 641—646).—Samples of anhydrous nickel oxide obtained by calcination, when submitted to the action of hydrogen, do not begin to show reduction below  $300^\circ$ , and even at more elevated temperatures the action ceases when the reduction is about two-thirds complete; this stage of the reduction is not a definite one, and cannot be regarded as proof of the existence of an oxide,  $\text{Ni}_2\text{O}$ ; the mixture of oxide and metallic nickel is pyrophoric, and shows fair catalytic activity. If the temperature is raised higher (above  $420^\circ$ ), the reduction can be completed, but the resultant metal, although pyrophoric, is not so effective as a catalyst.

Samples of nickel hydroxide, whether dehydrated before heating in the current of hydrogen or not, can be reduced more easily than the above oxides, the completion of the reduction again requiring a higher temperature than the main portion of the process. The final products show good catalytic activity.

Nickel oxide resulting from the oxidation (spontaneous or otherwise) of pyrophoric nickel is reducible even more easily than nickel hydroxide, and the nickel obtained shows greater catalytic activity than any of the preceding. The importance of this lies in the fact that the nickel catalyst may lose its activity by overheating, or by long use in the reduction of one substance may become passive to others (compare Bouveault, *Abstr.*, 1908, i, 117). By oxidising the nickel and then subjecting it once more to reduction, the original activity can be fully restored. Any excessive activity of the regenerated nickel can be moderated by raising it to a suitable temperature.

D. F. T.

**Chromites from Basic Chromates.** MAX GRÖGER (*Zeitsch. anorg. Chem.*, 1912, 76, 30—38).—When basic chromates are ignited, only a part of the second metallic oxide present is extracted by hydrochloric acid, although the residue is in a very fine state of division. Experiments with magnesium, zinc, cadmium, copper, nickel, and cobalt chromates show that the residue always contains more of the base than corresponds with the formula  $\text{MO}, \text{Cr}_2\text{O}_3$ , either as a basic chromite or as a solid solution. Basic iron chromate, even if heated in hydrogen, leaves a residue which contains a part of the iron as  $\text{Fe}_2\text{O}_3$ , whilst the precipitate obtained from manganous chloride and sodium chromate is not a manganous chromate, but a chromimanganite, and the ignited residue is completely soluble in concentrated hydrochloric acid.

C. H. D.

**Uranic Anhydride and its Hydrates.** PAUL LEBEAU (*Compt. rend.*, 1912, 154, 1808—1811. Compare this vol., ii, 650).—Uranic anhydride,  $\text{UO}_3$ , as prepared from the nitrate by the ordinary methods,

always retains some water and nitrogen. It may be obtained pure by heating in a current of oxygen, uranic acid, or the mixture of anhydride and acid made by heating the nitrate at a low temperature, at 500°. On contact with water, it is transformed directly into uranic acid,  $\text{UO}_2(\text{OH})_2$ .

The concentrated solution of uranic nitrate dissolves considerable quantities of uranic acid. If the solution is evaporated at 100° and the residue extracted with ether, crystallised uranic acid is obtained. If evaporated at the ordinary temperature in a vacuum over sulphuric acid, extraction with ether leaves a residue of hydrated uranic acid,  $\text{UO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ , which loses  $1\text{H}_2\text{O}$  at 100°, even when boiled with water.

T. S. P.

**Solubility of Thorium Sulphate in Sulphuric Acid and in Solutions of Lithium Sulphate.** MAURICE BARRE (*Bull. Soc. chim.*, 1912, [iv], 11, 646—648. Compare Abstr., 1910, ii, 718).—The solubility of thorium sulphate in a solution of lithium sulphate at 25° increases continuously and considerably as the concentration of the lithium sulphate increases, the solid phase being always thorium sulphate. The great increase in solubility is probably due to the formation of a complex salt in solution.

In a solution of sulphuric acid the solubility at 25° of thorium sulphate increases until the concentration of the sulphuric acid is 3—4%, and then diminishes. The solid phase in contact with the solution is normal thorium sulphate, but it is possible that the maximum observed in the solubility curve is due to the formation of an acid sulphate in solution.

T. S. P.

**System  $\text{Sb}_2\text{S}_3$ — $\text{SnS}$ .** NICOLA PARRAVANO and PIETRO DE CESARIS (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 535—540).—In investigating the melting-point diagram of this system, the fusion and cooling were carried out in an atmosphere of nitrogen.

The results indicate the formation of a compound, probably of the formula  $\text{Sb}_2\text{S}_3 \cdot \text{SnS}$  or  $\text{Sn}(\text{SbS}_2)_2$ . Antimony sulphide does not give solid solutions, or does so only with very small concentrations of stannous sulphide; the latter, however, gives solid solutions containing up to about 15% of antimony sulphide.

T. H. P.

**Electrolytic Reduction of Columbic Acid.** FRIEDRICH OTT (*Zeitsch. Elektrochem.*, 1912, 18, 349—362).—In the majority of the experiments a lead cathode was used. When columbium pentachloride is reduced in hydrochloric or sulphuric acid solution, or in an alcoholic solution of hydrogen chloride, reddish-brown to black solutions are obtained, which contain tervalent columbium. Sodium columbate in hydrochloric acid solution yields on reduction a green solution, which contains quadrivalent columbium. Fused potassium fluoxycolumbate,  $\text{K}_2\text{CbOF}_5$ , yields on electrolytic reduction a bluish-black product, which also contains quadrivalent columbium. When columbium pentafluoride is reduced in sulphuric acid solution at a platinum cathode, a blue solution, which appears to contain a compound

of quadrivalent and quinquivalent columbium (corresponding with the oxide,  $\text{Cb}_3\text{O}_7 = \text{Cb}_2\text{O}_5, \text{CbO}_2$ , is obtained.

No definite solid compounds could be isolated from the hydrochloric acid solutions, but from a sulphuric acid solution a double salt was obtained in reddish-brown crystals, the probable composition of which is  $\text{Cb}_2(\text{SO}_4)_3, (\text{NH}_4)_2\text{SO}_4, 6\text{H}_2\text{O}$ , although they were not obtained quite free from adherent sulphuric acid. G. S.

**Reduction of Gold in Silicic Acid Gels and the Formation of Gold Deposits.** EMIL HATSCHEK and A. L. SIMON (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 265—268).—It is shown that the peculiarities in connexion with the occurrence of gold in quartz can be explained on the assumption that it was reduced from a salt solution in a silicic acid gel. In the experiments both solutions and gases were used as reducing agents; in the former case the reducing agent was poured over the gel which contained gold chloride in solution, in the latter case, the gel, contained in a test-tube, was exposed to the reducing gas. The gold was obtained in very different degrees of dispersion, depending on the nature of the reducing agent and the conditions, but under suitable conditions practically all the reducing agents caused the separation of gold in crystalline form. The gold is deposited either in the gel or at the surface of the gel, or in both positions, depending on the osmotic relationships of solution and gel. Further, the gold has been deposited in layers, and, finally, when acetylene is used as reducing agent, carbon and gold are deposited simultaneously. Similar phenomena are observed in the native deposits, and can be readily explained on the basis of the authors' experiments.

The paper is illustrated by photographs in three colours of the products obtained with different reducing agents, the layers appearing very clearly in several of the tubes. G. S.

**Colloidal Platinum.** CHB. KELBER and ANTON SCHWARZ (*Ber.*, 1912, 45, 1946—1952).—See this vol., i, 617.

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### Mineralogical Chemistry.

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The Practice of Krystallochemical Analysis. EUGRAPH STEPANOWITSCH FEDOROFF (*Zeitsch. Kryst. Min.*, 1912, 50, 513—575). —When a crystal is given the correct setting in either the cubic or hypohexagonal types of the author, there may be derived from the form-complex a complex-symbol depending on the reticular density of the faces, which is highly characteristic of the substance. Several examples are worked out, and in tables to be shortly published, the symbols are given for about 10,000 substances, from which it will be possible to identify any one of them by means of the crystal measurements alone.

L. J. S.

**Albanite.** CONSTANTIN I. ISTRATI and M. A. MIHAILESCU (*Chem. Zentr.*, 1912, i, 1587; from *Bul. Soc. Române Științe, București*, 1912, 20, 626—629).—This name is applied to a black, lustrous substance, with a resinous aspect, found in Albania; D 1.644. It fuses with bubbling between 85° and 110°, and it burns with a sooty flame. Nitrogen and sulphur are not present. Subjected to dry distillation, it gives off water at 100°, and between 195° and 305° much gas (12 litres per 100 grams); above 305° a yellow liquid distils over. The material is slightly soluble in chloroform, and pentane extracts 34.42% of a brown hydrocarbon, m. p. 185—210°. L. J. S.

**Analysis of Molybdenite from Calabria.** RAFFAELLE NASINI and ENRICO BASCHIERI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 692—696).—Molybdenite occurs, disseminated in quartz, in the Stilo district of Calabria. The molybdenum was found to be 57.84 and 59.30%, and the sulphur 41.20%. The reactions described by Ogawa (*Abstr.*, 1908, ii, 952) as characteristic of nipponium were not observed. C. H. D.

**The Identity of Synchysite and Parisite.** EMANUELE QUERCIGH (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 581—588).—The mineral found at Narsasuk was distinguished from parisite by Flink (*Abstr.*, 1900, ii, 410) under the name of synchysite. It was, however, considered by Palache and Warren (*Abstr.*, 1911, ii, 614) that synchysite was merely an altered parisite. In order to determine the question, the optical properties have been studied, a crystal of synchysite and one of typical parisite being taken, and a prism cut from each with the refracting edge parallel with the optic axis. The refractive indexes of the two minerals are not identical,  $\epsilon$  being greater for parisite and  $\omega$  for synchysite, throughout the spectrum, but the differences are small, and diminish towards the violet, both minerals showing anomalous dispersion. The anomaly is less for the ordinary than for the extraordinary ray. An analysis of synchysite gives  $R_2O_3$  60.95% and CaO 11.96%, against 60.71% and 10.70% for parisite. The density of the two minerals is also sensibly the same, and their identity is now certain. C. H. D.

**The Rutile Group.** WALDEMAR T. SCHALLER (*Bull. U.S. Geol. Survey*, 1912, No. 509, 9—39).—The several minerals (rutile, cassiterite, mosseite, tapiolite, nigrine, iserite, ainalite, ilmenorutile, and strüverite) of this group are tetragonal with  $a:c$  near 1:0.64, and by twinning they give rise to pseudo-orthorhombic forms. They are to be regarded as isomorphous mixtures of two or more of the following compounds: ferrous columbate,  $Fe(CbO_3)_2$ , ferrous tantalate,  $Fe(TaO_3)_2$  (tapiolite), ferrous titanate,  $Fe(TiO_3)$ , titanyl titanate,  $(TiO)(TiO_3)$  (rutile), stannyl stannate  $(SnO)(SnO_3)$  (cassiterite), and ferrous stannate,  $Fe(SnO_3)$ , sometimes with small amounts of zinc arsenate,  $Zn(AsO_3)_2$ , etc. The published analyses are discussed, and the percentages of these compounds present are calculated. For example, the strüverite from Piedmont (*Abstr.*, 1908, ii, 398) is interpreted as consisting of 29.9% ferrous columbate, 27.4% ferrous tantalate, 2.6% ferrous titanate, and

40·1% titanyl titanate; and that from South Dakota (Abstr., 1911, ii, 499) as 8·4% ferrous columbate, 41·4% ferrous tantalate, 48·8% titanyl titanate, and 1·4% stannyl stannate. Few of these minerals deserve special names, and are better described as columbium tapiolite (instead of mossite), iron rutile (instead of nigrine and iserite), etc.

L. J. S.

**A New Occurrence of Carnotite.** EDGAR T. WHERRY (*Amer. J. Sci.*, 1912, [iv], 33, 574—580).—An amorphous to minutely crystalline, bright yellow powder, occurring as an impregnation in conglomerate at Mt. Pisgah, Carbon Co., Pennsylvania, is identified by analysis with carnotite (Abstr., 1910, ii, 308). The small amount of material scraped together for analysis gave the results under I; deducting quartz, limonite, etc., the figures under II agree approximately with the ratios  $(\text{Ca}, \text{K}_2)\text{O}_2 \cdot 2\text{UO}_2 \cdot \text{V}_2\text{O}_5$ . This and the earlier analyses of material from Colorado and South Australia indicate that carnotite is a definite species with the formula  $(\text{Ca}, \text{K}_2)(\text{UO}_2)_2(\text{VO}_4)_2 \cdot x\text{H}_2\text{O}$ , and belonging to the uranite group:

	$\text{V}_2\text{O}_5$	$\text{UO}_2$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{K}_2\text{O}$	$\text{H}_2\text{O}$	Insol.	Total.
I.	7·2	23·8	6·1	1·5	[1·6]	10·5	49·3	100·0
II.	21·1	69·8	—	4·4	4·7	—	—	100·0

Suggestions are made as to the mode of origin of carnotite in sedimentary rocks.

L. J. S.

**Natrolite from San Benito Co., California.** B. JEŽEK (*Zeitsch. Kryst. Min.*, 1912, 50, 638; from *Rozpr. Böh. Akad.*, 1909, 18, 2 Kl., No. 26, 1—6).—The white matrix of the crystals of benitoite and neptunite from this locality consists of natrolite. In cavities, good crystals of unusual habit are developed, these show pyramid faces, but only small prisms. The new form  $\alpha\{535\}$  is noted. Analysis by J. Švéda gave the following results, corresponding with the formula  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot \text{H}_2\text{O}$ :

$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{Na}_2\text{O}$	$\text{H}_2\text{O}$	Total.	Sp. gr.
47·46	26·89	trace	16·52	[9·13]	100·0	2·23

L. J. S.

**The Binary System  $\text{Na}_2\text{Al}_2\text{Si}_2\text{O}_8$  (Nephelite, Carnegieite)— $\text{CaAl}_2\text{Si}_2\text{O}_8$  (Anorthite).** N. L. BOWEN (*Amer. J. Sci.*, 1912, [iv], 33, 551—573).—Mixtures in various proportions of these two compounds were heated up to 1549°, and from the heating curves and the results of microscopical examination of quenched samples an equilibrium diagram is constructed. The sodium compound is stable as soda-nephelite below 1248°, and as carnegieite above this inversion point. There is a eutectic with 45%  $\text{CaAl}_2\text{Si}_2\text{O}_8$  at 1302°. Mixed crystals range from Ne to  $\text{Ne}_{65}\text{An}_{35}$ , the former being optically negative and the latter positive. On the other hand, carnegieite takes up much less anorthite, the maximum being  $\text{Cg}_{95}\text{An}_5$ .

L. J. S.

**Druse Minerals from the Leucite-basanite of the Eulenberg near Leitmeritz, Bohemia.** JOSEF E. HIESCH and ARTHUR SCHEIT (*Tsch. Min. Petr. Mitt.*, 1911 [that is, 1912], 30, 459—474).—In the

marginal portions of this pipe of volcanic rock are numerous steam-cavities, the walls of which are lined with crystallised minerals, especially zeolites. These are described in detail, and analyses given of the following: Phillipsite, I colourless, II rose, by H. Walland; III colourless, by W. Widmar; these analyses are noteworthy in showing wide differences in composition:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	48·73	19·89	—	5·45	—	7·36	2·31	16·26	100·00
II.	51·31	18·31	—	4·94	—	6·96	2·37	16·12	100·01
III.	45·41	19·19	—	7·48	—	9·82	4·65	13·41	99·96
IV.	61·46	18·58	1·48	0·60	0·25	15·73	1·93	0·75	100·78

Sanidine occurs as minute, colourless crystals implanted on the phillipsite, and it was at one time mistaken for a second generation of phillipsite. Analysis IV corresponds with 93% of the orthoclase molecule, 2·8% of anorthite, and 4·4% of carnegieite (Or<sub>16</sub>AnCg<sub>3</sub>). L. J. S.

**Chemico-Mineralogical Observations on Beryls from Elba.** L. MADDALENA (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 633—639).—The author has investigated three samples of beryl from the pegmatites of S. Piero in Campo, Elba, I being colourless and quite clear, II delicate peach-blossom colour and clear, and III sky-blue and rather less clear. The analytical results are as follows:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	GIO.	CaO.	MgO.	Cs <sub>2</sub> O.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Li <sub>2</sub> O.	H <sub>2</sub> O.	Total.
I.	65·09	17·21	13·27	1·02	1·81	—	—	—	—	1·44	99·84
II.	64·39	20·08	11·40	1·06	0·56	—	0·41	—	—	1·27	99·17
III.	63·90	18·64	10·87	trace	trace	trace	1·61	2·28	—	1·62	98·92

The indices of refraction for sodium light are:

	I.	II.	III.
ω .....	1·57682—1·5769	1·57778	1·5916—1·59169
ε .....	1·57169—1·5717	1·57269	1·5850—1·58524

and the values of D, 2·6891, 2·6917, and 2·7639 respectively.

These results indicate for beryls from Elba the same quantitative relations between proportion of alkali, index of refraction, and specific gravity as were pointed out by Lacroix (Abstr., 1909, ii, 58) and confirmed by Ford (Abstr., 1910, ii, 873) and other authors for American and Madagascar beryls.

Comparison of the chemical and physical properties of these different beryls shows that neither by the chemical composition, nor by the optical properties, nor by the specific gravity is it possible to distinguish two well-defined types of beryls, as was assumed by Duparc, Wunder, and Sabot (Abstr., 1910, ii, 221, 312; 1911, ii, 1105). Rather is the conclusion to be drawn that there exists a continuous series of beryls (compare Lacroix and Rengade, Abstr., 1911, ii, 736). The presence of a small proportion of alkali seems to cause marked increase in the solvent power of beryls towards pigments.

Subjection of the three beryls from Elba to the action of radium radiation is without effect on the colour or refractive index.

T. H. P.

**Hatchettite [and Glauconite] from Bonarka, near Cracow.** JÓZEF MOROZEWICZ (*Zeitsch. Kryst. Min.*, 1912, 50, 661; from *Kosmos, Lemberg*, 1909, 34, 610—624).—Small cavities in glauconitic marl contain crystals of quartz and calcite, and on these occurs the hatchettite. Kaolin (nacrite) was also observed. These minerals appear to have been deposited by hot springs at a temperature of at least 80°. The glauconite fills the cells of foraminifera: analysis by Starzyński gave:

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	Total.	Sp. gr.
50·72	9·86	12·66	4·18	1·52	3·71	7·73	2·29	7·46	100·13	2·623

L. J. S.

**Two French Meteorites.** STANISLAS MEUNIER (*Compt. rend.*, 1912, 154, 1739—1741).—The one meteorite, which fell on June 30th, 1903, had  $D_4^{16} = 3·500$ . Analyses give the following results:

SiO <sub>2</sub> .	MgO.	CaO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	NiO.	Total.
36·60	24·14	trace	1·64	1·70	8·00	2·90	21·60	1·20	97·78

The meteorite is apparently a stone of the leucite group which has been considerably altered by lying in the ground.

The analysis of the other meteorite, which fell on July 4th, 1890, is not given.

T. S. P.

## Physiological Chemistry

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The Respiratory Exchange at Extreme External Temperatures in Relation to the Body Surface. The Time Course of Carbon Dioxide Production and Oxygen Consumption at Such Temperatures. HANS MURSCHHAUSER (*Zeitsch. physiol. Chem.*, 1912, 79, 301—326).—In dogs the percentage increase of carbon dioxide production at 5° as compared with that at 35° varied between 46 and 131; and of oxygen consumption between 36 and 91. The greatest increases occurred in the smallest animals. For medium temperatures there is parallelism between the surface of the body and metabolism, and even at extreme temperatures, the same holds if the body temperature remains constant. In some cases the rectal temperature fell considerably in the cold. Tables are given to show the time relationships of the alterations in gaseous exchange. W. D. H.

The Effects of Atmospheres Enriched with Oxygen on Living Organisms: (a) Micro-organisms; (b) Mammals Inoculated with Tuberculosis; (c) Normal Mammals. Oxygen Pneumonia. ALFRED ADAMS (*Bio.-Chem. J.*, 1912, 6, 297—314).—With *Bacillus tuberculosis*, *B. pestis*, and *Staphylococci*, increase of oxygen inhibits their growth, but does not kill them. It, however,

kills organisms on the border line of anaerobic life, such as *Actinomyces* and *Mycetoma*. The effect on *B. tuberculosis* does not hold in vivo, and the beneficial effects of fresh air are probably due to a physical stimulus. If less than 70% of oxygen is present, it can be inhaled without harm; above this percentage it causes pneumonia if inhaled beyond short periods.

W. D. H.

**The Reaction of the Blood.** CHRISTEN LUNDGAARD (*Biochem. Zeitsch.*, 1912, 41, 247—267).—The author gives a critical survey of the electrometric methods for measuring the alkalinity of the blood, and draws attention to the value of Hasselbalch's apparatus for this purpose. He calls attention more especially to the influence of the carbon dioxide tension on the hydroxyl-ion concentration, and recommends that the measurements should be referred to the concentration at the mean alveolar tension of carbon dioxide (40 mm.). When the measurement is made at other tensions, the true measurement at 40 mm. can be deduced from curves (given in the paper) showing the variations of the hydroxyl-ion concentration with the carbon dioxide tension. The concentration varies slightly with different animals. For the human subject,  $p_H = 7.19$  ( $CO_2 = 40$  mm.), a mean derived from the measurement of several cases, none of which show a great deviation therefrom.

S. B. S.

**The Heat Production of Chemical Processes in Living Cells (Blood Corpuscles).** OTTO MEYERHOF (*Pflüger's Archiv*, 1912, 146, 159—184).—The present research follows up the author's previous work on egg cells. Bird's corpuscles lend themselves very well to the work, as the oxidation rate is readily measured. The effect of varying conditions and different reagents was studied; thus narcotics produce no change in the caloric quotient, showing that their effect is not on the oxygen consumption, but on the energy-production. A number of observations on mammalian blood corpuscles are also given.

W. D. H.

**Simplification of Enzymes by Combined Autolysis and Dialysis.** BALDUINO BOCCI (*Proc. verb. R. Accad. Fisiocritici, Siena*, 1912).—Experiments with gastric and pancreatic juice indicate parallelism between the peptic, tryptic, rennetic, and lipolytic activities. The conclusion is drawn that in many tissues, more especially glandular tissues, there exists an enzyme for which the name *analase* is proposed. The blood plasma that transudes from the capillaries, the products of specific treatment of the tissues, and ions in general and hydrogen- and hydroxyl-ions in particular, activate the enzyme, which may be at one and the same time proteolytic (peptic, tryptic), rennetic, and lipolytic in character.

T. H. P.

**Presence of Erepsin in the Organs and its Distribution in the Mucous Membrane of the Digestive Tract.** GIUSEPPE AMANTEA (*Arch. Farm. sper. e Sci. affini*, 1911, 12, 1—12, Reprint).—For investigating the distribution of erepsin in organs and tissues the author employs Sørensen's method (*Abstr.*, 1908, i, 115), which is more suitable than the biuret reaction formerly in general use.

In the case of the dog, the greatest ereptic effect is obtained with the pancreas, and then follow the intestinal mucous membrane, the kidneys, the spleen, liver, lungs, muscles, and blood-serum. With the other animals examined (birds, reptiles, and amphibia) small differences are found in the order of the organs.

Erepsin occurs in the whole of the mucous membrane of the digestive channel from the œsophagus to the rectum. It is found to the least extent in the œsophageal and gastric mucus, and to the greatest in that of the duodenum.

T. H. P.

**Human Pancreatic Juice.** KARL GLAESSNER (*Biochem. Zeitsch.*, 1912, 41, 325—327).—The author criticises certain statements in a recent paper by Wohlgemuth (this vol., ii, 460). He does not accept as trustworthy, Wohlgemuth's method for detecting rennet in pancreatic juice, and he claims priority for the demonstration of the non-identity of trypsin and erepsin, having employed the same method as that described by Wohlgemuth.

S. B. S.

**The Action of Mineral Substances in the Animal Body.** OSKAR HAGEMANN (*Pflüger's Archiv*, 1912, 146, 455—483).—In growing lambs and calves the amount of mineral substances, especially lime and phosphoric acid, is important; poverty of these in the diet reduces nitrogenous assimilation. A factor of importance is the fine subdivision of the inorganic materials; unless this is observed, their beneficial (antirachitic) action is not so well manifested.

W. D. H.

**The Conditions of Formation of Ethereal Sulphates in the Animal Body.** FRITZ LADE (*Zeitsch. physiol. Chem.*, 1912, 79, 327—348).—The present experiments on dogs with Eck's fistula lend no support to the view that the liver is the seat of the synthesis involved in the formation of ethereal sulphates. Any action this organ may possess in relation to these substances is of another and unknown kind.

W. D. H.

**The Synthesis and Degradation of Sugars in the Animal Organism.** JAKOB PARNAS and JULIUS BAER (*Biochem. Zeitsch.*, 1912, 41, 386—418).—Two methods of experiments were adopted: (1) The injection of various substances into fasting rabbits after treatment with phloridzin, the estimation of the sugar excreted in the urine, and comparison of the amount formed when phloridzin had been injected without the substance under investigation; (2) the perfusion of the substances in Ringer's solution through a tortoise heat, of which one lobe had been ligatured, and comparing the amounts of glycogen found in the ligatured and unligatured parts. It was found that lactic, glyceric, and dihydroxymaleic acids, and also glycolaldehyde, give rise to dextrose and glycogen in the organism. On the other hand, hydracrylic,  $\alpha$ -hydroxybutyric, glycollic,  $\alpha\beta$ -dihydroxybutyric, glyoxylic, and pyruvic acids do not. It is therefore assumed that lactic acid is converted into dextrose with the formation of glyceric acid, dihydroxymaleic acid, and glycolaldehyde as intermediate products. The first stage is an oxidative process, and the

second stage an oxidative process accompanied by the scission of the elements of water, the third stage a scission of carbon dioxide, and the fourth a polymerisation. From 3 molecules of lactic acid is formed one of dextrose. The reactions are in all stages exothermic.

S. B. S.

**The Appearance of Glycogen after Feeding on Sugars and Fat, and Morphological Observations on the Snail (*Helix pomatia*).** H. ERHARD and F. ZIEGLWALLNER (*Zeitsch. Biol.*, 1912, 58, 541—557).—Glycogen was detected by microscopic means (Best's method). After some weeks' inanition, glycogen entirely disappears, from the body of the snail. Normally it is most abundant in the liver and ganglion cells. The fat of the body also disappears in inanition. Feeding on dextrose, galactose, mannose, lactose, oleic acid, stearic acid, and glycerol led in all cases to the reappearance of glycogen in the tissues. Palmitic acid, however, gave a negative result. W. D. H.

**Feeding Experiments Illustrating the Importance of Accessory Factors in Normal Dietaries.** F. GOWLAND HOPKINS (*J. Physiol.*, 1912, 44, 425—460).—Groups of young rats were fed on a basal diet of caseinogen, fat, carbohydrate and salts, and compared with those on the same diet plus a minute ration of fresh milk. The former soon ceased to grow; the latter grew normally. The consumption of food was practically the same throughout, but the milk addendum reduced the food necessary for a given weight increment to one-half or less. Cessation of growth occurred before loss of appetite appeared. What the actual substances are in the milk which thus markedly, although in a secondary way, affect growth is not yet known.

W. D. H.

**The "Sparing Action" of Fat.** ALFONS BARTMANN (*Zeitsch. Biol.*, 1912, 58, 375—419).—Fat exercises a small "sparing action" in nutrition, at most 7%. This taken as a function of the total intake is treated on mathematical lines. The varying increase in nitrogen output when fat is given in large amounts is due to its action as a stimulus, probably in the main to the digestive tract. The large amount of faeces and their high nitrogen content speak in favour of this view.

W. D. H.

**Feeding Experiments with Fat-free Food Mixtures.** THOMAS B. OSBORNE and LAFAYETTE B. MENDEL [with EDNA L. FERRY] (*J. Biol. Chem.*, 1912, 12, 81—89).—It is generally recognised that proteins and carbohydrates are indispensable in a diet. No such clear statement can be made in reference to fats; the lipoids, it is true, are constant constituents of protoplasm, and Stepp's experiments (*Abstr.*, 1911, ii, 1002) point to the view that they are indispensable for life and growth. Several observers, however, have shown the possibility that the phosphatides may be synthesised in the body from inorganic phosphates. In the present experiments rats were employed, and they continue to grow and thrive on a diet completely free from fat and almost free from lipoids; certainly any significant quantity of phosphatides or cerebrosides was absent.

W. D. H.

**Nitrogen Retention and Equilibrium on Feeding with Ammonium Salts.** WILHELM VÖLTZ (*Zeitsch. physiol. Chem.*, 1912, 79, 415—420).—A question of priority. The results published by Grafe and Schläpfer (this vol., ii, 363) are only confirmatory of the author's previous work. W. D. H.

**Purine Metabolism in Man. II. Are the Endogenous Purine Substances the Products of the Activity of the Digestive Glands?** WALTER O. SIVÉN (*Pflüger's Archiv*, 1912, 146, 499—516).—The answer given to the above question is in the negative. Endogenous purine formation is regarded as the expression of certain physiological processes in the cell-nuclei, but as to the nature of the processes or the organs involved, no opinion is pronounced. The paper is mainly critical of the work of others (Mareš, Smetanka, etc.). W. D. H.

**Protein Metabolism from the Standpoint of Blood and Tissue Analysis. III. Further Absorption Experiments with Especial Reference to the Behaviour of Creatine and Creatinine and to the Formation of Urea.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1912, 12, 141—162).—The author's previous work (this vol., ii, 271, 364) has shown that during the absorption of amino-acids from the intestine, it is possible to detect them in the blood and tissues, and the increase in non-protein nitrogen there practically accounts for all the nitrogen absorbed. The theory that protein is synthesised in the intestinal wall, which was put forward by those who were unsuccessful in finding amino-acids in the blood, is therefore superfluous and untenable. Another theory to account for the supposed absence of amino-acids in the blood during digestion is that deamidation occurs immediately; this is supported by the rapid appearance of urea in the urine after a protein meal; but the word rapid is a comparative one. In the authors' two previous papers they dealt with minutes rather than hours, and no evidence of increased urea formation was discovered in those experiments which lasted an hour or less. The accumulation of the amino-acids showed that deamidation is not the instantaneous or immediate result which the writings of some physiologists infer.

In the present research, these experiments of feeding cats on alanine or glycine have been repeated, only the observations have in these cases been extended over some hours after the material was introduced into the ligatured intestine; they all show the same result, and the protocols of only four therefore are given in detail. After a hour or more, the formation of urea is demonstrable. If Witte's peptone is used instead, urea formation begins earlier, but the exact explanation of this is not clear; one can only say that Witte's preparation is a complex mixture, containing more or less ammonia and amide nitrogen in addition to proteoses and peptones. But even with such a product the urea nitrogen in the hepatic is not greater than that in the iliac blood; that is, the liver is not proved to be a specialised seat of deamidation; the view is advanced that urea formation has no special seat, but it probably occurs in all the tissues, and therefore probably

the largest amount comes from the muscles, the most abundant of the tissues. Whether special tissues form urea more readily from some amino-acids than they do from others is left unsettled, but such specific action is regarded as improbable.

A number of experiments are also recorded with other amino-acids than those previously employed, which, in general, confirm the earlier results. Thus asparagine feeding was followed by an unmistakable increase in the non-protein nitrogen both of blood and muscle. The figures obtained are less than were expected, but this is largely explicable by the method of analysis employed, for asparagine is precipitated with the proteins by the methyl alcohol used as a precipitant, and it is very difficult to recover it from the precipitate. In the case of tyrosine, no attempt was made to estimate it, but its presence was shown by the very delicate phosphotungstic-phosphomolybdic colour reaction recently introduced by Folin and Macallum. Creatinine presents much the same analytical difficulty as asparagine, and the various experiments exhibit some discrepancy, in some more creatinine being found in the blood, in others more in the muscles. Mellanby's view that it is transformed into creatine is not supported, neither was any evidence found of enzymes capable of transforming one substance into the other, or either of them into urea. During creatine absorption, no increase of urea could be found; and the blood, which contained large quantities of it and was examined after it must have passed many times through the liver, gave no stronger creatinine reaction than did the control blood.

W. D. H.

**The Water Balance in the Human Organism when at Rest and at Work in High Altitudes.** E. GALEOTTI and E. SIGNORELLI (*Biochem. Zeitsch.*, 1912, 41, 268—286).—The water formed by metabolism of the food and that excreted by the kidneys, fæces, skin, etc., was measured, and also the water ingested. Changes in the body-weight were also measured. The measurement of the water excreted by the skin was indirect, and calculated from the balance. It was found that under normal conditions the daily variations of weight, which are assumed to be due entirely to the water, are very small during rest, there being retention of water in high altitudes as compared with excretion of water at sea-level (Naples). In climbing mountains there is a loss of water and diminution of body-weight, which varies with the amount of exertion and meteorological conditions. On the next day following muscular work, there is again retention of water, and return to the original weight. The changes in the conditions due to muscular exertion can be ascribed to the loss of water by the skin.

S. B. S.

**The Control of the Suprarenal Gland by the Splanchnic Nerves.** T. R. ELLIOTT (*J. Physiol.*, 1912, 44, 374—409).—The two suprarenals contain almost exactly equal amounts of adrenaline. Fright induced by morphine or  $\beta$ -tetrahydronaphthylamine exhausts the residual adrenaline; so also does anæsthesia induced by ether, chloroform, or urethane. Excitation of afferent nerves and direct injury to the brain cause also loss of adrenaline. The centre controlling such loss is close to the bulb vaso-motor centre. The efferent

path is by the splanchnic nerves. Cutting these nerves prevents the exhaustion of the adrenals under the conditions mentioned above; anæsthetics, pilocarpine, eserine, and diphtheria-toxin have no direct action on the glands.

Faradisation of the splanchnic nerves discharges adrenaline into the blood.

W. D. H.

**The Relationship between the Pancreas and Suprarenals.** KARL GLAESSNER and ERNST P. PICK (*Biochem. Zeitsch.*, 1912, 41, 328—330).—A reply to criticism of the work of the authors by Minami (this vol., ii, 461).

S. B. S.

**The Presence of Active Principles in the Thyroid and Suprarenal Glands Before and After Birth. II.** FREDERIC FENGER (*J. Biol. Chem.*, 1912, 12, 55—59. Compare this vol., ii, 660).—Additional observations support the author's previous conclusion that the thyroid and suprarenal glands contain their active principles and play their part in the growth and development before birth. Sex makes no difference.

W. D. H.

**The Gaseous Metabolism of the Submaxillary Gland with Reference Especially to the Effect of Adrenaline and the Time-relation of the Stimulus to the Oxidation Process.** JOSEPH BARCROFT and H. PIPER (*J. Physiol.*, 1912, 44, 359—373).—The oxygen used by the submaxillary gland in decerebrate cats is 0.016 to 0.028 c.c. per gram per minute, a figure practically the same as that obtained with anæsthetised cats. This is much increased by injection of adrenaline, and therefore appropriate stimulation of the sympathetic nerve does cause increased metabolism of the gland. The vascular dilatation caused by adrenaline is probably due to metabolic products rather than to the dilator nerves. Increased oxygen consumption reaches its maximum when the saliva almost ceases to flow, and persists for some minutes later, as in the case of stimulation of the chorda tympani nerve. Probably therefore gland resembles muscle in being a mechanism in which oxidation serves to replenish a store of potential energy which is liberated in the act of secretion.

W. D. H.

**The Feeding of Young Dogs on the Anterior Lobe of the Pituitary Body.** THOMAS B. ALDRICH (*Amer. J. Physiol.*, 1912, 30, 352—357).—Although in some instances the addition of anterior lobe of the pituitary to the diet of puppies may stimulate growth, this is not the rule. The growth is neither retarded nor impeded by the addition of desiccated anterior lobe, ovary, or testicle to their food.

W. D. H.

**Extraction of a Substance from the Sperm of a Sea-urchin (*Strongylocentrotus purpuratus*) which will Fertilise the Eggs of that Species.** T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1912, 12, 1—12).—The spermatozoa freed from sea-water by an isotonic solution of sodium chloride can be extracted by hypotonic salt solution containing ether. The extract contains two substances precipitable

by barium. One is soluble in dilute acid, and the other insoluble in dilute acid, but soluble in dilute alkali. Both are precipitable by acetone. The former substance is a powerful fertilising, agglutinating, and cytolytic agent on the eggs, and is probably identical with the fertilising agent (oöcytase) in blood-serum. The alkali-soluble substance appears to be devoid of action. W. D. H.

**The Enzymes of the Ovaries.** WALTHER LÖB and S. GUTMANN (*Biochem. Zeitsch.*, 1912, 41, 445—460).—The following ferments are present in the ovaries of pigs: catalase, diastase, lecithase, lipase, proteoclastic ferments of the trypsin and pepsin type, urease and nuclease. The following enzymes were absent: peroxydase, invertase, lactase, glycolytic enzymes, deamidase, and tyrosinase. S. B. S.

**The Colouring Matter of Egg-Yolk or Ovochromin.** N. ALBERTO BARBIERI (*Compt. rend.*, 1912, 154, 1726—1729).—The author has separated and examined the colouring matter from egg-yolk. The yolks of two thousand eggs are left in contact with carbon disulphide for several days, and the solution so obtained is treated with excess of alcohol. The alcoholic solution is filtered, and the alcohol distilled off. The semi-solid residue is taken up with chloroform giving three layers: (a) an aqueous layer, which contains the colouring matter; (b) a white solid layer of paravitellin; (c) a chloroform layer.

From the aqueous solution, the ovochromin can be obtained by extraction with acetone and re-dissolving in water after distilling off the acetone, this process being repeated until all sodium chloride is removed. A simpler method is to submit the liquid to polydialysis and subsequent evaporation at 37°.

*Ovochromin* is a yellow, colourless, very hygroscopic powder. It is soluble in its own weight of water, but insoluble in all the ordinary organic solvents. In aqueous solution it has no characteristic absorption band, and gives no biuret reaction. Hydrogen peroxide decolorises it. Alkalis and concentrated acids have no action in the cold. It decomposes without melting at 270°, and is not toxic. W. G.

**The Central Nervous System under Normal and Pathological Conditions. I. The Indophenol Oxydase in the Central Nervous System, the Choroid Plexus, and Cerebrospinal Fluid.** GIACOMO PIGHINI (*Biochem. Zeitsch.*, 1912, 42, 124—136).—Investigations were undertaken to find the presence in different parts of the central nervous system of the oxygenase capable of oxidising the mixture of  $\alpha$ -naphthol and dimethyl-*p*-phenylenediamine to indophenol. It was found in the glandular tissue of the choroid, in the cerebrospinal fluid, and in the grey substance and in the grey matter of the brain and spinal chord. S. B. S.

**The Central Nervous System under Normal and Pathological Conditions. II. The Catalase of the Cerebrospinal Fluid.** GIACOMO PIGHINI and PIETRO BARBIERI (*Biochem. Zeitsch.*, 1912, 42, 137—144).—Catalase (capable of decomposing hydrogen

peroxide) was not found in any normal or pathological case in the cerebrospinal fluid. S. B. S.

The Central Nervous System under Normal and Pathological Conditions. III. The Esterase and Lecithase in Normal and Pathological Cerebrospinal Fluids. GIACOMO PIGHINI and FLAMINIO NIZZI (*Biochem. Zeitsch.*, 1912, 42, 145—149).—In the normal and pathological cases investigated, no esterase capable of causing hydrolysis of mono- or tri-butyryl was found. A lecithase was also absent. S. B. S.

Theory of Muscle Contraction. HENRY R. PROCTER (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 281—283).—It is pointed out that nearly all the phenomena described in a recent paper by Fischer and Streitmann (*ibid.*, 65) has previously been explained on a physico-chemical basis by the author (compare Abstr., 1911, i, 342).

A theory of muscle contraction is described, based on the assumption that the muscle-fibres consist of alternating transverse layers of different colloidal substances, and that the contraction is due to the formation of acid. These alternating plates might form a galvanic cell made up of oxidisable and oxidising substances, and when the circuit is completed, acid is produced and the contraction follows. On this theory the function of the nerve system is not to develop an *E.F.M.*, but to complete the circuit and bring the battery into action. G. S.

Absorption of Water by Nerve Tissue. MARIAN O. HOOKER and MARTIN H. FISCHER (*Zeitsch. Chem. Ind. Kolloide*, 1912, 10, 283—294).—As objections have been advanced to the view of the authors (compare Abstr., 1911, ii, 510) that the colloids in tissues and the form in which they occur are the chief factors in determining the amount of water contained in the tissues (compare, for example, Hober, *Biol. Zentr.*, 1911, 31, 575) a detailed comparison of the behaviour of fibrin (a typical colloid) and the nerve tissue of the brain and spinal marrow of the guinea-pig as regards swelling and power of absorbing water from acid and salt solutions has been made, and the results are given in tabular and in graphic form. They show that there is a very close parallelism of the two classes of material under a great variety of conditions, and therefore confirm the authors' views. G. S.

Heat Production of Surviving Amphibian Muscle during Rest, Activity, and Rigor. ARCHIBALD V. HILL (*J. Physiol.*, 1912, 44, 466—513).—Using the author's micro-calorimeter, heat-production was found to be immediately after death as high as during life. It then falls to a constant level for a long period, which corresponds with a constant rate of production of carbon dioxide and lactic acid. When decomposition sets in, it rises again. The rate of heat production is increased by the presence of oxygen; the formation of lactic acid is exothermic. The liberation of carbon dioxide is at first due to oxidation, and later to lactic acid turning it out from sodium hydrogen carbonate. The combination of alkali and lactic acid does not account

for any appreciable development of heat. In chloroform rigor and heat rigor, the heat production is about 1·3 cal. per gram of frog's muscles; this is due to the chemical processes, which liberate lactic acid, and it occurs before coagulation sets in. Any factors which liberate lactic acid cause a fall in heat-production. The total energy of the lactic acid precursor is about 10% greater than that of lactic acid itself, and the precursor is therefore not dextrose, but some unknown chemical compound of greater energy; the breakdown of muscular substance into lactic acid may thus liberate a large store of free energy.

W. D. H.

**Nitrogenous Compounds in Meat Extract.** TEMISTOCLE JONA (Pamphlet, 87 pp., Fossano, 1911).—A critical summary of the divergent results obtained in this direction.

T. H. P.

**Dipeptides in the Extractive Substances of the Muscles.** TEMISTOCLE JONA (Pamphlet, 19 pp., Fossano, 1911).—Micko (Abstr., 1908, ii, 644, 713) was unable to detect dipeptides in Liebig's extract of meat. The author's experiments on this extract and on an Italian preparation (Zardoni's) show that both contain small proportions of taurine, whilst the presence of any large amount of glycine is excluded. From Zardoni's extract, but not from that of Liebig, the anhydride of *d*-alanyl-*d*-alanine was isolated.

Both extracts, and also others which were examined, contain a considerable proportion of gelatin or, at any rate, of substances behaving like gelatin towards Schmidt's reagent (Abstr., 1910, ii, 911).

T. H. P.

**Cryoscopy of Meat Extracts.** TEMISTOCLE JONA (Pamphlet, 15 pp., Fossano, 1911).—Cryoscopic investigation of a number of commercial meat extracts and of an experimental extract prepared in the laboratory shows that in each case the lowering of the freezing point is proportional to the concentration of the solution. The curves representing the depressions as a function of the concentration are not, however, parallel, and it is found that the differences between the various extracts in this respect depend principally on differences in the proportions of mineral matter present.

Liebig's extract contains 8·36% of nitrogen, 6·87% being dialysable and 1·76% non-dialysable. Multiplication of the latter figure by 6·25 gives 11·0% of protein, which is in good agreement with the proportion (10·2%) found by Micko (Abstr., 1902, ii, 369) to be precipitable by zinc sulphate. As, in the author's experiments, the dialysate is not precipitated by saturation with ammonium sulphate or zinc sulphate, whilst the residue is precipitated, it is evident that the latter is colloidal in character. This result is in disagreement with that obtained by Rona and Michaelis (Abstr., 1907, i, 370).

Measurements of the freezing point during the preparation of the extract show that the extractive matters of the meat do not undergo appreciable hydrolysis to soluble products of lower molecular weight.

T. H. P.

**Presence of Manganese in the Animal Series.** GABRIEL BERTRAND and FLORENTIN MEDIGRECEANU (*Compt. rend.*, 1912, 155, 82—84. Compare this vol., ii, 459, 662).—The authors have continued their researches, and estimated the manganese content of the lower orders of animals down to and including the echinoderms. Of the invertebrates, the gastropod molluscs and the lamellibranchia are the most abundantly supplied with manganese. The animal kingdom as a whole is, however, very poor in manganese as compared with the vegetable kingdom.

W. G.

**Secretion and Composition of Human Bile.** J. A. MENZIES (*Bio.-Chem. J.*, 1912, 6, 210—218).—Bile obtained from a case of biliary fistula on an ordinary diet was secreted at the rate of 350 c.c. per diem. Increase of nitrogenous intake raised this to 600 c.c. On analysis the following figures were obtained :

Water.	Solids.	Bile salts.	Cholesterol.	Lipoids.	Mucin and pigments.	Ash.
97.747	2.253	0.416	0.094	0.298	0.929	0.516 %

W. D. H.

**Changes in the Composition of the Milk of the Cow on Different Diets.** KARL HELLE, PAUL TH. MÜLLER, WILHELM PRAUSNITZ, and HEINRICH PODA (*Zeitsch. Biol.*, 1912, 58, 355—374).—Data in tabular form are given from observations on two cows; they relate in part to chemical composition, and in part to certain physical constants (osmotic pressure, etc.). The amount of fat, the total solids, and the calorific value vary a good deal from day to day; the protein, sugar, and ash remain very constant. The effect of the various diets adopted appears to be very slight.

W. D. H.

**Proteins of Ascitic Fluid. Remarks on Rivalta's Reaction.** GEORGES PATEIN and R. WEITZ (*J. Pharm. Chim.*, 1912, [vii], 5, 521—530, 591—598).—I. The authors have examined five specimens of ascitic fluid, drawn from a man within a period of six months. The results of a detailed examination in each case are tabulated and compared with the results from blood plasma. Particular attention has been paid to the "acetoglobulin," the substance precipitated by acetic acid (compare Abstr., 1907, i, 570). It is found to consist entirely of globulin, the greater part being euglobulin and the rest  $\psi$ -globulin (compare Freund and Joachim, Abstr., 1903, ii, 87).

II. As a further proof that the acetoglobulin obtained from ascitic fluid is a globulin and not a nucleoprotein, several specimens were examined for phosphorus and gave negative or very feeble reactions for it.

The ascitic liquids examined all gave Rivalta's reaction. Rivalta considers the formation of the precipitate in the reaction to be due to the presence of euglobulin and  $\psi$ -globulin, and the authors find that if in a liquid giving a positive reaction, the acetoglobulin is first precipitated, the reaction is no longer obtained. Further they find that this reaction cannot be depended on as a positive proof of inflammatory ascites.

W. G.

**The Creatine Content of Muscle in Malignant Disease and other Pathological Conditions.** ROBERT A. CHISOLM (*Bio.-Chem. J.*, 1912, 6, 243—249).—In the healthy adult, the fresh muscles contain 0.3% of creatine. This is not reduced in rapidly fatal acute disease, but falls in chronic diseases where there is loss of body-weight. This is so in malignant disease, especially of the liver, and is probably due to diminished production as well as to increased loss. W. D. H.

**Fate of Secretin in Pancreatic Diabetes.** C. LOVATT EVANS (*J. Physiol.*, 1912, 44, 461—465).—After complete removal of the pancreas in dogs, prosecretin rapidly disappears from the intestine, but the depressor substance does not diminish. If sufficient pancreas is left to prevent diabetes, no appreciable loss of secretin occurs. The loss of secretin in pancreatic diabetes is simply one symptom in the general train of metabolic disturbances consequent on a loss of the pancreatic internal secretion. W. D. H.

**The Influence of Sodium Tartrate on the Elimination of Certain Urinary Constituents during Phloridzin Diabetes.** FRANK P. UNDERHILL (*J. Biol. Chem.*, 1912, 12, 115—126).—Baer and Blum's observation that subcutaneous injection of sodium tartrate lessens the output of nitrogen and dextrose in the urine of phloridzinised dogs is substantiated, but their interpretation of the result is disputed. The salt induces disintegrative changes in the renal tubules sufficient to account for the decreased elimination in question. The same result is obtained in normal animals. W. D. H.

**The Excretion of Iron in the Urine in Pneumonia.** EDWARD H. GOODMAN (*J. Biol. Chem.*, 1912, 12, 37—42).—The excretion of iron in the urine has been mainly studied in blood diseases. In pneumonia only one mention of this occurs in the literature. It was found in the present research that it is lessened during the height of the infection, and is greatly increased at the crisis and on the following day. W. D. H.

**Glycolysis After Pancreatectomy and with the Addition of Antiseptics.** HUGH MCGUIGAN and C. L. VON HESS (*Amer. J. Physiol.*, 1912, 30, 341—351).—Normal muscle extract with pancreatic extract has no greater glycolytic power than the extracts taken separately. An objection has been raised to this, that normal muscle already contains sufficient of the internal secretion of the pancreas to exert a maximum glycolysis. Accordingly, the muscles of animals with "pancreatic hunger" due to removal of the pancreas were employed, and the same results were obtained.

No substantial evidence of glycolytic enzymes in the body exists, and in the blood glycolysis is due to surviving cells. The influence of the pancreas if it exists must be exerted on cellular processes which are not enzymic. W. D. H.

**The Condition of the Digestive Tract in Parathyroid Tetany in Cats.** ANTON J. CARLSON (*Amer. J. Physiol.*, 1912, 30, 309—340).—In parathyroid tetany in dogs and cats, gastric and

pancreatic digestion is usually retarded, often seriously so, but they may be normal, and in rare instances in gastric digestion (cat) even accelerated.

In other sympathetic mechanisms (pilo-motor nerves, sweat nerves, uterus, bladder, etc.) the deviation from normal activity in parathyroid tetany is in the direction of depression. This effect is probably due to direct action of substances in the blood, or to the absence of the parathyroid secretion.

W. D. H.

**A Phosphatide as Activator for Tuberculin.** H. J. BING and V. ELLERMANN (*Oversigt K. Danske Vidensk. Selsk. Forh.*, 1912, No. 2, 153—167\*).—The authors have isolated from the yolk of eggs a diaminophosphatide which intensifies the tuberculin reaction. The substance is called *albin*, and is the same as Stern and Thierfelder's "white substance." None of the other lipoids tested, such as lecithin, kephalin, cholesterol, oleic acid, sodium oleate, etc., has any intensifying action.

It is possible that the activation of the tuberculin may play a part in its action on the organism of tuberculosis.

T. S. P.

**Chemistry of Silver Therapy.** THEODOR PAUL (*Zeitsch. Elektrochem.*, 1912, 18, 521—528).—The silver ion concentration in a number of silver preparations used in medicine has been determined in aqueous solution and in mixtures with blood serum. For use in infectious diseases and for other purposes a distinction must be drawn between the power of silver preparation to destroy germs and to hinder their development. The destructive action on germs depends chiefly on the concentration of silver ions in the solution and on the possibility of the formation of new silver ions; these factors are also of importance as regards the efficiency of the solution in hindering development.

When silver nitrate is added to blood serum, silver chloride is precipitated, and it is found that the  $Ag^+$  ion concentration in the serum is approximately the same as that in aqueous solution of sodium chloride of the same concentration in this salt as blood or blood serum. Silver protein compounds are therefore less soluble than silver chloride, and by addition of sodium chloride are converted into silver chloride.

The effect of dilution on the  $Ag^+$  ion concentration in a number of commercial silver preparations has been determined, and the results are represented graphically. The  $Ag^+$  ion concentration increases with dilution in the case of argentamine, lysargin, collargol, and the silver-ammonia compounds, remains practically constant in the case of sophol, and in the case of protargol diminishes on dilution.

G. S.

**Behaviour of Carbohydrate-phosphoric Acid Esters in the Animal Body.** HANS VON EULER [with E. THORIN and D. JOHANSSON] (*Zeitsch. physiol. Chem.*, 1912, 79, 375—397).—These esters are split by an intestinal enzyme, by *Bacterium coli*, and by an enzyme found in the kidney of the horse. The calcium salt of the

\* and *Biochem. Zeitsch.*, 1912, 42, 289—301.

ester passes as inorganic phosphate into the urine. The calcium salt of glycerophosphoric acid ester is split by *Bacterium coli*. The calcium salt of carbohydrate-phosphoric acid ester when given to the dog in its food passes in greatest measure as inorganic phosphate into the urine. The normal amount of organic  $\text{PO}_4$  in the urine of the dog is about 10% of the total  $\text{PO}_4$ . This is very little altered by feeding on the ester salts. The physiological actions of phosphates depend very largely on their strong effects on vital enzyme reactions.

W. D. H.

**The Influence of Adrenaline on the Respiratory Quotient and its Mode of Action.** G. G. WILENKO (*Biochem. Zeitsch.*, 1912, 42, 44—58).—The experiments were carried out on rabbits by the Zuntz-Geppert method. Injection of adrenaline into the fasting animal altered the respiratory quotient, either not at all, or only very slightly. If carbohydrates are administered to the animals, the respiratory quotient normally rises. This, however, does not happen after injection of adrenaline. Furthermore, dextrose, if injected into the veins of animals, after administration of adrenaline, reappears quantitatively in the urine. It is suggested that adrenaline inhibits the capacity of the organism to burn the sugar, and does not act merely in "mobilising" the sugar in the blood, as has been suggested by previous investigators.

S. B. S.

**The Influence of Adrenaline Modified by Salts on the Blood Pressure of the Cat.** I. R. BURKET (*Amer. J. Physiol.*, 1912, 30, 382—387).—The after depressing effect of adrenaline on the blood pressure, which may be due to an impurity, can be counteracted by very small doses of barium chloride. This salt alone strengthens the heart's action, and sustains high blood pressure for some time. Uric acid also raises the pressure, but antagonises the high pressure due to adrenaline. Salts which cause a rise in pressure are: sodium chloride ( $m/2$ ), barium chloride ( $m/128$ ), and sodium dihydrogen phosphate ( $m/16$ ); those which lower it are: potassium chloride ( $m/16$ ), calcium chloride ( $m/16$ ), and magnesium sulphate ( $m/8$ ). Ringer's solution, sodium chloride ( $m/8$ ), calcium chloride ( $m/32$ ), and disodium hydrogen phosphate ( $m/16$ ) have no effect.

Adrenaline pressure is augmented by barium chloride ( $m/28$  and  $m/32$ ) and potassium chloride ( $m/16$ ). Salts which depress the action of adrenaline are: sodium chloride ( $m/2$ ), calcium chloride ( $m/16$ ), and magnesium sulphate ( $m/8$ ).

W. D. H.

**The Actions of Pituitrin, Adrenaline, and Barium on the Circulation of the Bird.** D. NOËL PATON and A. WATSON (*J. Physiol.*, 1912, 44, 413—424).—Pituitrin causes in the duck a fall of blood pressure due to vascular dilatation; this is antagonised by adrenaline and by barium chloride. Pituitrin powerfully stimulates all the chambers of the avian heart, whether the vagi are cut or not; but this action is not seen after the inhibitory mechanism has been paralysed by atropine. Adrenaline does not increase the amplitude of contraction of the heart of the bird as it does that of the mammal. This appears to be

due to the absence of any augmentor response. Pituitrin and adrenaline have an antagonistic action on the avian heart. This is in part due to the dilatation of peripheral vessels by which the decrease in the amplitude of cardiac contractions is removed. The antagonism of pituitrin to barium chloride is of the same kind. W. D. H.

**The Action of Gitalin on the Excised Frog's Heart.** W. LEGGE SYMES (*Proc. physiol. Soc.*, 1912, xxvii—xxix; *J. Physiol.*, 44).—Gitalin is a glucoside originally prepared by Kraft from digitalis leaves. It is amorphous, soluble in 600 parts of cold water, and in the presence of alcohol readily takes up water, and is converted into a crystalline hydrate. On evaporating its aqueous solution on a water-bath, it readily loses water, and yields an insoluble, crystalline glucoside, anhydrogitalin. The best samples of digitoxin are said to contain both these crystalline products. When perfused in Ringer-Locke solution through an excised frog's heart, there is first augmentation and, in slow hearts, acceleration before characteristic slowing occurs. After removal of the drug, recovery is gradual but good. Solutions of 2 to 5 per million were used. It has no hæmolytic action. W. D. H.

**The Active Substance of Opium Smoke.** PAUL POTT (*Biochem. Zeitsch.*, 1912, 42, 67—81).—That morphine is the substance producing the characteristic effect of opium smoke is made evident by the following facts: (1) It is possible to sublime morphine unchanged, even under ordinary atmospheric pressure. (2) It is possible to show the presence of morphine in the smoke by the two following physiological reactions: (a) by the narcotic action of the smoke on the breathing centre of rabbits, as shown by both diminution of frequency and volume of respiration, both in air, and air containing 5 and 10% of carbon dioxide; (b) by the production of the catatonic condition in mice, which is characteristic of morphine (Straub's reaction). S. B. S.

**The Pharmacodynamic Action of Narcotine in Opium.** WALTHER STRAUB (*Biochem. Zeitsch.*, 1912, 41, 419—430).—In the case of cats, morphine does not produce the excitant action if administered after a dose of narcotine. The effect of the two alkaloids is a pure (if weak) narcotic action. The same effect is produced if the two alkaloids are administered subcutaneously. The effect of the two drugs on the breathing centre of rabbits was also investigated, the result of stimulation of the breathing centre by air containing 10% of carbon dioxide (measurement of volume of expired air on respiration) on animals without alkaloid administration, and after administration of narcotine and morphine, both singly and combined, being measured. It was found that in presence of narcotine, the breathing centre was less narcotised by morphine, the regulation of the breathing mechanism being left intact when the two alkaloids were injected. In experiments on mice, it was found that the addition of narcotine to morphine increased the toxic effect of the latter. The results partly explain the better effect of opium as compared with morphine. S. B. S.

**The Action of Scopolamine.** ERNST HUG (*Arch. exp. Path. Pharm.*, 1912, 69, 45).—*l*-Scopolamine acts on the vagus three to four times, and on the oculo-motor nerve almost twice, as strongly as

*i*-scopolamine. An aqueous solution of the former does not lose its activity on keeping. In therapeutics, the two preparations must therefore be distinguished.

W. D. H.

**Selective Tissue Colouring (Vitalfärbung) and Chemico-therapeutics.** WERNER SCHULEMANN (*Arch. Pharm.*, 1912, 250, 252—279).—By selective tissue colouring is denoted the power of certain cells in living tissues to absorb certain dyes and to retain them for a long time, whilst other cells are not coloured at all. This selective action of the cells is regarded by some investigators as a chemical process, by others as a physical process. The author attempts to explain it by the chemical constitution of the dye.

Stated broadly, Ehrlich's theory of the local action of a remedial medicine is as follows. The large molecule of the protoplasm contains labile chemical groups, (side-chains) which react with corresponding groups (acceptors) of the remedy. By this process the molecules of the remedy are attached to the protoplasm. Then the toxophoric groups of the remedy exert their specific action, which must, therefore, be purely local. The distribution of the remedial molecules is conditioned by the acceptors, whilst the specific action of the medicine is determined by the toxic groups. For example, in salvarsan the ortho-hydroxyl and amino-groups are the acceptors, and the  $\cdot\text{As}\cdot\text{As}\cdot$  is the toxic group. A similar explanation can be advanced of the selective colouring action of certain dyes. Trypan-blue, for example, contains amino- and hydroxyl-groups in the peri-position, and these may act as acceptors. A large number of other dyes which exhibit selective colouring action are mentioned, but the author cannot state at present that the theory stated above is applicable generally. All such dyes contain sulphonic acid groups. The number and position of these groups affect the solubility of the dyes, and thus indirectly influence their selective colouring action.

The author also attempts to answer the following two questions: (1) What relations exist between the chemical constitution of the dye and the physico-chemical character of the solution? (2) In what state must the dye be in solution in order that it may exhibit selective colouring action? Here, again, the evidence is somewhat conflicting. Substances which do not show selective colouring power are suspensory colloids. The fundamental character of solutions of selective colouring dyes is determined by a definite position of the chromophoric relative to the auxochromic groups; the number and position of the sulphonic acid groups are without influence on the character of the solution, except in so far as they increase the solubility and thereby diminish the tendency to gel-formation. Indirectly, therefore, the selective colouring power of a dye is dependent on its chemical composition, which conditions a definite physico-chemical character of the solution, whereby the substance may be brought into a state in which it can be absorbed.

C. S.

**The Combined Action of Fluorescent Materials and Alcohol.** JOSEPH SZÜCS and BRUNO KISCH (*Zeitsch. Biol.*, 1912, 58, 558—570).—Contrary to the statements of Hausmann and Kolmer

(Abstr., 1909, ii, 78), it was found that in all cases the photodynamic action of fluorescent substances is increased by combination with alcohol.

W. D. H.

**Reciprocal Cation Ratio with Different Diets and in the Case of Acid Poisoning.** FRIEDRICH LUTHLEN (*Arch. exp. Path. Pharm.*, 1912, 68, 209—230).—When guinea pigs are fed on oats they become richer in sodium and magnesium and poorer in calcium and potassium, but the equilibrium as regards the equivalent amount of bases is not disturbed. On the other hand, when the animal is poisoned with acid (by subcutaneous injection of hydrochloric acid), it becomes relatively richer in calcium and magnesium and relatively poorer in potassium and sodium. When fed with green food, it becomes richer in calcium, magnesium, and potassium, but poorer in sodium. The most important factor in this connexion is the ratio of the different cations to one another, the so-called equivalent equilibrium of bases which can be disturbed by quite different causes, poisoning by hydrochloric acid leading to demineralisation, and the taking of green food to mineralisation.

G. S.

**Nitrogen Distribution in the Urine of Dogs in Cases of Sub-acute Phosphorus Poisoning.** HIROMU ISHIIHARA (*Biochem. Zeitsch.*, 1912, 41, 315—324).—It was found when phosphorus was administered in such small quantities (even over a prolonged period) that the animal still ingested normal amounts of food, that there was no change in the nitrogen distribution as regards ammonia, amino-acids, creatine, and creatinine. In the earlier stages of phosphorus poisoning, it appears, therefore, that the liver function remains normal.

S. B. S.

**The Synergic Action of Poisons. I. The Combination of Heart Poisons (Methyl-violet) with Alcohol and Glycerol.** HERMANN FÜHNER (*Arch. exp. Path. Pharm.*, 1912, 69, 29—44).—Methyl-violet can be easily estimated colorimetrically; its action on the heart resembles that of digitalis, and was studied both by subcutaneous injection and on the isolated heart of the frog. Injection of 2 mg. stops the heart in eight hours, and of 4 mg. in four hours. Addition of alcohol or glycerol hastens the onset of cardiac arrest. Glycerol increases the rate of absorption, whereas alcohol lessens it. The combination of alcohol and pigment in acting more rapidly is regarded as an instance of synergic action. The experiments on the isolated heart gave corresponding results.

W. D. H.

**The Phosphatides in the Organs of Rabbits Killed by Injection of the Tubercle Bacillus.** OTOLSKI and BIERNACKI (*Biochem. Zeitsch.*, 1912, 41, 375—385).—These preliminary investigations indicate that the injection of tubercle bacilli causes a general diminution of phosphorus in the organs, as a whole; a decrease of lecithin in the liver, which is accompanied by an increase of jecorins, and an increase in the phosphorus content of the lecithans.

S. B. S.

## Chemistry of Vegetable Physiology and Agriculture.

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**Bacterial Metabolism. I.** ARTHUR I. KENDALL and CHESTER J. FARMER (*J. Biol. Chem.*, 1912, 12, 13—18).—The experiments recorded show the extent, and in a measure the nature, of the sparing action which dextrose exerts for protein in ordinary media for a number of micro-organisms. The more pathogenic bacteria exhibit less proteolytic activity measured in terms of ammonia production and alkali formation than the more saprophytic organisms.

W. D. H.

**Bacterial Metabolism. II.** ARTHUR I. KENDALL and CHESTER J. FARMER (*J. Biol. Chem.*, 1912, 12, 19—21).—Further evidence in relation to other micro-organisms is presented to confirm the conclusions arrived at previously (see preceding abstract).

W. D. H.

**Production of Lævulose by Biochemical Methods.** AUGUSTE FERNBACH and MARCEL SCHOEN (*Compt. rend.*, 1912, 155, 84—86).—The authors have discovered an anærobic bacillus, which they name "gommobacter," which in a nutritive medium attacks sucrose giving a gum, which is precipitated from solution by alcohol, acetone, or barium hydroxide. When dry its weight is approximately 50% of that of the sucrose used, and it is readily and completely hydrolysed by a trace of acid to the same weight of lævulose. The authors conclude that the gum is a lævulan (compare Lippmann, *Abstr.*, 1881, 888). The gommobacter only produces this gum at the expense of sucrose. Although it commences by inverting the sucrose, no gum is obtained by using completely inverted sugar or an equimolecular mixture of dextrose and lævulose. The production of gum only seems to take place in the presence of nascent lævulose. The other half of the sucrose molecule is transformed into volatile and gaseous products.

W. G.

**Indole Reaction.** HUGO ZIFFEL (*Centr. Bakt. Par.*, 1912, i, 64, 65—80).—The production of indole by bacteria depends on the presence of the tryptophan group (indole- $\alpha$ -aminopropionic acid) in the nutritive medium. Solutions containing tryptophan are preferable to peptone, owing to the absence of any colour, and have the further advantage of being constant in composition. The solution employed contained ammonium lactate (0.5), dicalcium phosphate (0.2), magnesium sulphate (0.02), and tryptophan (0.03%). N. H. J. M.

**Chemical Composition and Formation of Enzymes. V. Formation of Invertase.** HANS VON EULER and HERMANN MEYER (*Zeitsch. physiol. Chem.*, 1912, 79, 274—300. Compare this vol., ii, 376).—Previous treatment of yeast with either dextrose or sucrose increases the amount of invertase; there is no material difference in the influence exercised by the two sugars.

Substitution of glycine or ammonium sulphate for asparagine in the solution used for the preliminary treatment has no effect on the amount of invertase formed. Treatment causes an increase of 10% in the amount of nitrogen in the yeast, but a total loss of 20% of the dried substance.

Transference of a yeast undergoing treatment to a second portion of solution, causes a further increase in the invertase produced, indicating that young cells have a greater power of forming the enzyme than old cells. The sugar vanishes from solution after some twenty-four hours' treatment, so that the increase in the invertase after this time takes place in a solution free from sugar. A third transference to fresh solution had but little further effect on the amount of enzyme. The greatest amount formed corresponded with about five times that in the original yeast.

In addition to the formation of invertase under the conditions described, there is an increase in the power of the yeast to synthesise carbohydrate phosphoric acid ester, to ferment dextrose, or to hydrolyse nucleic acid.

A distinction is drawn between specific enzyme formation for which a definite substrate is necessary and general enzyme formation dependent on the general nutrition of the yeast without reference to a particular substrate. E. F. A.

The Anti-neuritic Bases of Vegetable Origin in Relationship to Beri-Beri, with a Method of Isolation of Torulin, the Anti-Neuritic Base of Yeast. E. S. EDIE, W. H. EVANS, BENJAMIN MOORE, G. C. E. SIMPSON, and A. WEBSTER (*Bio.-Chem. J.*, 1912, 6, 234—242).—The anti-neuritic bases are not confined to rice, but can also be obtained from yeast. The yeast is extracted with alcohol, and the alcohol evaporated at room temperature. The aqueous residue is mixed with plaster of Paris to make it set, and the powdered material is extracted with acidified spirit. This extract is freed from alcohol, and precipitated with basic lead acetate, freed from lead, and concentrated to a syrup. This is treated with alcohol, and crystals of creatinine, etc., filtered off; it is again freed from alcohol and precipitated with baryta and silver nitrate. The precipitate is decomposed with hydrogen sulphide, and taken to dryness in a vacuum at 38°. A brown, sticky, hygroscopic mass remains, easily soluble in water, and intensely active. It can be further purified with alcohol; it is insoluble in ether and acetone, and on keeping yields feathery crystals. The name *torulin* is proposed for it. On treatment with barium hydroxide, it gives off trimethylamine. Its formula may be written  $C_7H_{16}O_2N, HNO_3$ . Its investigation is being continued. W. D. H.

The Biolytic Scission of Gelatin. I. and II. W. S. SADIKOFF (*Biochem. Zeitsch.*, 1912, 41, 287—297, 298—314).—I. By the expression biolytic scission is understood the degradative changes produced by living organisms as opposed to those produced by enzymes. Certain moulds (*Penicillium*) and bacteria (*Proteus* and varieties of *Sarcina*) can grow on pure gelatin alone, and produce liquefaction. The "biolysates," chiefly produced by the action

of *Proteus vulgaris* at 37° were studied. The liquefied gelatin obtained by the growth of the living culture was shown, on steam distillation after acidification with sulphuric acid, to yield volatile organic acids, which vary with the species of organism used for the production of the biolysate, and on distillation after making alkaline with sodium hydroxide, volatile bases were obtained. Analysis of the acid distillate from the proteus biolysate revealed the presence of formic, acetic, propionic, butyric, isobutyric, and valeric acids. The chief bases obtained were ammonia and methylamine. A large percentage of volatile acids is obtained, and the amount of nitrogen in the bases of the distillate and in the residue from distillation is larger than the amount originally in the gelatin, a fact that indicates that the nitrogen of the air has been assimilated. The biolysate yielded also sulphur in a form which directly produced lead sulphide on heating with a lead salt.

II. An account is given of the biolysate produced by the growth of *Penicillium glaucum* at room temperature, the medium being kept slightly acid. In this case, a product is obtained which on boiling with water yields ammonia and carbon dioxide in the proportion of approximately two parts of the former to one part of the latter. It is assumed that ammonium isocyanate is formed which yields these substances on hydrolysis. It is also assumed that the isocyanate is formed from some complex polymeride. These phenomena can be produced only by the living organism, and the first stage of the process takes place in the presence of a good air supply. An intermediate compound appears to be formed, which undergoes further change in the presence of air. To get the best yield of ammonia and carbon dioxide, the biolysate should be formed under good conditions of aeration, and then kept, in the presence of micro-organisms, in well-corked flasks. The medium for production should be slightly acid, and various organisms (*Proteus* and *Sarcina*) are effective in addition to *Penicillium*. Nitrogen in these cases is also, during the formation of the biolysate, assimilated from the air. Similar results were obtained with hydrolysed gelatin. The author suggests that amino-acids are only secondary products of hydrolysis of living proteins, and are formed by the hydrolysis of other substances, such as isocyanates.

S. B. S.

**The Behaviour of Moulds to Sucrose.** G. E. RITTER (*Biochem. Zeitsch.*, 1912, 42, 1—6).—It is generally recognised that the capacity of plants and animals to utilise sucrose depends on the fact that the organism contains an invertase. It has been shown, however, by Butkewitsch, that certain moulds, for example, *Rhizopus nigricans*, which contain no invertase can grow on sucrose. This can happen when ammonium nitrate is used as a source of nitrogen, but not with ammonium oxalate, the explanation of this fact being that the organism rapidly absorbs the ammonia, and the nitric acid set free hydrolyses the sucrose. In this way the invertase can be dispensed with. The author has investigated this hypotheses by experiments on the following moulds which are supposed to contain no invertin: *Mucor spinosus*, *Thamnidium elegans*, *Rhizopus nigricans*, *Rhizopus tonkinensis*, *Mucor Javanicus*, and *Penicillium purpurogenum*. With the exception

of the last named, all were found to be capable of growing in sucrose solutions only when ammonium sulphate (and not ammonium tartrate or potassium nitrate) was used as the source of nitrogen. The exception in the case of *Penicillium purpurogenum*, which could grow in all solutions, was found to be due to the fact that, contrary to the statement of other investigators, it contains invertase. S. B. S.

**Alcohol Consumption in the Respiration of Plants.** W. ZALESKI and A. REINHARD (*Biochem Zeitsch.*, 1912, 42, 39—43).—It has been suggested that the production of carbon dioxide by powdered pea-seeds is due to an alcoholic fermentation. The amount of alcohol that can be recovered is, however, less than that corresponding with the carbon dioxide produced. Experiments by the authors show, however, that alcohol exposed to animal charcoal under physical conditions similar to that in which it might exist in the presence of pea-seeds, is partly oxidised, even when kept in closed flasks. Alcohol is also oxidised by powdered pea-seeds, and more strongly still by wheat-seeds under similar conditions. It is conceivable that in the original experiments on pea-seeds, an intermediate product of alcoholic fermentation is oxidised. S. B. S.

**Influence of the Concentration of Solutions of Nutritive Substances on their Absorption by Plants.** ISIDORE POUGET and D. CHOUGHAK (*Compt. rend.*, 1912, 154, 1709—1711).—If the concentration of a solution of a nutritive substance is very small (less than 0.1 mg. per litre for phosphoric acid), absorption does not take place, but, on the contrary, the plant tends to excrete some of the substances which it has already absorbed. If the concentration increases continuously, the absorption increases at first more rapidly than the concentration up to a certain limit, when it is exactly proportional. On further increasing the concentration, a point is reached where the absorption increases less rapidly, and is then controlled by the consumption of the nutritive substance by the plant (compare Schloesing, Abstr., 1899, ii, 119). W. G.

**Relation of the Plant to the Nutritive Elements of the Soil. Law of the Minimum and the Law of Physiological Ratios.** PIERRE MAZÉ (*Compt. rend.*, 1912, 154, 1711—1714).—The author maintains that, as a result of his experiments, the law of the minimum does not hold good, but that the relations of a plant to its nutritive substratum depend on conditions which obey a law of "physiological ratios."

Working with maize plants, he grows them in a given water culture, to which he adds nitrogen in the form of a nitrate or ammonium salts. After the plants have obtained a dry weight of about 10 grams, they are removed from the culture, the roots well washed, and inserted into other nutritive solutions. The best increase is found to result in plants which continue their growth with their roots in pure distilled water. All solutions constituted of a single nutritive element containing neither sulphur nor iron produce more or less intense chlorosis.

Working with *Aspergillus niger* grown on Raulin's solution, the

author finds that by increasing the quantity of ammonium nitrate present to sixteen or thirty-two times its correct amount, a marked diminution is shown in the weight of mycelium produced. W. G.

**New Theory of Nitrogen Fixation by Plants.** ÉMILE HENRY (*Bied. Zentr.*, 1912, 41, 391—393; from *Ann. Sci. Agron.*, 1909, i, 102).—A criticism of Jamieson's theory of nitrogen fixation by special organs (protein generators) present in all kinds of plants. Jamieson's results indicating fixation of nitrogen are attributed to assimilation of atmospheric ammonia. N. H. J. M.

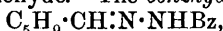
**Nitrogen Assimilation and Protein Formation in Plants.** OSCAR LOEW (*Biochem. Zeitsch.*, 1912, 41, 224—240).—The author reviews the literature of this subject, and draws the following conclusions. The reduction of neither nitrates nor sulphates in plants is a photochemical reaction. The alkaline reaction to phenolphthalein of aquatic plants is due to the conversion of the calcium hydrogen carbonate into the normal carbonate, and not to the formation of alkali carbonates, as Baudisch supposes. The protein synthesis is due neither to the partial oxidation of ammonia (nitrosyl formation) nor to the action of light, as can be demonstrated by experiments on the moulds. The increased protein formation can be ascribed partly to increased energy of the living protoplasm and partly to increased carbohydrate formation. Asparagine acts as a store for ammonia, and for intermediary products of protein formation. Many facts indicate that protein formation is a condensation process.

S. B. S.

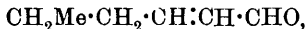
**Presence of Formaldehyde in Plants.** THEODOR CURTIUS and HARTWIG FRANZEN (*Ber.*, 1912, 45, 1715—1718).—The reactions supposed to identify formaldehyde in plants are given also by other aldehydes. Accordingly, until now, formaldehyde has not been identified in plants with certainty. Formic acid, formed from formaldehyde by oxidation with silver oxide, can be positively identified by the formation of an insoluble silver salt which turns black, by the formation of a precipitate of mercuric chloride on warming, and by the formation of carbon monoxide when it is decomposed with concentrated sulphuric acid. The distillate from 1500 kilos. of hornbeam leaves was tested in this manner after oxidation with silver oxide. Formaldehyde was proved conclusively to be present, but the amount was only 0.0008613 grams per kilo. of leaves. E. F. A.

**Chemical Constituents of Green Plants. I. Leaf Aldehydes.** THEODOR CURTIUS and HARTWIG FRANZEN (*Annalen*, 1912, 390, 89—121).—It has long been known that the distillate, obtained by the distillation with steam of the juices expressed from leaves after neutralisation with sodium carbonate, contains a substance or substances exhibiting the reactions of an aldehyde. Curtius and Reinke (*Ber. Deut. bot. Ges.*, 1897, 15, 201) showed that *m*-nitrobenzhydrazide is a good reagent for the isolation of the aldehydic substance, and that the condensation product obtained in the case of many plants has m. p. 154° and the composition  $C_{15}H_{17}O_4N_3$ .

The authors have now worked up about 600 kilog. of the leaves of the hornbeam and have obtained therefrom 209.4 grams of the crude condensation product with *m*-nitrobenzhydrazide. After purification by benzene, the substance has the composition  $C_{15}H_{15}O_5N_3$ , and m. p. 167—168°, and is proved, as shown below, to be the *m*-nitrobenzhydrazone of  $\Delta^6$ -hexenaldehyde. The benzhydrazone,



m. p. 112—113°, forms colourless leaflets.  $\Delta^6$ -Hexenaldehyde,



b. p. 47—48°/17 mm., obtained by the hydrolysis of the hydrazone by dilute sulphuric acid, is a colourless oil with a peculiar, characteristic odour. It has  $D_4^{17.9}$  0.8470, and  $n_D^{17.9}$  1.44235,  $n_D^{17.9}$  1.44602,  $n_D^{17.9}$  1.45559, and  $n_D^{17.9}$  1.46377. The *p*-nitrophenylhydrazone,  $C_{12}H_{15}O_2N_3$ , reddish-brown leaflets, has m. p. 137°. The constitution of the aldehyde is proved by the fact that by oxidation by silver oxide by Délepine's method it yields  $\Delta^6$ -hexenoic acid, identical with that obtained by Fittig and Baker from hydrosorbic acid (Abstr., 1905, i, 206).

The leaves of the vine (*Vitis vinifera*), edible chestnut (*Castanea vesca*), common short-stalked oak (*Quercus sessiliflora*), elder (*Sambucus racemosa*), lupin (*Lupinus polyphyllus*), black alder (*Alnus glutinosa*), hazel-nut (*Corylus avellana*), horse-chestnut (*Aesculus hippocastanum*), birch (*Betula alba*), beech (*Fagus silvatica*), white clover (*Trifolium repens*), raspberry (*Rubus Idaeus*), willow, walnut (*Juglans regia*), Norway maple (*Acer platanoides*), poplar, acacia (*Robinia pseudacacia*), and ash (*Fraxinus excelsior*), have been examined and contain  $\Delta^6$ -hexenaldehyde, which has been isolated as the *m*-nitrobenzhydrazone. The leaves of many other trees and shrubs have been examined for the presence of the aldehyde, and always with positive results.

The formation of the aldehyde is intimately connected with the assimilation of carbon dioxide by the leaves, because the distillates obtained from leaves of plants which have been kept in darkness for some days do not exhibit the reactions of an aldehyde, but after the plants have been again exposed to light the distillates contain the aldehyde.

The authors point out the simple changes whereby  $\Delta^6$ -hexenaldehyde could yield the unsaturated alcohol, or hexyl alcohol, or hexoic aldehyde, or hexoic acid, all of which are substances which have been detected in various plants. A theory is put forward whereby the production of  $\Delta^6$ -hexenaldehyde from an aldohexose such as dextrose is plausibly explained.

C. S.

**Presence of Free Hydrocyanic Acid in Plants. II.** CIRO RAVENNA and V. BABINI (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 540—544. Compare Ravenna and Tonegutti, Abstr., 1910, ii, 884).—In order to avoid slight enzymic decomposition of the cyanogenetic glucoside, the authors suggest the following procedure for detecting free hydrocyanic acid in plants.

Not less than 25—30 grams of the leaves (of the cherry-laurel, etc.) are immersed one at a time for a minute in boiling very dilute potassium hydroxide solution, no interruption of the boiling occurring.

The cold alkaline liquid is neutralised with tartaric acid and distilled in a current of steam, the distillate being tested for the acid. This method does not work perfectly with old leaves, as these do not instantly assume the temperature of the boiling alkali.

Examination in this way of the cherry-laurel, peach, sorghum, flax, and medlar shows, when the distillates are tested by the Prussian-blue reaction, absence of free hydrocyanic acid in these plants. In some cases, however, sodium picrate paper indicates traces of hydrocyanic acid, and it is yet undecided whether such indications are due to the presence of the free acid in the plants or to a defect in the method of investigation.

T. H. P.

**Ammonia as a Decomposition Product of the Nitrogenous Compounds in Higher Plants. II.** WL. BUTKEWITSCH (*Biochem. Zeitsch.*, 1912, 41, 431—444. Compare Abstr., 1909, ii, 424).—In seedlings (lupins) which have been developed for a long time at the expense of their carbohydrate reserve there is formation of ammonia, the nitrogen of which is about one-fifth of the total in the dying plants. The material for this ammonia formation is, at any rate partly, the amide group of asparagine. The formation of the ammonia is a result of the exhaustion of the carbohydrate, and artificial nutrition of the seedlings with dextrose diminishes the amount formed. The ammonia, furthermore, is formed only in the presence of air, no appreciable amount above the normal being found even after prolonged growth in an oxygen-free atmosphere at 24—26°. The author is of the opinion that ammonia formation is not due to the presence of a deamidising ferment, although he admits the possibility that under aerobic conditions a deamidising ferment, if present, might be inhibited in its action. The seeds used for experiment were sterilised by concentrated sulphuric acid and bromine water, and the methods by means of which this sterilisation is carried out, and the seeds transferred to the flasks in which the plants are grown, are described in detail, and the apparatus employed is figured.

S. B. S.

**Betaines of Plants. III.** ERNST SCHULZE and GEORG TRIER (*Zeitsch. physiol. Chem.*, 1912, 79, 235—242. Compare this vol., ii, 287).—Betonicine is accompanied by other isomeric bases corresponding in composition with the dimethylbetaine of hydroxyproline. These betaines are present in *Betonica officinalis* and in *Stachys silvatica*; they are readily separated from the ordinary betaines, since as free bases they are sparingly soluble in absolute alcohol. The separation of the individual betonicine bases has not been effected; betonicine itself forms a hydrochloride, which is the most sparingly soluble in alcohol.

Young tare plants (*Vicia sativa*) contain bases which in many respects correspond with betonicine, but there are also points of difference which at present prevent their classification as betonicines; they react as amino-acids containing methyl groups attached to nitrogen.

E. F. A.

**Presence of Betaine in Green Tobacco Leaves.** N. T. DELEANO and GEORG TRIER (*Zeitsch. physiol. Chem.*, 1912, 79, 243—246).—Ordinary glycinebetaine has been isolated from green tobacco leaves. Betaine has previously been found in other *Solanaceae*. E. F. A.

**Influence of Various Oxidising Agents on the Work of Proteolytic Enzymes in Dead Plants.** WLADIMIR I. PALLADIN, W. G. ALEXANDROFF, NICOLAUS N. IWANOFF, and A. N. LEVITSKY (*Bull. Acad. Sci. St. Pétersbourg*, 1912, 677—695).—The principal results of a series of experiments with hefanol, wheat germs, pea meal, etc., are as follows :

Proteolytic enzymes act anaerobically, and are retarded or completely inhibited in their action by various oxidation reactions. In the living cell the functions of the proteolytic enzymes are protected from the injurious influence of the oxidation processes occurring simultaneously. After the death of the plant, the oxidising reactions begin to poison the proteolytic enzymes, owing to the removal of the regulating influence of the living protoplasm. Atmospheric oxygen has no immediate action on the autolysis of protein: thus, with zymin, the degradation of protein is the same in the air as in absence of oxygen. If plants contain a substance (or if such is added, for instance, as taka-diastrase) capable of transmitting the oxygen absorbed by them (peroxydase or respiratory chromogens), autolysis in the air always results in less degradation of protein than when oxygen is absent (compare Palladin and Kraule, this vol., ii, 291).

In small proportions, hydrogen peroxide has no influence on the autolysis of protein, as it is immediately destroyed by catalysis. But by larger amounts of the peroxide, the resolution of protein is retarded or entirely inhibited. The autolytic products must not be boiled in presence of hydrogen peroxide, as under these conditions they undergo rapid decomposition with formation of considerable quantities of ammonia.

Dihydroxybenzenes retard the autolysis, and in presence of peroxydase the retarding action depends on the oxidisability of the dihydroxybenzene by the peroxydase; thus, with resorcinol, the retardation is 14%, with quinol 35%, and with catechol 63%. But in absence of peroxydase, such wide differences are not observed, resorcinol and catechol then causing retardations of 46% and 59% respectively.

The autolysis of protein is delayed by methylene-blue, isatin, and sodium selenite. Potassium nitrate, which produces considerable stimulation of the autolysis of protein in zymin (Gromoff and Grigorieff, *Abstr.*, 1904, i, 960), has no effect in the case of wheat germs.

Taka-diastrase contains a very energetic proteolytic enzyme, the action of which is greatly enhanced by citric acid. T. H. P.

**Formation of Chlorophyll in Plants.** II. N. A. MONTEVERDE and V. N. LUBIMENKO (*Bull. Acad. Sci. St. Pétersbourg*, 1912, 609—630).—Further experiments (compare *Abstr.*, 1911, ii, 424) show that the formation of chlorophyll in green plants comprises two stages. The first of these includes the reactions by which a colour-

less substance, leucophyll, is converted into the coloured chlorophyllogen without the direct action of light, whilst the second consists of those chemical or photochemical transformations by which chlorophyllogen is converted into chlorophyll itself. With conifers and other plants which become green in the dark, the chlorophyllogen is acted on by unknown chemical reagents, but with most green plants the energy required for the change of chlorophyllogen into chlorophyll is supplied by light. Under the influence of light rays, chlorophyllogen is transformed rapidly into an intermediate pigment, this change occurring both in living plants and in those killed by drying; this pigment is moderately resistant to the action of light, and its conversion into chlorophyll is hence slow, and, further, only takes place in living plants. Accumulation of chlorophyllogen or of the intermediate pigment in appreciable amount occurs only in etiolated plants. Both pigments are chemically very labile, and their absorption spectra can be observed only in living etiolated leaves or in those which have been carefully dried at the ordinary temperature. When treated with various solvents, chlorophyllogen gives solutions showing the spectrum of protochlorophyll, whilst the intermediate pigment yields solutions characterised by the chlorophyll spectrum. When left too long in the dark, etiolated plants lose their power of transforming the intermediate pigment into chlorophyll under the influence of light.

The part played by light is a complicated one. The maximal accumulation of chlorophyll corresponds with an optimal light intensity, the absolute value of which varies with different species of plants. With excessive intensity of light, both etiolated and non-etiolated plants turn green more slowly, and the latter exhibit a kind of adaption to strong light which shows itself in accelerated accumulation of chlorophyll during the development of the young plants. The chlorophyll accumulated by leaves developed in daylight possesses considerable resistance to strong light, and it seems improbable that the retarding influence of such light is due to the destruction of chlorophyll already formed, although direct sunlight does cause appreciable decomposition of the intermediate pigment before its conversion into chlorophyll; on the other hand, the fact that even brief exposure of etiolated plants to sunlight greatly retards their subsequent greening under the influence of diffused light can be explained only by the destruction of the colourless substance which gives rise to the chlorophyll.

A well defined quantitative relation exists between chlorophyll and the yellow pigments accompanying it in the chloroleucites, and, as a general rule, the accumulation is similarly influenced by the same physical and chemical factors in the two cases. But these pigments are not combined chemically with the chlorophyll, so that the destruction of the latter in autumn leaves does not affect the yellow pigments.

T. H. P.

**The Latex of the Fig Tree, a Vegetable Pancreatic Juice with Proteolytic Diastase Predominating.** C. GERBER (*Compt. rend.*, 1912, 155, 56—59).—A comparison of the latex of the fig tree (*Ficus carica*) with that of the mulberry tree as regards the enzymes

they contain. The former contains a lipodiastase but slightly active in neutral medium, being about one-twelfth the strength of that of the latter. It is much more active in an acid medium, and is not resistant to heat.

The fig tree latex possesses marked amylolytic properties, but again is much weaker than that of the mulberry tree. Its action is not weakened by dialysis, and is favoured by an acid medium and by weak solutions of calcium chloride. It is inhibited by small doses of cadmium or mercuric chlorides.

The proteolytic action of the fig tree latex is one hundred times stronger than that of the mulberry tree. The rennet of the former is more resistant to heat than its accompanying amylase or lipase. It is distinguished from that of the mulberry tree in that it more readily coagulates boiled milk, whilst the latter more readily coagulates fresh milk. It loses the greater part of its activity by dialysis, and its action is inhibited by small quantities of mercuric chloride.

The curve of the diastatic activity of the fig tree latex is sinusoidal, exhibiting two maxima, the first at the time of flowering, and the second when the figs begin to develop. The two minima occur at the time of flower maturity and when the tree is bare of leaves and fruit.

W. G.

**Composition of the Seeds of *Funtumia elastica*, the Rubber Tree of the Ivory Coast.** ALEXANDRE HÉBERT (*Bull. Soc. chim.*, 1912, [iv], 11, 612—614).—The seeds of *Funtumia elastica* contain about 20% of fatty matter, which is mainly composed of the glycerides of oleic, myristic, margaric, and perhaps a little lauric acids. The oil obtained by ether extractions resembles drying oil in its behaviour, and could probably be employed for the same purpose. The residue after extraction of the oil could be used as a feeding-stuff for cattle on account of the percentage (3.4%) of nitrogen present as proteid matter.

W. G.

**The Fruit of Solomon's Seal (*Polygonatum Biflorum*).** ERNEST A. RAYNER (*Chem. News*, 1912, 105, 289—290).—The results of an analysis of this fruit are recorded, the fruit being obtained from N. Carolina, U.S.A., in the summer of 1910. The figures obtained were: ash, 2.27%; sugars, 12.48%; nitrogen, 1.88%; oil, 2.00%; cellular tissue, water, etc., 81.37%. Although the berries when crushed yielded an odour resembling that of tobacco, neither nicotine or coniine could be detected.

W. P. S.

**Changes in the Osmotic Pressure of the Sap of the Developing Leaves of *Syringa vulgaris*.** HENRY H. DIXON and W. R. G. ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1912, 13, 219—222).—A series of freezing-point determinations of the sap of *Syringa vulgaris* has been made with the object of tracing the changes in the osmotic pressure during the unfolding of the buds and the maturing of the leaves. The recorded data show that these processes are accompanied by appreciable variations in the osmotic pressure of the sap. During

the period of opening of the buds, the sap of the older leaves and that of the leaves still cohering in the bud were separately examined. It was found that the osmotic pressure of the former was 9.97 atmospheres, whilst that of the latter was 11.60 atmospheres. A similar, although smaller, difference was found at a later stage in the development of the leaves.

H. M. D.

**Distribution of the Mineral Bases in Barley During Growth.** GUSTAVE ANDRÉ (*Compt. rend.*, 1912, 154, 1817—1819).—Having previously examined the variations in the amounts of the acid-forming elements (nitrogen, sulphur, etc.) in barley during growth (compare this vol., ii, 675), the author has now carried out a similar investigation with respect to the bases lime, magnesia, potassium oxide, and sodium oxide, determining the quantities of these substances present in the ear, stalk, leaves, and roots. The chief point brought out is that the plant as a whole contains the maximum amount of potassium oxide at the commencement of flowering; after this date the amount diminishes. When the barley has attained maturity, the ear contains the maximum amount of potassium oxide, but the plant as a whole has lost 17.6% of the oxide. The amount of sodium oxide present decreases continually during the growth of the barley, the first analyses being made just as the ear makes its appearance. There is no loss of lime or magnesia during growth.

T. S. P.

**Action of Calcium Carbonate in Manuring Oats with Mono- and Di-calcium Phosphate.** W. SIMMERMACHER (*Landw. Versuchs.-Stat.*, 1912, 77, 441—471).—Application of calcium carbonate in conjunction with monobasic calcium phosphate reduced the amount of phosphoric acid taken up, but not the yield. When dibasic calcium phosphate was employed, both the amount of produce and the amount of phosphoric acid in the produce were considerably diminished. The experiments were made in zinc pots (covered with paraffin) holding 6.2 kilos. of sand.

N. H. J. M.

**Non-protein Nitrogenous Constituents of the Sugar Beet. II.** KAZIMIR SMOLENSKI (*Zeitsch. Ver. deut. Zuckerind.*, 1912, 791—807).—From the pressed beet-juice of a Russian sugar-factory (season 1909—1910) there has been obtained allantoin amounting to 0.005%, asparagine 0.01%, and betaine 0.2%. In addition, glutamine, vernine, tyrosine, choline, trigonelline, stachydrine, and lysine are present. After treatment with lead acetate and mercuric nitrate, betaine is the only organic base remaining in the sap. The vernine is identical with that obtained from other sources; it is probably present as a nucleo-protein in the beet, which is partly hydrolysed during diffusion. Allantoin is present as such or as a very easily decomposed compound. Russian beets contain almost exclusively asparagine, which replaces the glutamine present in beets from West Europe.

E. F. A.

**Contamination of Water by the Combustion of Turf.** ACH. GRÉGOIRE and J. HENDRICK (*Bull. Soc. chim. Belg.*, 1912, 26, 276—280).—Following the extensive turf fires of 1911, the brooks

crossing the burnt area became contaminated, and destroyed the fish in the rivers.

Examination of the waters made some time subsequently showed the presence of organic acids and reducing products resulting from the distillation of the turf. These either act directly as toxic agents or lower the amount of dissolved oxygen in the water below that necessary to maintain the fish alive.

E. F. A.

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### Analytical Chemistry.

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**An Automatic Universal Burette.** FRANZ MICHEL (*Chem. Zeit.*, 1912, 36, 595).—The burette is provided with a three-way tap, through one opening of which the solution may be forced up from the containing vessel by pressure on a rubber ball. C. H. D.

**Improvements in Ludwig and Sipöcz's Method for the Estimation of Water in Silicates.** MAX DITTRICH and W. EITEL (*Zeitsch. anorg. Chem.*, 1912, 75, 373—381).—In the usual method of estimating water in rocks by heating with a mixture of potassium and sodium carbonates, a platinum crucible is used, enclosed in a porcelain tube, or else the whole apparatus is of platinum. A silica tube may be used with great advantage. The tube is conveniently 45 cm. long and 22 mm. in diameter. One end is drawn out, and a ground joint made with the absorption apparatus, whilst at the other end a silica tube is widened and ground in. The ground joints are made tight by means of graphite. The mixture is contained in a platinum-iridium boat wrapped round with foil. With this arrangement, sodium carbonate, previously dried at 270—300°, may be used in place of the hygroscopic mixture of sodium and potassium carbonates. The air must be thoroughly dried, best by using a gasometer filled with sulphuric acid, and drying tubes are also used. 0.4 to 1 Gram of the powdered rock is mixed with 5.5—6 grams of sodium carbonate, and heated gradually to 1000—1050°, preferably in an electric furnace. At this temperature the expulsion of water is complete.

In order to prevent devitrification of the silica, the tube should be wiped with a cloth moistened with alcohol just before being used, and not again touched with the fingers. C. H. D.

**A Metallographic Hygroscope.** CARL BENEDICKS and RAGNAR ARPI (*J. Inst. Metals*, 1912, 7, 246—248).—Alloys of antimony and zinc containing about 20% of zinc are etched with hydrochloric acid vapour and exposed to moist air. The thin film of chloride yields interference colours, and acts as a sensitive hygroscope. The thickness of the film increases with falling temperature, the rate of increase becoming higher as the dew point is approached. Alloys containing more than 30% of zinc do not show the effect. C. H. D.

**Estimation of Iodine in Iodides. and in Particular in the Ash of Seaweed.** VICTOR AUGER (*Bull. Soc. chim.*, 1912, [iv], 11, 615—617).—The process employed is a modification of that of Bernier and Péron (*Abstr.*, 1911, ii, 435). To the solution containing about 0.05 gram of iodine is added 5 c.c. of sodium hydroxide solution (36° B), and the whole is heated on a water-bath and a concentrated solution of potassium permanganate is run in slowly until in excess. The liquid is then diluted to 250 c.c., freely acidified with acetic acid, and the excess of permanganate destroyed by the addition of hydrogen peroxide. One gram of potassium iodide and 5 c.c. of hydrochloric acid are added, and the liquid is titrated with sodium thiosulphate. The process can be used in the presence of chlorides, bromides, cyanides, thiocyanates, sulphides, nitrites, or ammonium salts. W. G.

**Colorimetric Estimation of Very Small Quantities of Fluorine.** ARMAND GAUTIER and PAUL CLAUSMANN (*Compt. rend.*, 1912, 154, 1670—1677).—According to the method previously described (this vol., ii, 681) the fluorine present in the substance to be analysed has all been carried down as fluoride in the presence of barium sulphate; generally there are also present some silicate, carbonate, and chloride. The fluorine is then completely separated and estimated as follows: The barium sulphate precipitate is washed with a minimal amount of aqueous alcohol, dried and weighed, and then heated with concentrated sulphuric acid in a special gold crucible, which is fully described, in such a way that the gases evolved are absorbed by moistened, pure potassium hydroxide. The fluorine present is thus collected as potassium fluoride and silicofluoride, but it may still be contaminated with chloride. The potassium hydroxide is then dissolved in water, the solution boiled for an instant, almost neutralised with hydrochloric acid, and ammonium chloride is added until the warm solution is neutral to phenolphthalein. Excess of ammonium carbonate is then added, and the solution evaporated to dryness. The residue is dissolved in water, filtered from the silica, sodium sulphate added, and the boiling solution precipitated with a slight excess of barium nitrate. The whole is evaporated to dryness, water added, and an equal volume of 95% alcohol; the precipitate is collected on a centrifuge, and washed with 65% alcohol to remove traces of chloride or nitrate.

This precipitate is then treated with concentrated sulphuric acid in a platinum crucible similar to the gold one above mentioned, and the vapour absorbed by coarsely powdered lead glass, whereby lead fluoride is formed. The lead glass is then dried, and washed with boiling 85% alcohol to remove any lead chloride or nitrate which may be present. The lead fluoride is dissolved out of the lead glass by treatment with a saturated solution of potassium chloride diluted with four volumes of water, a small quantity of a 1% solution of gelatin added, and the lead precipitated as the colloidal sulphide by means of hydrogen sulphide. The amount of lead present in this solution is estimated colorimetrically by comparison with a standard, and hence the amount of fluorine combined with the lead determined.

T. S. P.

**Control of the New Method for the Estimation of, and Tests for the Merest Traces of, Fluorine.** ARMAND GAUTIER and PAUL CLAUSMANN (*Compt. rend.*, 1912, 154, 1753—1758).—The control experiments in the authors' method for the estimation of fluorine (this vol., ii, 681, and preceding abstract) were carried out by adding known weights of potassium fluoride to distilled water, various natural waters, the brain of a dog, calf's blood and sheep's bones, and then carrying out the analytical process. In all cases, a blank was made to determine the amount of fluorine present before the addition of the potassium fluoride. It is shown that as little as 0.1 mg. of fluorine present in 1 litre of a potable or mineral water or in 100 grams of animal or vegetable tissue can be accurately determined. The method has been devised only for those cases where very small quantities of fluorine are present, but it may be used in the estimation of mineral fluorides which can be obtained only in very small quantity.

Before the final conversion of the fluoride into lead fluoride is proceeded with (this vol., ii, 681), it is necessary to test for the presence of fluorine. This is done by treating a portion of barium sulphate-fluoride precipitate with concentrated sulphuric acid and noting whether it etches glass or not. A special apparatus has been devised for carrying out the test, by the use of which it is possible to detect the presence of 0.002—0.001 mg. of fluorine. T. S. P.

**Fluorine Analyses.** PAUL DRAWE (*Zeitsch. angew. Chem.*, 1912, 25, 1371—1372).—The usual process, heating with silica and sulphuric acid and passing the silicon fluoride into water, etc., is only accurate when care is taken to exclude all traces of moisture from the generating apparatus.

The following process is recommended: 0.3—0.4 of the fluoride and 0.5—0.6 of felspar (this is preferable to quartz powder) are well mixed; 5 grams of anhydrous copper sulphate are added, and the whole heated in a current of dry purified air with 50 c.c. of sulphuric acid in a Sarnström flask. The temperature for the first two hours is kept at 200°, and the current is then kept up for another three hours. Before reaching the absorption vessel, the gas passes through an empty tube, and then through another one containing calcium chloride.

L. DE K.

**Volumetric Estimation of Combined Sulphuric Acid.** GEORGE FINCH (*Chem. Zeit.*, 1912, 36, 782—783).—The solution is acidified with acetic acid, heated to boiling, and precipitated with standard lead acetate, a little filter paper pulp being added to obtain a clear liquid. When cold, an equal volume of alcohol (in the case of ammonium sulphate double the volume) is added to complete the precipitation. The deposit is collected and well washed with dilute alcohol (1:1), and the excess of lead in the filtrate is then titrated, as usual, with standard ammonium molybdate, using tannin as external indicator.

When dealing with sulphates other than those of the alkalis, the metal may be removed, say, with ammonia (aluminium) or with potassium hydroxide (iron, copper).

L. DE K.

**Use of Physico-chemical Volumetric Methods in the Analysis of Waters.** F. DIENERT (*Compt. rend.*, 1912, 154, 1701—1702. Compare this vol., ii, 687).—In the case of a soft water, assuming that the electrical conductivity is the sum of the individual conductivities of the dissolved salts, the following relation holds:  $a \times \text{alkalinity (expressed as CaO)} + b \times \text{nitric nitrogen} + c \times \text{chlorine} + d \times \text{SO}_3 = 100,000/\text{electrical resistance}$ , where  $a$ ,  $b$ ,  $c$ , and  $d$  are constants.  $a$  is determined by the analysis of various waters in which  $b$ ,  $c$ , and  $d$  are known, and the latter constants are evaluated by adding to water of known conductivity, known weights of either sodium nitrate, sodium chloride, or sodium sulphate, and again determining the conductivity.

The following values have thus been obtained:  $a = 0.29$ ,  $b = 0.77$ ,  $c = 0.30$ , and  $d = 0.21$ . If the alkalinity, nitric nitrogen, chlorine, and electrical resistance of any water are known, the amount of sulphate present can readily be calculated, and results given by the author show a fairly good agreement between calculation and experiment. T. S. P.

**Estimation of Total Nitrogen in Blood.** JULIUS LÖWY (*Zeitsch. physiol. Chem.*, 1912, 79, 349—351).—Kjeldahl's method (von Jaksch's modification) gives good results in the estimation of nitrogen in blood, being only very slightly lower than those obtained by Dumas' method. For clinical purposes, it is the best method. W. D. H.

**Estimation of Nitric and Nitrous Acids in Acetic Acid Solution. The Stability of Nitric Acid in Acetic Acid Solution.** KENNEDY J. P. ORTON and WILLIAM H. GRAY (*Analyst*, 1912 37, 303—306).—The method described is based on the fact that all the nitric acid in acetic acid solution is retained as potassium nitrate if the solution is evaporated to dryness on the water-bath with a slight excess of potassium carbonate; any nitrous acid present is destroyed by this treatment. The potassium nitrate, which is mixed with some acetate, is then estimated by the Lunge process, the precautions mentioned by Marquoyrol and Florentin (*Abstr.*, 1911, ii, 437) being observed. The nitrous acid is best estimated by Raschig's permanganate process (*Abstr.*, 1906, ii, 50). Nitric acid is very stable in acetic acid solution, and reduction does not take place even after prolonged exposure to diffused light, but nitrous acid is oxidised gradually to nitric acid. W. P. S.

**Use of Oxygen Under Pressure for the Estimation of Carbon in Iron Alloys.** P. MAHLER and E. GOUTAL (*Compt. rend.*, 1912, 154, 1702—1705).—The method previously described (*Abstr.*, 1911, ii, 937) is extended to the estimation of carbon in iron alloys. The alloy is mixed with iron and oxide of lead or copper, burnt in oxygen under pressure, the carbon dioxide absorbed in sodium hydroxide, and estimated by titration. A blank is performed at the same time on the iron and oxide of lead or copper used to mix with the alloy.

Examples are given of the results of analyses of ferro-manganese, spiegeleisen, ferro-chrome, ferro-silicon, ferro-tungsten, ferro-vanadium,

ferro-molybdenum, ferro-aluminium, ferro-titanium, and chromium prepared by the thermit process. T. S. P.

**A Clinical Method of Estimating the Amount of Calcium in the Urine and Other Physiological Fluids.** W. BLAIR BELL (*Bio.-Chem. J.*, 1912, 6, 205—209).—The principle of the method is to centrifugalise the urine to which a solution of oxalic acid and acetic acid, and alcohol are added in a specially graduated tube. The depth of the precipitate is compared with that in a similar tube containing a known amount of calcium salts. W. D. H.

**Assay of Zinc Ores; Separation of Iron by Ammonia.** LUCIEN L. DE KONINCK and EDM. VON WINIWARTER (*Bull. Soc. chim. Belg.*, 1912, 26, 238—243).—The chief source of error in the estimation of zinc in the usual method of separation of iron by ammonia is the retention of zinc by ferric hydroxide; this is usually stated to be due to adsorption, but it is here regarded as occasioned by the formation of a double hydroxide.

To reduce or obviate the error, the effect has been studied of adding to the solution of zinc and iron a metal such as magnesium, for which ferric hydroxide has at least an equal affinity. Solutions of zinc, iron, and magnesium chlorides in varying proportions have been used, the zinc being estimated by titration with sodium sulphide.

The effect of the addition of magnesium chloride is to reduce the loss of zinc, and when sufficient ammonium chloride is present to prevent the precipitation of magnesium hydroxide by ammonia, the loss of zinc is completely obviated when 5% of magnesium (as chloride) is added to the solution; smaller quantities are insufficient.

The method gave satisfactory results when applied to the analysis of an ore containing 45% of zinc and 10% of iron; the addition of magnesium and ammonium chloride avoided a loss of 1.04% of zinc by the ordinary method. E. F. A.

**Detection of Lead in Colouring Matters.** EDUARD SPAETH (*Pharm. Zentr.-h.*, 1912, 53, 703—704).—A portion of the substance is boiled with hydrochloric acid, the hot solution is filtered, and the lead chloride allowed to crystallise from the filtrate; the crystals obtained may be identified as lead chloride by means of the reactions with potassium iodide, sulphuric acid, hydrogen sulphide, etc. Should only traces of lead be present in the colouring matter, portions of the hydrochloric acid extract may be evaporated on microscope slides, and the residues obtained then tested with the reagents. Chromium may also be detected in the acid extract by adding alcohol and applying the usual tests. W. P. S.

**The Use of Arsenious Acid in Volumetric Analysis. II. The Estimation of Mercury.** FRANZ M. LITTERSCHEID (*Chem. Zeit.*, 1912, 36, 601. Compare Abstr., 1909, ii, 348).—Mercuric salts are conveniently estimated by the following reaction:  $\text{As}_2\text{O}_3 + 2\text{HgCl}_2 + 8\text{NaHCO}_3 = 2\text{Hg} + 4\text{NaCl} + 8\text{CO}_2 + 2\text{Na}_2\text{HASO}_4 + 3\text{H}_2\text{O}$ .

The reduction is performed by means of *N*/10-arsenious acid in a boiling-water bath until the precipitate consists entirely of grey particles of mercury. After cooling and diluting to a definite volume, a little precipitated chalk is added and the solution filtered. An aliquot part of the clear filtrate is titrated with *N*/10 iodine solution.

C. H. D.

**The Estimation of Iron in Water.** O. MAYER (*Chem. Zeit.*, 1912, 36, 552).—The water is evaporated to dryness with hydrochloric acid and bromine. The residue is mixed with 5 c.c. of hydrochloric acid (1:4) and 5 c.c. of 10% potassium thiocyanate, and diluted to 20–100 c.c., according to the proportion of iron present. In another vessel, the same quantity of reagent is titrated with an acid solution of iron alum until the same tint is reached.

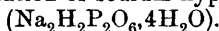
In the second method, 100 c.c. of the water, without evaporation, are mixed with 10–20 drops of hydrochloric acid containing bromine, and also with 20–40 drops of thiocyanate solution and 10 c.c. of a mixture of ether and amyl alcohol. The colour of the upper layer is compared with that of a solution obtained in the same manner from distilled water and the standard iron solution.

C. H. D.

**Estimation of Chromium in Bronzes containing Tin and Antimony.** H. SCHILLING (*Chem. Zeit.*, 1912, 36, 697).—Two grams of the turnings are dissolved in 25 c.c. of *aqua regia*, and after adding 40 c.c. of dilute sulphuric acid (1:1), the whole is evaporated and heated until white fumes of sulphuric acid appear. Two hundred c.c. of water are added, and the whole boiled vigorously. Without troubling about any lead sulphate, the copper and antimony are removed by digestion with two grams of iron wire, and the filtrate is diluted to about 500 c.c. in an Erlenmeyer flask. After heating to boiling, a few drops of silver nitrate solution (1:20) are added by way of a catalyst, and then 10 c.c. of cold saturated solution of ammonium persulphate. On boiling, the chromium is converted into chromate, and the excess of the persulphate is decomposed; the last portions, also any permanganate formed, are removed by adding 5 c.c. of hydrochloric acid and boiling a little longer. When cold the chromic acid is titrated as usual by means of ferrous sulphate.

L. DE K.

**A New Reagent for Thorium.** MARKUS KOSS (*Chem. Zeit.*, 1912, 36, 686–687).—In order to separate thorium from the cerium and yttrium earths, the solution is acidified with hydrochloric acid and the thorium precipitated by adding solution of sodium hypophosphate



The precipitate has the composition  $\text{ThP}_2\text{O}_6, 11\text{H}_2\text{O}$ . In the presence of titanium, which is also precipitated, this should be oxidised with hydrogen peroxide before adding the reagent.

Zirconium is also co-precipitated. In this case the precipitate should be heated with sulphuric acid and a few drops of nitric acid; on adding solution of oxalic acid, the thorium only is precipitated.

L. DE K.

**Separation and Estimation of Antimony in White Bearing Metal.** I. COMPAGNO (*Atti R. Accad. Lincei*, 1912, [v], 21, i, 473—478).—In this electrolytic method, use is made of a rectangular platinum-iridium cathode, roughened in a sand-blast, provided with two horizontal slits to facilitate diffusion of the electrolyte from the anode to the outer surface of the cathode, and bent into the form of an open cylinder.

One gram of the alloy in chips is treated in a covered tall 300 c.c. beaker with 4 c.c. of concentrated hydrochloric acid and 4 c.c. of dilute nitric acid (D 1.2), the nitrous fumes being expelled by gentle heating. The solution is neutralised, and rendered alkaline with about 10 c.c. of sodium hydroxide solution of 43° Baumé, 80 c.c. of sodium sulphide (D 1.225) and about 6 grams of potassium cyanide being then added. It is then boiled for five minutes and shaken, and the sides of the beaker washed down with 20 c.c. of water. When the liquid is cool, electrolysis is carried out in the beaker. The anode consists of a platinum wire of about 1 mm. diameter, surrounded by three or four coils about 1 cm. in diameter. A current density of 0.1 ampere is used, and the action allowed to proceed during the night. The deposit of antimony is subsequently washed, without interrupting the current, with a jet of water, then in a beaker of water, and finally with alcohol.

The method is found to give accurate results.

T. H. P.

**The Direct Estimation of Small Amounts of Platinum in Ores and Bullion.** FREDERIC P. DEWEY (*Chem. News.*, 1912, 106, 8—9).—The silver button obtained in the usual manner and containing besides gold also a minute proportion of platinum is treated with nitric acid, which dissolves both the silver and the platinum. The solution is diluted copiously, and a very dilute solution of hydrogen sulphide (1:20) is then added until a decided precipitate forms, which contains all the platinum together with some silver.

The sulphides are then converted into the metals by burning the filter containing them, and the ash is wrapped up in lead foil and cupelled. The silver is then parted from the platinum by means of sulphuric acid; the latter may then be tested as to purity in various ways. If from appearance the platinum shows the presence of gold, it must be re-alloyed with silver and the treatment repeated.

L. DE K.

**Estimation of Ash in Coals.** FRANZ WEISSER (*Chem. Zeit.*, 1912, 36, 757—759).—The true amount of ash is found by burning the sample in a muffle, and making the following corrections. Weight of ash—total iron oxide—sulphur trioxide in the ash + carbon dioxide in the coal + pyrites + soluble ferrous oxide in the coal.

The soluble iron is obtained by treatment of the coal with sulphuric and hydrofluoric acids; pyrites is not affected, and is found by calculation from the insoluble iron.

L. DE K.

**Influence of Metallic Carbonates Occurring in Coals on the Estimation of the Volatile Matter.** EUGÈNE PROST and MAURICE UBAGHS (*Bull. Soc. chim. Belg.*, 1912, 26, 216—222).—Determinations

of the carbon dioxide liberated as the result of the action of 5% hydrochloric acid on coal indicate that this frequently amounts to more than 1%, and may in some cases exceed 2.5%. This error is contained in the determinations of volatile matter effected in the ordinary manner, and in the case of a rigid classification of coals according to their volatile matter it may lead to false assumptions as to the value of a coal.

E. F. A.

**Net Calorific Power of Fuels (Calculated from the Results Obtained with the Mahler Bomb Calorimeter and the Proximate Analysis).** R. LUCION (*Bull. Soc. chim. Belg.*, 1912, 26, 255—262).—Ultimate and proximate analyses of a large number (63) of coals of all types and from various countries are recorded. From these the percentage of volatile matter at 100° and hydrogen in the moisture and ash-free coal are calculated. By multiplying the hydrogen values by 9, values are obtained for the percentages of water of combustion, and by dividing these by the corresponding values for the percentages of volatile matter, a series of coefficients ( $N$ ) are obtained varying in magnitude from 0.9 to 3.7.

The coal samples are grouped according to their character and origin, and average values for each group have been calculated. From a selection of these a curve has been plotted connecting  $N$  with the percentages of volatile matter.

To calculate the net calorific power ( $P'$ ) of a coal, the formula  $P' = P - 6(M + NV)$  is used, in which  $P$  is the gross value of the calorific value determined in the Mahler bomb,  $M$  and  $V$  are the percentages of moisture and volatile matter, and  $N$  is deduced from the curve.

It is claimed that this net value is as accurate as the gross value.

The same method of calculation is applied to cokes.

E. F. A.

**Action of Potassium Permanganate on Organic Compounds.** II. JOSEF HETPER (*Zeitsch. anal. Chem.*, 1912, 51, 409—429. Compare Abstr., 1911, ii, 339).—The author has previously shown that the behaviour of organic compounds towards potassium permanganate and phosphoric acid is dependent on their constitution, and has worked out a schematic representation for their analysis. Many of the substances, however, exhibit a behaviour contrary to that expected, and one of the objects of the present paper is to clear up the discrepancies. For this purpose the author has examined the behaviour of many organic compounds towards alkaline potassium permanganate. It is generally known that the oxidising action of potassium permanganate is weaker in acid than in alkaline solution. A somewhat concentrated, alkaline solution must be employed for the quantitative oxidation of most organic substances; the author employs  $N/2$ -potassium permanganate containing 40 grams of sodium hydroxide per litre, and effects the oxidation on the water-bath.

As the outcome of a large number of experiments, the following generalisations are made: (1) The oxidation of compounds of the aliphatic series by alkaline potassium permanganate proceeds the more

easily the smaller the carbon chain of the substance under examination. Conversely, in acid solution, substances are more easily oxidised the higher they are in the homologous series. (2) Compounds containing alkyl groups are oxidised by alkaline potassium permanganate always through the formation of the corresponding fatty acid. (3) Substances which are not attacked, or only slightly, by acidified potassium permanganate are also only slightly oxidised in alkaline solution. (4) Substances of acid character are more easily oxidised by potassium permanganate in acid solution, whilst basic substances are more easily oxidised in alkaline solution. C. S.

**The Oils of Copaiba Balsam.** ERNST DEUSSEN and BENNO EGER (*Chem. Zeit.*, 1912, 36, 561—562. Compare Deussen and Hahn, *Abstr.*, 1910, i, 687).—Caryophyllene, copaiba oils, and mixtures of copaiba and gurjun oils have been investigated by the nitrogen oxides method (this vol., i, 368). The yield of  $\beta$ -caryophyllene is 14—16% from Para oil and 5—8% from Maracaibo oil. The presence of 10% of gurjun oil in Para copaiba oil may be detected by the much lower optical rotation and by the higher m. p. of the hydrochloride. For the qualitative detection of gurjun oil, 1 drop is mixed with a drop of 10% sodium nitrite solution, and added cautiously to concentrated sulphuric acid. The reaction is only regarded as positive if the coloration appears within five minutes. If a reaction is given, 170 grams of the oil are distilled under 10—12 mm. pressure, three fractions being collected below 145°. Each fraction is dissolved in 300 grams of aqueous acetone, and oxidised by the gradual addition of 160 grams of potassium permanganate in the course of twelve hours. The solution is then decanted, and the residue is washed with 200 grams of acetone and then with 200 grams of ether. The solvent is then removed by distillation, and the residual oil dried and distilled under 3 mm. pressure. The fractions 130—140° and 140—165° are treated with semicarbazide. For the test, 1.1 gram of semicarbazide hydrochloride is dissolved in water, a solution of 1 gram of potassium acetate in 3 grams of alcohol added, and then 2 grams of the oil, followed by alcohol until the solution is clear. The semicarbazone is precipitated in two days. After recrystallisation, the pure semicarbazone of gurjunene ketone has m. p. 234°, and rotation + 317°. C. H. D.

**The Forensic-Chemical Detection of Oil of Savin.** JUHO HÄMÄLÄINEN (*Biochem. Zeitsch.*, 1912, 41, 241—246).—Oil of savin can be distinguished from turpentine oil and thuja oil by the fact that, on administration to a rabbit, it is excreted in the form of a glycuronate, which can be isolated best in the form of the strychnine salt in the following way. The urine is first precipitated by normal lead acetate, and the filtrate is then precipitated with basic lead acetate. The second precipitate is then treated with 5% sulphuric acid, and the filtrate from the lead sulphate is neutralised with barium carbonate. The filtrate from barium sulphate is concentrated in a vacuum, and hot strychnine sulphate solution is added. On cooling, strychnine glycuronate,  $C_{37}H_{49}O_9N_2 \cdot 2H_2O$ , m. p. 196—197°,  $[\alpha]_D^{20} = -39.66^\circ$ , separates. On evaporating the mother liquor, a second salt,  $C_{37}H_{49}O_9N_2 \cdot 3H_2O$ ,

m. p. 192—193°,  $[\alpha]_D^{20} = -37.08^\circ$  separates. The strychnine salt can be converted into the barium salt, from which a free amorphous acid, m. p. 82—83°, can be obtained. S. B. S.

**New Method of Estimating Glycerol in Wines.** CONSTANTIN BEIS (*Bull. Soc. chim.*, 1912, [iv], 11, 618—623).—The author has made a critical examination of the methods employed for the estimation of glycerol in wine where oxides of the alkaline-earth metals are used to render the acids and sugar insoluble. From his results he draws the conclusion that the discrepancies shown in several determinations of the same wine are due to variation in the amount of oxide employed, and as a result of further investigations suggests the following method of analysis.

One hundred c.c. of wine (50 c.c. if a sweet wine) are run into a porcelain basin, just neutralised with barium hydroxide, and concentrated to a syrup at a temperature below 70°. Sand is then well incorporated into the syrup, and the mixture extracted with 50 c.c. of acetone by warming on a water-bath and then leaving to cool before filtering. The extraction is repeated three times, and the filtrate made up to 200 c.c. Two lots of 100 c.c. of this filtrate are separately evaporated without boiling. In one residue, the sugar is estimated by Fehling's solution. The other is dissolved in five times its weight of water, and to it is added powdered barium hydroxide in amount varying according to the sugar found in the first residue. For sugar under 0.05 gram, use a few mg. more of barium hydroxide, if between 0.05 and 0.3 gram use the same weight, and if between 0.3 and 0.5 gram use four-fifths of the weight. After leaving for some time, it is mixed with sand and again extracted with acetone as above, using 40 c.c. for the first extraction and 25 c.c. for the other. The filtrate is evaporated at 50°, the glycerol dried for one hour at 60°, and weighed. W. G.

**New Method for the Estimation of Sugars in Potatoes.** OSWALD CLAASSEN (*Chem. Zeit.*, 1912, 36, 741—744, 771—772).—The method consists in determining the optical activity of an extract of the potatoes before and after inversion. The amounts of dextrose and sucrose present are then calculated from the readings obtained. It is recommended that the potato pulp be digested with alcohol on the water-bath in order to obtain the solution of the sugar for the polarimetric examination; the alcohol is removed from the extract before inversion, and a correction made for the volume of the insoluble potato-substance. The results obtained in the investigation show that, when potato juice is kept for some length of time, the sucrose is inverted, and the quantity of total sugar present corresponds with the amount of dextrose. W. P. S.

**The Estimation of Lactic Acid in the Presence of  $\beta$ -Hydroxybutyric Acid.** JULIUS MONDSCHIEIN (*Biochem. Zeitsch.*, 1912, 42, 91—104).—By von Fürth and Charnass's method, lactic acid can be estimated by oxidising with permanganate in sulphuric acid solution, and the aldehyde thus formed can be titrated by Ripper's bisulphite method.  $\beta$ -Hydroxybutyric acid, on the other hand, can be estimated by oxidation with dichromate and sulphuric

acid mixture, according to Schaffer's process, and the acetone formed can be estimated by an iodine titration method. If mixtures of the two acids are present, small quantities of acetone are formed in the permanganate oxidation, and small quantities of aldehyde in the dichromate oxidation. Accordingly, both acetone and aldehyde are found in the oxidation mixtures, whichever process is employed, if both acids are present. If the oxidation products are treated with hydrogen peroxide in alkaline solution, the aldehyde is oxidised to acetic acid, and on distilling the mixture, pure acetone alone distils over. If, therefore, it is required to estimate lactic acid in a mixture, von Fürth and Charnass's process is employed, and an aliquot part of the distillate is oxidised by hydrogen peroxide in alkaline solution, and the acetone found in the distillate from this is estimated by Ripper's process. The quantity thus found is subtracted from the quantity found in another aliquot portion titrated by Ripper's method and not previously oxidised. The  $\beta$ -hydroxybutyric acid can be estimated by oxidising by Schaffer's method, and estimating the acetone formed after previously oxidising the aldehyde by peroxide.

S. B. S.

**The Estimation of Lactic Acid in the Presence of Proteins.** JULIUS MONDSCHIEIN (*Biochem. Zeitsch.*, 1912, 42, 105—123).—When estimating lactic acid in muscular tissue by the ordinary method, according to which the protein is coagulated by heat, it is found that about one-third of the acid is precipitated with the coagulum. In the filtrate from the coagulum the lactic acid can be estimated with sufficient accuracy by simply titrating in the presence of phenolphthalein. The author shows that  $\beta$ -hydroxybutyric acid is also present, but in quantities which are practically negligible. The acid carried down in the coagulum can be estimated by conversion of the protein into alkali albumin by dissolving it in strong sodium hydroxide. On saturation of this solution with sodium chloride, the protein is precipitated, and in the filtrate the lactic acid can be estimated by von Fürth and Charnass's method.

S. B. S.

**Estimation of Uric Acid in Urine by means of Iodine.** TORQUATO GIGLI (*Boll. Chim. Farm.*, 1912, 51, 39—40).—Pizzorno's method for estimating uric acid in urine (*Abstr.*, 1911, ii, 667) gives results which gradually increase with the time during which the iodine and uric acid are left in contact. This is also the case when potassium urate solutions are employed. Further, urine contains substances other than uric acid which combine with iodine; thus, the iodine absorbed by two normal urines was found by immediate titration with thiosulphate to be 1.98 and 2.33 grams per litre, which would correspond respectively with 1.31 and 1.54 grams of uric acid per litre, such large amounts being improbable.

T. H. P.

**Estimation of Uric Acid in the Urine.** S. M. VELLER (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 647—652).—Kowarsky's method for the estimation of uric acid in urine (*Deut. med. Woch.*, 1906) is rapid, and, with normal and pathological urines and also with uric acid solutions

containing urea, albumin and sugar, gives results in close agreement with those obtained by the Ludwig-Salkowski (Abstr., 1895, ii, 538) and Hopkins' methods. Ruhemann's uricometer gives inaccurate results. T. H. P.

**Analysis of Soap Powders.** JAMES J. POLAK (*Chem. Weekblad*, 1912, 9, 470—472, 548).—For the estimation of sodium carbonate in soap powders, the author recommends incineration of the powder, and titration of the residual sodium carbonate. Subtraction of the soda equivalent of the fatty acids present from the residual carbonate gives the amount of sodium carbonate in the sample.

The ordinary method of extracting with absolute alcohol is costly, and the water always present in the soap dilutes the alcohol and induces solution of the carbonate.

In the second paper, the incineration of the powder before titration is stated to be unnecessary. A. J. W.

**New Oxygen Absorption Method for Oils.** LEONARD P. WILSON and G. S. HEAVEN (*J. Soc. Chem. Ind.*, 1912, 31, 565—568).—The following method was used for determining the quantity of oxygen absorbed by various oils: a mixture of 0.2 gram of the oil and 1 gram of kieselguhr was placed in a flask of about 250 c.c. capacity. The neck of this flask was provided with a side-tube on which was a bulb, and, after the side-tube had been sealed, the flask and its contents were heated to 100° for one hour. The flask was then cooled, the side-tube attached to levelling tubes filled with water, and on breaking the end of the side-tube the difference in level of the water gave the volume of the oxygen absorbed by the oil from the air in the flask. Linseed oil absorbed about 20% of oxygen, poppy-seed oil 17%, cotton-seed oil 11.1%, sesame oil, 5.8%, and olive oil none.

W. P. S.

**The Bromine Absorption of Certain Vegetable Oils and Fats.** H. SPRINKMEYER and A. DIEDRICHS (*Zeitsch. Nahr. Genussm.*, 1912, 23, 679—687).—The following quantities of bromine compounds were obtained when various oils were examined by the process described by Hehner and Mitchell (Abstr., 1899, ii, 190): Linseed oil, 27.3 to 30.8%; candlenut oil, 8.8%; hemp oil, 8.82%; walnut oil, 2.22%; soja bean oil, 3.62%; sesame oil, 0.14%; mustard oil, 1.30%; rape oil, 1.92%; poppy oil, sunflower-seed oil, maize oil, cotton-seed oil, castor oil, tea oil, and earthenut oil, butter, margarine, tallow, lard, cocoanut oil, palm kernel oil, cacao butter, stillingia tallow, tulucuna fat, dika fat, and malukang butter, none. Shea butter, however, yielded from 7 to 8.6%, mowrah butter from 0.4 to 0.95%, enkabang tallow, 0.17%, and adjab fat, 2.2%. There is some evidence that the insoluble bromine compound is due, in certain cases, to the unsaponifiable constituents of the fats. W. P. S.

**Detection of Earthenut Oil in Olive Oil.** LUDWIG ADLER (*Zeitsch. Nahr. Genussm.*, 1912, 23, 676—679).—The method proposed is based on the different solubility of the fatty acids of the oils

in alcohol. One c.c. of the oil is saponified under a reflux apparatus with 5 c.c. of an 8% alcoholic potassium hydroxide solution, the mixture is then cooled to about  $25^{\circ}$ , and 1.5 c.c. of dilute acetic acid (1 vol. of acid to 2 vols. of water) and 50 c.c. of 70% alcohol are added. The mixture is shaken and cooled to  $16^{\circ}$ ; if, after being kept at this temperature for five minutes, the solution is clear, the mixture is cooled to  $15.5^{\circ}$ . Should a precipitate not be obtained, the oil under examination contains less than 5% of earthnut oil. Fourteen samples of pure olive oil examined by this method yielded crystals at temperatures varying from  $11.8^{\circ}$  to  $14.3^{\circ}$ , whilst the addition of 5% of earthnut oil raised the crystallising point to  $15.9$ — $17.0^{\circ}$ . In the case of earthnut oil itself the crystallising point is  $40.5^{\circ}$ . W. P. S.

**Analysis of Fats.** ANTONIO MADINAVEITIA (*Anal. Fis. Quim.*, 1912, 10, 153—158).—In the determination of glycerol in fats, good results are obtained by the treatment of small quantities (0.15 to 0.35) of the fat with 10 c.c. of hydriodic acid (D 1.8); thus avoiding the preliminary hydrolysis necessary in Zeisel and Fanto's process.

In the determination of free hydroxyl by Lewkowitsch's acetic anhydride method, the author finds that interchange of acetyl and higher fatty radicles takes place; thus tristearin gives acetodistearin.

G. D. L.

**The Action of Twitchell's Reagent.** EDWIN GRIMLUND (*Zeitsch. angew. Chem.*, 1912, 25, 1326).—Statements that the hydrolysis of fats in the Twitchell process is brought about by the simultaneous presence of naphthalene and dilute sulphuric acid, or that the process consists in heating the fat with a 1% solution of naphthalenestearosulphonic acid, are incorrect. The reaction really takes place in two phases, the fat being first emulsified by that portion of the reagent which is insoluble in sodium chloride solution, and then hydrolysed by the sulphuric acid and aromatic sulphonic acids present. W. P. S.

**Beeswax and Carnauba Wax. Method of Analysis; Estimation of Foreign Hydrocarbons.** ALEXANDRE LEYS (*J. Pharm. Chim.*, 1912, [vii], 5, 577—588).—The method of indices (compare Buisine, *Abstr.*, 1891, 131; 1892, 251), as at present largely employed for the analysis of such waxes, leads to doubtful results, which on totalling up often give a content of 117—131%. The author details new methods for the estimation of hydrocarbons, alcohols, saturated and unsaturated acids in waxes. The procedure is as follows:

Into a specially designed combined flask and separating funnel is weighed 10 grams of the wax, which is then saponified by alcoholic potassium hydroxide in the presence of benzene. Water is added, and the heating is continued for some time. After settling, the lower layer, which contains the soap, is run off and used later for estimating the acids. The benzene layer is transferred to a dish, and the benzene evaporated off. The residue is dissolved in amyl alcohol, to which is then added an equal volume of fuming hydrochloric acid, the whole being boiled and then left to cool. The hydrocarbons separate on the surface in a solid cake, which can be removed, dried, weighed, and of

which the iodine number can be determined. The alcoholic liquid is transferred to a large dish, excess of water added, and the amyl alcohol driven off on the water-bath, after decanting the aqueous layer, when the alcohols remain.

For the acids, the above-mentioned soap solution is warmed until the whole is liquid, just neutralised with acetic acid, lead acetate added, and the mixture boiled for twenty minutes and cooled. The liquid is decanted off, and the lead salts dissolved in hot benzene and left overnight. The salts of the saturated acids, which separate, are collected, decomposed with acetic acid, and after dilution with water, the acids are extracted with benzene. The benzene is then evaporated off and the acids are weighed.

By determining the iodine number of the original wax and of the hydrocarbons when separated, the percentage of unsaturated acids in terms of oleic acid can be calculated from their difference.

W. G.

**The Action of Hydrazine and Hydroxylamine on Ferricyanides, and a New Method for the Estimation of Hydrazine and Ferricyanides.** PRIYADA RANJAN RÂY and HEMENDRA KUMAR SEN (*Zeitsch. anorg. Chem.*, 1912, **76**, 380—386).—An alkaline solution of hydrazine sulphate is quantitatively oxidised by potassium ferricyanide according to the equation  $\text{N}_2\text{H}_4 + \text{O}_2 = \text{N}_2 + 2\text{H}_2\text{O}$ . About 0.03—0.07 gram of hydrazine sulphate is introduced into a nitrometer, followed by 4—5 c.c. of 15% potassium hydroxide. A crystal of potassium ferricyanide is introduced, and the nitrometer is well shaken.

In the estimation of ferricyanides, solid hydrazine sulphate in excess is introduced into the nitrometer from below, and 0.3—0.7 gram of potassium ferricyanide is introduced through the funnel, followed by alkali as before. The method is preferable to the permanganate titration.

Phenylhydrazine is also oxidised by ferricyanide, giving nitrogen and benzene. Hydroxylamine is oxidised, yielding nitrogen and nitrous oxide:  $4\text{NH}_2\cdot\text{OH} + \text{O}_2 = 2\text{N}_2 + 6\text{H}_2\text{O}$ ;  $6\text{NH}_2\cdot\text{OH} + \text{O}_2 = 2\text{N}_2\text{O} + 2\text{NH}_3 + 6\text{H}_2\text{O}$ .

C. H. D.

**A New Reaction for Organic Bases.** K. W. CHARITSCHKOFF (*Chem. Zeit.*, 1912, **36**, 581).—A solution of inactive naphthenic acid in petroleum or ether is mixed with half its volume of a 3% solution of copper sulphate. If traces of an organic base are added, the upper layer becomes green on shaking. Caffeine and diphenylamine do not give the reaction. Oleic acid may be used in place of naphthenic acid.

C. H. D.

**Volumetric Analysis of Cinchona Bark.** MARTIN KLEINSTUCK (*Pharm. Zentr.-h.*, 1912, **53**, 643—651, 680—684, 705—718).—Twenty grams of the powdered bark are stirred for three hours with 50 c.c. of *N*/1-hydrochloric acid and 250 c.c. of water, and the extract is then filtered. After rejecting the first 50 c.c. of the filtrate, 150 c.c. of the latter are

diluted with 150 c.c. of water and neutralised with *N*/1-sodium hydroxide solution; to the turbid solution obtained is added 1 gram of clay, which has been treated with a copper salt and a platinum salt and ignited, and the mixture is oxidised by passing a current of air through it for one hour. The mixture is now filtered, the residue is washed with *N*/2-sodium chloride solution containing 5 c.c. of *N*-hydrochloric acid per litre, and the filtrate and washings are diluted to 500 c.c. The solution is next passed slowly through a clay filter in order to remove tannins, and 100 c.c. of the filtrate are treated with 50 c.c. of a solution containing 5.7285 grams of picric acid and 50 c.c. of *N*-hydrochloric acid per litre. The precipitate is removed by filtration, 15 c.c. of the filtrate are boiled for ten minutes with 50 c.c. of a 1.39% titanium trichloride solution in an atmosphere of carbon dioxide, and the excess of titanium trichloride is then titrated with a ferric chloride solution of equivalent strength. The percentage quantity of alkaloids present,  $x$ , is found from the formula:  $x = 0.775(t - 25)$ , where  $t$  is the number of c.c. required for the titration.

W. P. S.

**Creatine and Creatinine. IV. Estimation of Creatine in the Presence of Sugar.** WILLIAM C. ROSE (*J. Biol. Chem.*, 1912, 12, 73—80)—By the use of phosphoric acid instead of hydrochloric acid, and by allowing the diluted solutions to remain for a few minutes before making the readings, just as accurate estimations of creatine and creatinine may be made in diabetic as in normal urine.

W. D. H.

**Estimation of Morphine in Opiates, especially in Pantopon "Roche."** E. ANNELER (*Arch. Pharm.*, 1912, 250, 186—198).—In estimating the morphine in pantopon "Roche" (that is, the hydrochlorides of the total alkaloids in opium), the author finds that the usual methods of the pharmacopœia always yield results which are 4—5% too low. The difficulty is to remove the accompanying alkaloids without loss of morphine.

In examining the usual methods, the author has employed (1) known mixtures of the hydrochlorides of morphine, narcotine, papaverine, thebaine, codeine, and narceine; (2) known mixtures of morphine hydrochloride and pantopon free from morphine; (3) pantopon itself.

The Dieterich-Helfenberg process (*Deutsch Arzneibuch V*) gives results 4—5% too low, because during the filtration of the accompanying alkaloids a small quantity of morphine crystallises in and on the filter. Debourdeaux's modification of the method of the English and of the French pharmacopœiæ is the best for most purposes, because, although the results are about 3% too low, the error is constant, and it is only necessary to add to the weight of the morphine found 30 mg. for every 50 c.c. of mother liquor.

The author has devised a very convenient method. The alkaloids are liberated by sodium hydrogen carbonate, and those other than morphine are extracted by chloroform saturated with morphine; the morphine itself is then extracted by a mixture of equal volumes of isobutyl alcohol and chloroform, the extract is shaken with a known

amount of standard hydrochloric acid, the excess of which is found by titration. The results are about 1.5% too high. C. S.

**Chrysophanic Acid and Chrysarobin.** EUGÈNE LÉGER (*J. Pharm. Chim.*, 1912, [vii], 5, 588—591. Compare Tutin and Clewer, this Journ., 1912, 101, 290).—A suggestion that chrysarobin should be substituted for chrysophanic acid for medicinal purposes, since they both have the same physiological effect, and it is difficult to obtain the latter in a state of purity. The two substances can be distinguished (1) by their behaviour with concentrated sulphuric acid, chrysarobin giving an orange-yellow colour and chrysophanic acid, a red.

(2) Chrysophanic acid when triturated with alcohol and treated with aqueous sodium hydroxide, dissolves, giving a red solution. Chrysarobin when similarly treated is insoluble (compare Liebermann and Seidler, *Abstr.*, 1879, 326). W. G.

**Detection of Saponin.** J. RÜHLE (*Zeitsch. Nahr. Genussm.*, 1912, 23, 566—577).—Saponin may be detected by means of its hæmolytic action, the test being applied to the substance after the latter has been extracted from the article under examination (compare *Abstr.*, 1910, ii, 559). As the hæmolytic action of the saponin varies with the cholesterol-content of the blood corpuscles, its presence may be confirmed by making a second test after the addition of cholesterol to the blood corpuscle liquid; should the hæmolytic action fail in this second test, saponin is present, as the hæmolytic action of other substances is not inhibited by cholesterol. The test is not influenced by the presence of glycyrrhizin, but this substance renders Vamvakas' test untrustworthy, as it does also the colour reactions with  $\alpha$ -naphthol, thymol, etc. W. P. S.

**Detection of Saponin in Beverages and Foods by Hæmolysis.** CESARE SORMANI (*Zeitsch. Nahr. Genussm.*, 1912, 23, 561—566).—A synopsis of papers published by Rusconi is given, and the method described by him for the detection of saponin (*Abstr.*, 1910, ii, 559) is recommended. This method may also be employed for the detection of the seeds of *Agrostemma Githago*, *Sorghum*, *Atriplex*, and *Delphinium* in wheat flour, the injurious properties of these seeds being due to the presence of saponin as a constituent. W. P. S.

**Refractivity of the Products of the Hydrolysis of Caseinogen and a Rapid Method of Determining the Relative Activity of Trypsin Solutions.** T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1912, 12, 23—29).—The complete hydrolysis of sodium caseinogenate in trypsin does not alter the refractivity of its solution. This enables a simple and rapid method to be employed of determining from time to time the extent of digestion, namely, precipitating the undigested caseinogenate by a known amount of acetic acid, filtering off the precipitate, and measuring the refractive index of the filtrate.

W. D. H.

**The Gluten-content and the Baking Quality of Flour. Estimation of the Gluten-content.** O. RAMMSTEDT (*Pharm. Zentr.-h.*, 1912, 53, 673—680).—Although the results of an investigation carried out by the author show that there is no strict relation between the quantity of gluten yielded by a flour and its quality from a baking point of view, the estimation should not be discarded, as it may yield useful information regarding the qualities of different flours when the methods employed for the estimation have been improved. The weight of the gluten should be determined both in the moist and dry state, and the gluten should be dried under reduced pressure in order to prevent changes in its composition. W. P. S.

**Estimation of Humus, Especially in Heavy Clay Soils.** WILLIAM BEAM (*Cairo Sci. J.*, 1912, 6, 93—103).—In extracting soils, a Buchner funnel, with a layer of asbestos underneath the filter paper, was employed. The soil is mixed with sand, and covered with a layer of sand, over which a filter paper is placed. It was found that washing with water cannot be depended on for removing the excess of hydrochloric acid used for liberating the humic acids. The difficulty is overcome by washing with a solution of carbon dioxide.

For complete extraction of humus it is necessary to renew the ammonia repeatedly. Suspended clay is readily removed by ammonium carbonate; a part of the humus may, however, be precipitated with the clay, which should be separated by filtration and re-extracted.

Prolonged heating of the dried humus must be avoided, otherwise a portion may be rendered insoluble in ammonia.

The following colorimetric method was found to give accurate results. The soil (5 grams) is extracted with hydrochloric acid, and then (without working out the acid) boiled for ten minutes with 5% sodium carbonate. When cold, the liquid is diluted to 250 c.c. and left overnight, or centrifuged. The clear liquid is decanted through an asbestos filter, and the colour compared with that obtained with a soil in which the amount of humus has been estimated. N. H. J. M.

**Photometry of Blood-Pigment.** E. E. BUTTERFIELD (*Zeitsch. physiol. Chem.*, 1912, 79, 439—445).—The experiments recorded with the spectrophotometer show that the estimation of hæmoglobin by this instrument is possible. Various photometric constants with different kinds of blood are given. W. D. H.

**Quantitative Spectroscopy and Spectrophotography as Methods for Determining the Presence of Oxyhæmoglobin and its Derivatives.** OTTO SCHUMM (*Biochem. Zeitsch.*, 1912, 42, 304—315).—The author gives a general account of the methods already published, indicating in the case of spectroscopy the method of measuring various absorption bands and of determining the position of maximum absorption, and gives examples to illustrate the accuracy of the method. He calls attention to the various advantages and disadvantages in photographing the spectrum and using the photographs for measurements. S. B. S.

## General and Physical Chemistry.

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**The Ultimate Lines, and the Quantities of the Elements Producing these Lines, in Spectra of the Oxyhydrogen Flame and Spark.** SIR WALTER N. HARTLEY and HENRY W. MOSS (*Proc. Roy. Soc.*, 1912, *A*, 87, 38—48).—Wave-length measurements have been made of the ultimate lines in the oxyhydrogen flame and spark spectra of a number of metals, and the quantities of the various elements which are required for the appearance of the ultimate lines have also been determined.

In the case of the spark spectra, an arrangement has been devised by means of which the spectra produced by any desired number of discharges can be recorded on photographic plates. In utilising this arrangement, the usual procedure was to expose a series of plates to a gradually decreasing number of discharges, and thus to eliminate all but the most persistent lines. The smallest quantity of material necessary for the production of the ultimate lines was estimated from the loss of weight of the electrodes during a measured interval of discharge and the number of discharges per second.

A comparison of the ultimate lines in the two types of spectra shows that these are usually quite different. The ultimate line spectrum varies also according to whether the observations are made with the eye only, or by photography, and in the latter case it depends also on the sensitiveness of the photographic plate. H. M. D.

**Relationship between the Atomic Weights and Spectra of the Alkali Metals.** OTTO BÜRY (*Zeitsch. physikal. Chem.*, 1912, 80, 381—384).—The rule of Kayser and Runge, that the square root of the differences in the vibration velocity of certain pairs of lines of the third order in the spectra of the alkali metals are proportional to the atomic weights of the metals is only approximate, the deviations being the greater the higher the atomic weight. The author suggests that the law might be more nearly fulfilled if the sum of the vibration differences of all the pairs of lines of the principal series is taken into consideration, and finds an excellent agreement in the case of rubidium and a moderate agreement in the case of potassium. The data for caesium are not sufficient to permit of calculation. G. S.

**The Absorption of Ultra-violet Radiation by Ozone and its Application to the Estimation of Small Quantities of Ozone.** FRIEDRICH KRÜGER and M. MOELLER (*Physikal. Zeitsch.*, 1912, 13, 729—732. Compare Hallwachs, *Abstr.*, 1909, ii, 1050).—On the assumption that the photo-electric effect is proportional to the intensity of the incident light, the author has measured the absorption of ultra-violet light of wave-length  $\lambda = 254$  in ozonised oxygen with the aid of a photo-electric cell containing a potassium electrode in contact with hydrogen at a pressure of 0.3 mm. The results obtained

with different samples are in good agreement with those found by the iodine method, and it is shown that the optical method can be employed for smaller concentrations than the chemical method, the lower limit being about 0.001%.

The extinction-coefficient has also been determined for other lines in the region  $\lambda = 200$  to  $\lambda = 300$ , the values obtained differing very considerably from those given by Meyer (Abstr., 1904, ii, 2), which have been made the basis of previous attempts to estimate small quantities of ozone by the absorption of ultra-violet light. The curve showing the connexion between the extinction-coefficient and the wave-length is much more convex to the wave-length axis than the curve plotted from Meyer's data, and the magnitude of the extinction-coefficient at its maximum ( $\lambda = 254$ ) is much greater than the previously recorded value.

H. M. D.

**Metallic Compounds with Molecular Asymmetry.** ALFRED WERNER (*Bull. Soc. chim.*, 1912, [iv], 11, i—xxiv).—A lecture summarising the author's work on the optical isomerism of compounds in which the asymmetry is due to a cobalt, chromium, iron, or rhodium atom.

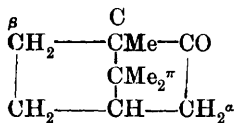
D. F. T.

**The Rotatory Dispersion of Some Camphor Derivatives.** LEO A. TSCHUGAEFF (*Bull. Soc. chim.*, 1912, [iv], 11, 718—722).—The author has observed (Abstr., 1911, ii, 450) that the ketonic derivatives of the terpenes are distinguished by an unusual elevation of the rotatory dispersion,  $[\alpha]_D/[\alpha]_C$ . The investigation is now extended to  $\alpha$ -chloro-,  $\alpha$ -iodo-,  $\alpha\alpha'$ -dibromo-,  $\alpha\alpha'$ -di-iodo-,  $\alpha\beta$ -dibromo-camphor, the ammonium salt of  $\alpha$ -bromocamphor- $\pi$ -sulphonic acid (see annexed formula), and also to the isomeric  $\beta$ -(epi)-camphor; these (in benzene, carbon disulphide, and methyl alcohol solutions at 20°) show exalted values for the rotatory dispersions  $[\alpha]_D/[\alpha]_C$  and  $[\alpha]_E/[\alpha]_C$ , the values being highest for the  $\alpha\alpha'$ -di-substituted derivatives and lowest for the  $\alpha$ -mono-substituted. For the  $\alpha$ -halogen derivatives the value is independent of the nature of the halogen.

The conclusion is drawn that the exaltation is probably general to all camphor derivatives containing the grouping C—CO—C, and is connected with the selective absorption in the ultra-violet portion of their spectra.

D. F. T.

**The Radiations Effective in the Photochemical Synthesis of Quaternary Compounds, in the Polymerisation of Different Gases, and in the Photolysis of Acetone.** DANIEL BERTHELOT and HENRI GAUDECHON (*Compt. rend.*, 1912, 155, 207—210).—Equal volumes of carbon monoxide and ammonia combine in a few hours to give formamide under the influence of the ultra-violet rays ( $\lambda < 0.2\mu$ ) from a mercury-quartz lamp. Combination also takes place slowly with medium ultra-violet rays ( $\lambda = 0.2$  to  $0.3\mu$ ), but there is no combination under the influence of initial ultra-violet or solar rays ( $\lambda > 0.3\mu$ ). On the other hand, formamide slowly decomposes when submitted to



ultra-violet rays, the reaction being complicated by dehydration and formation of hydrogen cyanide.

Light, less markedly than heat, produces polymerisation (compare *Compt. rend.*, 1910, 150, 1164). Cyanogen exposed to sunlight slowly polymerises. Acetylene, under the same conditions, is not changed, but it too polymerises under the influence of the ultra-violet rays from a mercury-quartz lamp.

Acetone is rapidly decomposed into carbon monoxide and ethane by the rays from the lamp, but is not acted on by sunlight. A 10% aqueous solution of acetone behaves similarly, except that with sunlight the acetone is hydrated and decomposed, giving methane and acetic acid.

W. G.

**The International Radium Standard.** WILLY MARCKWALD (*Physikal. Zeitsch.*, 1912, 13, 732—734).—The purity of the radium chloride, prepared by Mme. Curie for the International Radium Standard, and by Hönigschmid for the Austrian Standard, is called into question on the ground that (as is the case for mixed liquids with the vapour pressure), in the fractional crystallisation of isomorphous salt-mixtures the solubility of the mixed crystals may attain a maximum or minimum at a certain composition. Reasons are advanced for considering that the purest radium chloride capable of being prepared by fractional crystallisation of the mixed radium and barium chlorides still contains 1% of barium chloride, the spectroscopic evidence of Mme. Curie, that the addition of 0.6% of barium chloride to the final product considerably strengthened the barium lines, being considered inconclusive. The addition of five times the atomic weight of helium (3.99) to that of lead (207.1) gives for the atomic weight of radium 227.0, whereas Hönigschmid's value, 225.95, referred to that of lead and referred to that of uranium, makes the atomic weight of helium 3.77 and 4.14 respectively, on the usual view that three atoms of helium are expelled in the change of uranium into radium, and five atoms in the change of radium into lead. It is suggested that analogous fractionations should be carried out on the pure material, converted into a salt with another anion, such as the bromide, for it is improbable that the solubility relations of the new mixed crystals will be the same as for the chlorides.

F. S.

**The Transformations of the Active Deposit of Thorium.** E. MARSDEN and C. G. DARWIN (*Proc. Roy. Soc.*, 1912, A, 87, 17—29).—The product or products "thorium-C" give two types of  $\alpha$ -rays of ranges 4.8 and 8.6 cms. respectively, and produce thorium-D, which gives  $\beta$ - and  $\gamma$ -rays, and from Geiger and Nuttall's empirical relation between range and period, it is to be expected that the period (one hour) of thorium-C corresponds with the rays of range 4.8 cm., whilst the rays of range 8.6 cm. correspond with a period of  $10^{-12}$  second. The conclusions advanced are that thorium-C, a homogeneous substance of period of about one hour, undergoes two modes of disintegration: (1) 35% of the atoms expel an  $\alpha$ -ray of range 4.8 cms., and are transformed into thorium-D; (2) 65% of the atoms expel a  $\beta$ -ray of high velocity and penetrating power, but no  $\gamma$ -ray, and are transformed

into the product (called thorium- $C_2$ ), which expels the  $\alpha$ -rays of range 8.6 cms., and probably has a period of the order of  $10^{-12}$  second. Thorium- $D$ , on the other hand, gives relatively soft  $\beta$ -rays, and a very intense  $\gamma$ -radiation, which is the most penetrating known, and has probably six times as much energy as the  $\beta$ -rays. The products both of the  $C_2$ - and  $D$ -members are unknown, and are probably inactive, but subtracting six times the atomic weight of helium from that of thorium (six  $\alpha$ -particles being expelled in the series), the result is very nearly the atomic weight of bismuth, of which, however, there is very little confirmatory evidence. These conclusions, which are in agreement with all the known facts relating to the active deposit of thorium, have been drawn from the following lines of evidence.

(1) By counting the number of scintillations on a zinc sulphide screen receiving  $\alpha$ -particles, from a wire made active with thorium- $C$  after passage through a slit and strong magnetic field, the relative numbers of the more readily and less readily deviated rays were found to confirm the ratio (0.35 + 0.65) previously deduced in other ways. (2) No alteration of this ratio was observed when very short exposures to the thorium emanation of the wire being made active were employed. The  $\alpha$ -activity always rose to a maximum in 225 minutes, corresponding with a period of about an hour for the  $\alpha$ -ray-giving product. By dipping plates of various electrochemical potentials into the solution of the active deposit, the ratio of the two types of  $\alpha$ -particles was always the same. Thorium- $C$  separated by recoil from thorium- $B$  gave the ordinary ratio, and this was not affected by volatilising the product at various temperatures. (3) The  $\beta$ -ray absorption curve of thorium- $C$  and  $-D$  was compared with that of pure thorium- $D$ , and it was found that the former rays were the more penetrating. The rise of  $\beta$ -activity of thorium- $C$ , due to the production of thorium- $D$ , is rendered less marked when a screen cuts off the less penetrating  $\beta$ -rays, showing that thorium- $C$  gives a more penetrating  $\beta$ -radiation than thorium- $D$ . The effect of the  $\gamma$ -rays of thorium- $C$  and  $-D$  was only 1.15%, whilst that of thorium- $D$  was 2.5% of the  $\beta$ -radiation. In the recoil separation of thorium- $D$  from the active deposit, 31% of the activity as measured by  $\gamma$ -rays and only 8.8% of the  $\beta$ -activity result in the recoil product. A mathematical examination of the results favours the conclusions stated. According as to whether the breaking up of the atom or the expulsion of a radiant particle is considered the primary or fundamental event, the transformation constant of those atoms of thorium- $C$  giving  $\alpha$ -rays of range 4.8 cm. must be either that usually ascribed to thorium- $C$  ( $0.115 \text{ min.}^{-1}$ ) or 0.35 times this. This cannot be determined directly, but if Geiger and Nuttall's rule applies to the thorium series, and the ranges of the  $\alpha$ -rays could be determined to 0.33 mm., it may be possible to deduce it from the exact range of the  $\alpha$ -particles. F. S.

**The Branching of the Radium Disintegration Series.**  
KASIMIR FAJANS (*Physikal. Zeitsch.*, 1912, 13, 699—705).—The evidence that radium- $D$  results directly from the  $\alpha$ -ray change of radium- $C_1$ , and that radium- $C_2$ , a product of half-period 1.4 minutes giving  $\beta$ -rays, is a branch product of radium- $C_1$ , is considered in detail.

The proportion of the number of atoms of radium-*D* which recoil was found in three experiments to be 35%, 32%, and 30% of the total possible. This was deduced from the  $\alpha$ -radiation of the recoil product, due to radium-*F*, after the lapse of a known time. An upper limit to the ratio of the numbers of atoms of radium-*C*<sub>2</sub> and radium-*D* respectively produced is a few per cent., for the intensity of the  $\beta$ -radiation due to radium-*C*<sub>2</sub> in comparison with that of radium-*C*<sub>1</sub> is so small that the existence of the *C*<sub>2</sub> member cannot be detected in the  $\beta$ -ray growth curve from pure radium-*B*. A lower limit, which is perhaps nearer the true value, is 3/10,000th. Radium-*C*<sub>2</sub> is obtained by recoil from radium-*C*, but its  $\beta$ -activity is only of the order of 1/20,000th of that of the source. This small proportion was originally explained on the view that the change in which radium-*C*<sub>2</sub> results is a  $\beta$ -ray change, and only a small proportion of that formed is recoiled.

No other case of  $\beta$ -ray recoil is known—an experiment with a very powerful radium-*E* preparation giving no trace of radium-*F*—and it is considered probable that radium-*C*<sub>2</sub> is produced in an  $\alpha$ -ray change in very small relative proportion. Taking into consideration that, from the range of the  $\alpha$ -rays of radium-*C*, the change in which they result must be of the order of  $10^{-6}$  second, it is probable that the change of radium-*C*<sub>1</sub> into radium-*D* occurs through an intermediate product (called radium-*C'*) of this short period. From analogy to the thorium disintegration scheme of Marsden and Darwin (preceding abstract) it is considered likely that all but some ten-thousandths of the radium-*C*<sub>1</sub> atoms change with emission of  $\beta$ -rays into radium-*D* through the short-lived  $\alpha$ -ray product radium-*C'*, whilst the remainder change, with the emission of an hitherto undetected  $\alpha$ -radiation of low range, into radium-*C*<sub>2</sub>. The question whether the actinium series is also analogous is discussed. F. S.

[The Ionisation of Liquid Hydrocarbons.] TCHESLAS BIALOJESKI (*La Radium*, 1912, 9, 227—230. Compare Abstr., 1911, ii, 837).—A reply to the criticisms of Goldmann (this vol., ii, 515). H. M. D.

Mercury Lamps for Use in Spectroscopy, Polarimetry, and Saccharimetry. T. MARTIN LOWRY (*Trans. Faraday Soc.*, 1912, 7, 267—270).—A silica mercury lamp, consisting of a horizontal tube with a bulb at one end, is used in an end-on position. In order to avoid condensation of mercury globules on the surface, a silica window is mounted on a re-entrant tube in the bulb, so that it is kept hot by the mercury vapour. Another form having a straight tube, is used vertically, and gives a very intense line of light. C. H. D.

Electrolytic Dissociation of Sulphurous Acid. JOSEF LINDNER (*Monatsh.*, 1912, 33, 613—672).—Sulphurous acid has a maximum conductivity in concentrated solution at a little above 30°.

The conductivity measurements indicate considerable discrepancies when calculated according to the laws of dilution. The expression  $(\mu/\mu_\infty)^2/(1 - \mu/\mu_\infty)v$  could not be made constant by lowering or increasing the value of  $\mu_\infty$ . The observed increase in the conductivity during the estimation is due not to any oxidation, but to internal changes in the acid.

Sulphur dioxide departs from Henry's law in its behaviour towards water even at 50°. The differences observed at this temperature correspond with the dissociation of the acid as determined by the conductivity measurements; at lower temperatures other disturbing factors come into play. Accordingly, the solubility does not follow the usual laws of dilution.

The partition of sulphur dioxide between water and chloroform is not in agreement with the law of Berthelot and Jungfleisch. Sulphur dioxide further has not the normal molecular weight in chloroform.

Lower values for the dissociation of sulphurous acid in water are obtained by the cryoscopic method than by the other methods: here also the dilution laws are not obeyed. Phosphoric acid behaves similarly.

The magnitude of the heat of dissociation and the dependence of the dissociation constant on the temperature are as postulated by van't Hoff's laws.

E. F. A.

**Application of the "Scale of Combined Influence" to Explain the Ionisation Constants of Organic Acids, and a Reply to the Criticism of C. G. Derick.** ARTHUR MICHAEL (*J. Amer. Chem. Soc.*, 1912, 34, 849—855).—In an earlier paper (Abstr., 1900, i, 321) it was pointed out that the chemical properties and reactions of organic compounds can be best elucidated by considering the sum of the influence of the constituent atoms of the molecule, and a "scale of combined influence" was employed to explain the ionisation constants of organic acids. The objections raised by Derick (Abstr., 1911, ii, 713) to these views are discussed, and it is stated that they are based on misunderstandings and that his new scale of combined influence is fundamentally wrong.

E. G.

**Salt Solutions and the Law of Mass Action.** F. H. MACDOUGALL (*J. Amer. Chem. Soc.*, 1912, 34, 855—860).—It is suggested that the abnormal behaviour of strong electrolytes may be due to the influence of the electric charges of the ions in increasing the speed at which the molecules dissociate, and that the effect is proportional to some power of the total ion concentration. From these considerations, the following expression has been deduced:  $K = c\gamma^2/(1 - \gamma)[1 + m(c\gamma)^n]$ , where  $K$  is the dissociation constant,  $c$  the concentration (in gram-mols.) of the solution,  $\gamma$  the fraction ionised, and  $m$  and  $n$  constants. This has been applied to aqueous solutions of potassium chloride, potassium nitrate, and copper sulphate, and the value of  $n$  has been found to be approximately 0.66. The same formula has been obtained independently by Bray and Kraus (*Science*, 1912, 35, 433).

E. G.

**Dissociation of Hydrogen into Atoms.** IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1912, 34, 860—877).—In an earlier paper (this vol., ii, 231) it was shown that the energy required to maintain a tungsten wire at a given temperature in hydrogen increases at an abnormal rate with the temperature, and it was suggested that this was due to the dissociation of the hydrogen molecules into atoms.

A theory of the convection of heat from hot wires has now been developed, by means of which the loss of energy from heated wires in various gases can be readily calculated by simple equations. The results thus calculated for nitrogen and for mercury vapour agree well with the experimental results up to 3500° (abs. temp.), whilst those obtained with air and carbon dioxide show similar agreement up to the m. p. of platinum. In the case of hydrogen, the results do not agree above 2100°, but the energy loss increases very rapidly, and at 3300° is four or five times the calculated value. A theory of the conductivity of heat in a dissociating gas is presented, and the heat of the reaction and the degree of dissociation at various temperatures have been calculated and found to agree well with the results obtained from van't Hoff's equation. Experiments have been carried out at low pressures which show that the phenomenon is a true dissociation,  $H_2 = 2H$ , and evidence is adduced to show that it is not electrolytic. Nitrogen is not dissociated to an extent of more than 5% at a pressure of 1 atmosphere even at a temperature of 3500°.

The heat of reaction at constant volume for  $2H = H_2$  is 550,000 joules or 130,000 cal., whilst at constant pressure it would be about 575,000 joules or 136,000 cal. at 3000°. The degree of dissociation at any temperature  $T$  is given by the equation:  $\log p_1 / \sqrt{P - p_1} = 2.665 - 14400/T + \frac{1}{2} \log T$ , where  $p_1$  is the partial pressure (in atmospheres) of the hydrogen atoms and  $P$  the total pressure. This also permits of the calculation of the free energy of formation of hydrogen molecules. The degree of dissociation ( $p_1$ ) of hydrogen at a pressure of 1 atmosphere has been calculated at various absolute temperatures from 293° to 5000°.

E. G.

**An Amalgam Thermometer.** DOUGLAS MCINTOSH and FREDERICK M. G. JOHNSON (*J. Amer. Chem. Soc.*, 1912, 34, 910—911).—During the investigation of the properties of certain substances between  $-20^\circ$  and  $-80^\circ$ , attempts were made to prepare thermometers from various amalgams. The only satisfactory result was obtained with an 8.5% solution of thallium. Thermometers made with this amalgam have proved very useful down to  $-60^\circ$ . The amalgam expands with such regularity that the temperatures plotted against those given by a platinum thermometer are in a straight line.

E. G.

**Thermostats.** HUGH MARSHALL (*Trans. Faraday Soc.*, 1912, 7, 249—252).—The best electric lamps for heating thermostats are tubular, 30—40 cm. long with a terminal bulb; they are placed vertically in the thermostat, and run at a low voltage in order to prolong their life. A toluene regulator with platinum—mercury contact is used, actuating a relay.

A constant temperature of  $0^\circ$  is conveniently obtained by using a cylindrical vessel with non-conducting walls, with a false bottom of perforated metal, on which rests a rectangular inner vessel. Crushed ice is placed below as well as above the false bottom, and the vessel is then filled up with ice-water. The inner vessel is filled with finely crushed ice.

A temperature of  $12.5^\circ$ , or other temperature intermediate between

0° and 20°, is obtained by using an internally-heated glass vessel immersed in a larger vessel maintained at a temperature about 5° lower by the introduction of ice. C. H. D.

**Thermostats and Devices used in Connexion with Thermostats.** ALEXANDER C. CUMMING (*Trans. Faraday Soc.*, 1912, 7, 253—259).—The principal types of regulators are described, and an account is given of two new forms. In the first, a metal plunger floats on the mercury, and carries a re-curved platinum wire, which comes into contact with a platinum plate when the plunger sinks. In the second, current does not pass through the mercury, the plunger serving to raise or depress a platinum contact against a spring.

Good stirring is obtained by using a tubular stirrer with an open side-tube at right angles, or by bubbling air through a wide tube open at both ends. C. H. D.

**Two Thermo-Regulators.** WILLIAM R. BOUSFIELD (*Trans. Faraday Soc.*, 1912, 7, 260—266).—The current supplying an electric regulator passes through part of a column of mercury contained in a barometer tube, the lower end of which communicates with a bulb containing hydrogen, which serves as expansion vessel. The bulb at the top of the barometer tube should be about half full under normal conditions. The regulation is independent of variations of atmospheric pressure.

A modified form of Lowry gas regulator is designed in the form of a grid, to lie along the side of the thermostat. C. H. D.

**Physico-chemical Determinations at High Pressures by Optical Methods.** WALTER WAHL (*Phil. Trans.*, 1912, A, 212, 117—148).—A form of apparatus is described with the aid of which transition phenomena have been investigated at high pressures by an optical method. This apparatus consists of plant for the production and measurement of high pressures, the pressure-bomb, thermostat, and the optical installation, including the specially constructed windows of the pressure bomb.

With this apparatus the author has examined the influence of pressure on the melting point of the isotropic form, and on the transition temperature of the enantiotropic forms of carbon tetrabromide, and also on the melting points of the monotropic forms of  $\alpha\beta$ -dibromopropionic acid. Whereas the melting point of the isotropic form of carbon tetrabromide is raised 1° by a pressure of 16 kilograms per square cm., the corresponding transition temperature is only raised half as much by the same pressure. The melting-point and transition-point curves do not therefore intersect at high pressure, and it follows from this that the anisotropic modification of carbon tetrabromide cannot be melted at any pressure. The theoretical triple point deduced from the curves would lie at about 0° and a negative pressure of about 1500 kilograms per square cm. In the case of  $\alpha\beta$ -dibromopropionic acid, the melting point of the stable modification is raised 1° by a pressure of 51.28, and that of the unstable form the

same amount by a pressure of 53.48, kilograms per cm.<sup>2</sup>. It thus appears that the melting-point curves diverge as the pressure is increased, and the unstable form will therefore melt at a lower temperature than the stable form at all pressures, and will remain unstable.

H. M. D.

**Determination of Melting Points with the Aid of the Microscope.** MARSHALL P. CRAM (*J. Amer. Chem. Soc.*, 1912, 34, 954—956).—A method is described for the determination of the m. p. of a substance with the aid of the microscope, and is recommended for cases, such as sometimes occur in toxicological work, in which the quantity of material available is not sufficient for introduction into a capillary tube. The substance on the slide is heated by means of a coil of wire placed beneath it, and through which an electric current is passed. The coil is wound in a brass tube, and the thermometer is introduced into the middle of the coil through an opening in the side of the tube. The apparatus does not permit of accurate results, but is capable of yielding approximations within a few degrees of the true m. p. The highest readings obtainable were 64° with a current of 0.6 ampere, and 153° with a current of 0.95 ampere, whilst with a current of 1.25 ampere the temperature rose above 200°.

E. G.

**Vaporisation. VI.** HANS VON JÜPTNER (*Zeitsch. physikal. Chem.*, 1912, 80, 299—318. Compare Abstr., 1908, ii, 663, 810; 1909, ii, 21; 1910, ii, 583, 689).—A theoretical paper in which the author's theory of ideal liquids is applied to certain liquids the properties of which have been very fully investigated. The meaning of the symbols is the same as in previous papers of the series.

The density of the ideal liquid, of a real liquid, and of its saturated vapour are represented diagrammatically, and the changes observed in cooling a vapour of high tension discussed. In a previous paper several formulæ have been given for the calculation of the density of the saturated vapour and of the real liquid from the density of the ideal liquid in terms of the expression  $\gamma = (d - D)/2D_k$ . The formula  $\gamma = A \sqrt[3]{1 - T/T_k}$ , where  $A$  is a constant (2 or, more accurately, 1.91), is shown from the experimental data for fluorobenzene not to be quite accurate, and better results are obtained when  $A$  is not taken as constant, but is represented by the expression  $A = 1.953 - 0.291(1 - T/T_k)$ . The same formula, with slightly different values of the constants, is also shown to hold for ammonia and for carbon dioxide. The full density-temperature diagram for carbon dioxide is given, and it is shown that the inner latent heat of evaporation increases at first and then diminishes as the temperature rises, whilst the internal pressure of the saturated vapour shows the converse behaviour.

It is shown that the relationships between a solid substance and its vapour can also be deduced on the assumption of the existence of an ideal solid, and the considerations are illustrated by means of the data for phosphorus and sulphur.

G. S.

**A Thermodynamic Measure of the Degree of Polymerisation of Liquid Substances.** MADISON M. GARVER (*J. Physical Chem.*, 1912, 16, 454—470. Compare this vol., ii, 536).—The opinion recently expressed by van der Waals that all liquid substances must consist more or less of polymerised molecules is incompatible with the assumption made by Ramsay and Shields that substances giving a normal temperature-coefficient of surface tension are not polymerised.

According to the relation previously established by the author, the molecular attraction in the surface film is proportional to the density instead of to the square of the density as assumed by van der Waals. If Maxwell's law of distribution of molecular energies is applicable to both liquids and gases, any polymerisation in passing from the gaseous to the liquid state will be accompanied by a liberation of internal molecular energy. Conversely, if it be found that the heat liberated during the isothermal conversion of a vapour to its liquid is in excess of the equivalent of the work done by all the forces concerned, both internal and external, the excess must be attributed to polymerisation having occurred.

Thus if  $p$  is the external pressure and  $\gamma$  the internal pressure,  $L$  the latent heat of vaporisation, and  $H$  the heat liberated by polymerisation changes on passing isothermally from vapour to liquid :

$$H = L - \int_1^2 (p + \gamma) dv.$$

If no polymerisation occurs,  $L = \int_1^2 (p + \gamma) dv$ , and the ratio  $r = L / \int_1^2 (p + \gamma) dv = 1$ . The value of the ratio  $r$  has been calculated for a number of liquids. Theoretically  $r$  is closely related to the  $k$  in Eötvös' formula. The normal value of  $k$  indicating that no association occurred was assumed to be 2.12 in Ramsay and Shields' work. The value of  $r$  for the same liquids is now found to be about 0.2 less than  $k$ , and as it is considerably more than unity it indicates considerable polymerisation in Ramsay and Shields' "normal" liquids. The one liquid which gives values of  $r$  in any way approximating to unity is acetic acid.

When two molecules unite to form a single molecule isothermally, one half of the total energy of the two molecules must leave the system as heat. The two molecules act about a common mass centre, and there can be no force or pressure between them. The function  $p\gamma$ , which represents energy, may yield consistent numerical results even when the symbols  $p$  and  $\gamma$  separately have no physical meaning, as in the osmotic theory of electromotive force. Thus the supposed "internal pressures" of liquids (Tammann), amounting to thousands of atmospheres, have no physical existence as pressures in the ordinary sense of the word.

The author's view is confirmed by the fact that it leads to a theory of osmotic pressures which is consistent with the conclusion drawn by Morse and Fraser, namely, that the volume of the solvent must be considered instead of the volume of the solution.

R. J. C.

**Molecular Attraction in Liquids and in Liquid Films.** MADISON M. GARVER (*J. Physical Chem.*, 1912, 16, 471—474. Compare preceding abstract).—The author's view of molecular attraction necessitates the conclusion that surface tension, that is, the attraction in the surface film, depends on the number of molecules present irrespective of their mass. A heavy, polymerised molecule exerts no more attraction in the film than a lighter and less complex one.

To account for this apparent departure from the ordinary Newtonian laws of mass attraction, the assumption must be made that a polymerised molecule occupies the same volume as a simple one. This is admittedly the case in a gaseous system, being the basis of the law of Avogadro, and the existence of an attractive force which is not a function of the mass is held to be quite reconcilable with molecular mechanics.

The author's theory lends no support to the view that surface attraction is so great as materially to increase the density of the surface film.

R. J. C.

**Densities of Some Gases and Vapours.** ANATOLE LEDUC (*Compt. rend.*, 1912, 155, 206—207).—The author has calculated the densities of a large number of gases and vapours, and in some cases also determined them experimentally. The results are set out in a table. The method of calculation has already been published (compare *Ann. Chim. Phys.*, 1910, [viii], 19, 459).

W. G.

**Relationship between the Molecular Volume and Structure of Solid Chemical Compounds.** FRIEDRICH TELTSCHER (*Zeitsch. physikal. Chem.*, 1912, 80, 319—337).—The suggestion that one element in a compound may have a predominant influence in determining the molecular volume of a compound has been tested by means of the available data for compounds containing chlorine. There is no evidence of such an influence in the case of binary compounds, since their molecular volumes are very different, and although the molecular volumes of the chlorides of bivalent compounds are not very different, from which it might be concluded that the volume-determining property of chlorine increases with the number of atoms of this element in the molecule; this conclusion is not borne out by the data for compounds containing three chlorine atoms, since the molecular volumes differ considerably among themselves.

The attempt is made to account for this apparent want of conformity with the theory on the basis of speculations regarding the structure of the molecules. One assumption is that one atom can approach another only up to a certain distance depending on the nature of the other atom; this distance is known as the chemical radius, and is proportional to the cube-root of the atomic weight. Evidence is given that when the molecular volumes of two elements of given structure are known, the molecular volumes of all other stages of valency and types of structure can be calculated. The radii and molecular volumes of a number of elements found in this way are in

most cases only in moderate agreement with the experimental values. The structural formulæ of certain oxides and oxy-salts are discussed.

G. S.

**Viscosity of Carbon Dioxide.** P. PHILLIPS (*Proc. Roy. Soc.*, 1912, *A*, 87, 48—61).—In order to carry out measurements of viscosity at high pressures, the author has modified the simple form of apparatus described by Rankine (*Abstr.*, 1910, ii, 188), and with this, measurements of the viscosity have been made at pressures ranging from 1 to 120 atmospheres. The data obtained at 20°, 30°, 32°, 35°, and 40° are plotted in the form of curves which show the variation of the coefficient of viscosity ( $\eta$ ) and also of the kinematic viscosity ( $\eta/\rho$ ) with the pressure at each temperature.

The viscosity-pressure isothermals are very similar in form to the density-pressure isothermals, the only difference being that the former cross one another, whereas the latter do not. The crossing of the curves occurs before the gas undergoes liquefaction, indicating that the gas begins to behave like a liquid, as regards viscosity, before condensation takes place.

The curves, which are obtained when the viscosity is plotted against the density or the square of the density, seem to show that the viscosity is almost entirely dependent on the density, for the points corresponding with different temperatures are all similarly situated with reference to the curves. Between densities of 0.2 and 0.7, the viscosity is approximately a linear function of the square of the density, which means that the change in viscosity is due almost entirely to the change in attraction between two adjacent layers of the fluid.

H. M. D.

**The Viscosity of Solutions.** C. CHÉNEVEAU (*Compt. rend.*, 1912, 155, 154—155).—The author has determined the viscosity of aqueous solutions of ethyl alcohol sulphuric acid, and nitric acid by means of a viscometer based on Poiseuille's law. Comparing his results with those obtained by a study of the refractive indices of the same substances, the hydrates indicated by the two methods are, in general, different. The viscosity, however, does not appear to indicate the possibility of a large number of hydrates.

W. G.

**The Viscostagmometer. Method for Estimation of Surface Tension, Viscosity, and Adsorption.** ISIDOR TRAUBE (*Biochem. Zeitsch.*, 1912, 42, 500—503).—The principle of the apparatus described (which is figured in the text) is the measurement of the relative volumes of a drop falling from a given capillary tube, and comparison of this with the volume of a drop of water falling from the same apparatus. The volumes are proportional to the surface tension. The liquid is contained in a tube with scale divisions which ends in a fine capillary. The size of the drop is indicated by the number of scale divisions. The same apparatus can be employed for measurement of viscosity. A method is also indicated by means of which the apparatus can be employed for the measurement of adsorption.

S. B. S.

**Adsorption Phenomena.** L. GURWITSCH (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 17—19).—In connexion with the decolorisation of mineral oil residues, the author has examined the influence of the size of the particles of floridin on the extent to which the colouring matters are removed and on the velocity with which this removal is effected. Although with increase in the fineness of subdivision of the granules, the speed of decolorisation increases, the final result is independent of the size of the particles. This is also true for the sum total of the substances which are adsorbed by the floridin, although the courses of the two phenomena are not quite parallel.

When the porous hydrosilicate is brought into contact with amylene, a considerable amount of heat is evolved, and experiments are described which indicate that this is due to polymerisation of the hydrocarbon.

Similar results are obtained with hexylene.

H. M. D.

**Traube's Theory of Cohesion Pressure.** FRANZ BUBANOVIĆ (*Pflüger's Archiv*, 1912, 146, 484—498. Compare Abstr., 1911, ii, 469).—In recent papers (summarised *loc. cit.*) Traube has developed the theory that the so-called "cohesion pressure," which may be defined as the difference between the surface tension of the solution and that of the solvent, is the principal factor, not only in osmosis, but in other properties of solutions. The author points out, more particularly on the basis of the experiments of Forch (Abstr., 1899, ii, 640), that the agreement between the results of surface tension measurements by different observers is not sufficiently good to enable generalisations to be founded on them with confidence. Traube has further suggested that in their effect on the cohesion pressure and on certain other properties of solutions, the cations and anions can be arranged in a definite order. The author confirms this view to some extent by a recalculation of the data for the surface tension of aqueous solutions obtained by Röntgen and Schneider (compare *Ann. Phys. Chem.*, 1886, [iii], 29, 165). Finally, it is pointed out that no definite relationship has been shown to exist between the osmotic pressure of a solution and the so-called cohesion pressure.

G. S.

**Dissociation Pressures of Phosphonium Bromide and Iodide.** FREDERICK M. G. JOHNSON (*J. Amer. Chem. Soc.*, 1912, 34, 877—880).—The dissociation pressures of phosphonium chloride have been investigated by Tammann (Abstr., 1902, ii, 69). In the case of the bromide and iodide, only the temperatures at which the dissociation pressures are one atmosphere have hitherto been recorded, and these substances have therefore been further investigated. The method employed for measuring the pressures was similar in principle to that used in earlier work (Abstr., 1908, ii, 157; 1909, ii, 23; 1911, ii, 727). The dissociation pressures of phosphonium bromide have been determined at temperatures from  $-80^{\circ}$  to  $38.8^{\circ}$ , and those of the iodide from  $0^{\circ}$  to  $61^{\circ}$ . The results have been plotted as curves, which show that the bromide and iodide have a dissociation pressure of one atmosphere at  $38^{\circ}$  and  $62^{\circ}$  respectively.

E. G.

**Dissociation [Tension] of Hydrated Salts.** H. BOLTE (*Zeitsch. physikal. Chem.*, 1912, 80, 338—360).—The vapour pressures of a number

of salt hydrates have been measured by a static method, the salts being kept at constant temperature in a vessel, free from air, connected with a mercury manometer, on which the pressure was read off from time to time.

Hydrates of magnesium sulphate containing 7, 6, 5, 4, 3, 2, and 1 molecule of water exist; their tensions have been measured at 30·75°. The vapour tension is independent of the form of the salt, whether crystal or powder. The alteration of vapour pressure from one hydrate to another is discontinuous, as is also the case with the hydrates of manganous sulphate. The maximum tensions of the hepta- and hexa-hydrates of manganous sulphate are the same, and there is also no difference in the tensions of the tri- and tetra-hydrate. There are three hydrates of potassium hydroxide, containing 2, 1, and  $\frac{3}{4}$  molecules of water respectively to one molecule of salt, and it was found that with change from one hydrate to another there is a slow continuous fall of pressure, as well as a discontinuous change. No steady vapour pressure was observed either for carnallite or kainite from 30° to 70°.

It has been suggested by Müller-Erzbach that the ratio between the vapour pressures of a salt hydrate and water increases continuously with the temperature, but the author shows by observations with hydrated manganous sulphate that this is not the case; the ratio attains a maximum at 18°. Evidence has been obtained that hydrates poorer in water cannot always exist as stable substances in contact with higher hydrates.

G. S.

**The Theory of Emulsification. II.** WILDER D. BANCROFT (*J. Physical Chem.*, 1912, 16, 345—372. Compare this vol., ii, 542).—The paper consists of a critical summary of the work of Chichkoff (1880), Gad (1878), Rachford (1891), and Moore and Krumbholz (1898). The significant facts which emerge are as follows:

Olive oil when added in drops to a  $\frac{1}{4}$ % solution of sodium carbonate spontaneously emulsifies if it contains 5·5% of free fatty acid. Spontaneous emulsification occurs less readily if the oil contains more or less free acid than 5·5%. A mixture which does not emulsify spontaneously is often emulsified by moderate shaking, but excessive shaking may be detrimental. The protecting soap solutions do not reach their maximum insolubility and strength instantaneously.

There is no evidence that the mixture of acids formed by the partial hydrolysis of any given fat is the best possible mixture for emulsifying that particular fat. Blood albumin and egg albumin have very little power of maintaining an oil emulsion. The acid and alkali albumins prepared from them are very effective emulsifying agents, however. In comparison with many artificially prepared emulsions, milk is rather unstable.

R. J. C.

**The Theory of Emulsification. III.** WILDER D. BANCROFT (*J. Physical Chem.*, 1912, 16, 475—512. Compare preceding abstract).—Pickering's paper on kerosene emulsions (*Trans.*, 1907, ii, 2001) is reproduced verbatim, followed by a critical discussion. The conclusions drawn, in so far as they are novel, are as follows:

The theory of surface tension is not so important for the understanding of emulsification as has generally been supposed. For instance, colloidal ferric oxide which has practically no effect on the surface tension of water is an excellent emulsifier. The pellicle theory of Pickering does not entirely exclude the electrostatic charge theory of emulsions, since both causes may co-operate. If the conditions are such that a brittle instead of an elastic film tends to form, for example, with a too concentrated soap solution, emulsification will be unsatisfactory. The nature of the soap employed is of importance from this point of view.

Pickering considered that emulsification will be produced by any insoluble particles in a sufficiently fine state of division, which have only a slight tendency to agglomerate, which are more readily wetted by water than by oil, and are not crystalline. In the author's view this statement is inadequate because it does not specify that the precipitate must be of such a nature and in such a state that it can and does form a coherent film, that is, one in which the particles are not discrete. The conditions which determine this cannot yet be stated. The corollary to Pickering's hypothesis is that fine insoluble particles which do not emulsify kerosene, because they are more readily wetted by it than by water, should emulsify water in kerosene, but such emulsions have not been observed.

It is held that the segregation into several distinct layers of the emulsion of "Solar distillate" with basic copper sulphate observed by Pickering had no objective existence. Pickering's experiments have been repeated by the author, using benzene instead of kerosene.

R. J. C.

**Osmotic Pressure of Sucrose Solutions at High Temperatures.** HARMON N. MORSE, WILLIAM W. HOLLAND, CHESTER N. MYERS, G. CASH, and J. B. ZINN (*Amer. Chem. J.*, 1912, 48, 29—94).—In an earlier paper (Abstr., 1911, ii, 701) it was shown that the osmotic pressures of all aqueous sucrose solutions containing from 0.1 to 1.0 gram-mol. per litre obey Gay-Lussac's law for gases between 0° and 25°. It was not evident, however, whether they obey Boyle's law. The fact that the osmotic pressures appeared excessive and not proportional to the concentration of the solution was not regarded as evidence against the validity of Boyle's law in such cases, for it was considered possible that the anomalies might be due to unknown molecular relations between the sucrose and portions of the solvent which would cause the solutions to become more concentrated. It was thought likely that such relations, if they exist, would become simpler at higher temperatures, and a study of this question has now been carried out. The osmotic pressures have been determined of solutions containing 0.1 to 1.0 gram-mol. of sucrose per litre at 30°, 40°, 50°, 60°, 70°, and 80°.

The results show that the 0.1*N*-solution between 30° and 60° and the 0.2*N*-solution between 50° and 60° obey strictly Gay-Lussac's law for gases. Between 25° and 30° the ratio of osmotic to gas pressure (which is constant but greater than unity from 0° to 25°) begins to decrease at all concentrations, but more rapidly in the more dilute

solutions. This decrease continues at the higher temperatures until the osmotic pressure becomes, in every instance, equal to the calculated gas pressure of the sucrose. Boyle's law is found to hold in the 0.1 and 0.2 *N*-solutions at 50°; in the 0.1, 0.2, 0.3, and 0.4 *N*-solutions at 60°; in the 0.5, 0.6, and 0.7 *N*-solutions at 70°; and in the 0.8, 0.9, and 1.0 *N*-solutions at 80°.

E. G.

**The Solution Volumes of Nitric Acid.** VICTOR H. VELEY (*Trans. Faraday Soc.*, 1912, 7, 229—236).—The solution volume of nitric acid in water increases with the concentration, the rate of increase falling off between 94 and 100%, owing to polymerisation of the nitric acid molecules. The greatest simplicity is reached at about 50%.

C. H. D.

[Fused Salts as Solvents.] WILLIAM C. BRAY (*Zeitsch. physikal. Chem.*, 1912, 80, 378—380); OTTO SACKUR (*ibid.*, 308. Compare this vol., ii, 744).—The first-named author further criticises the views of Sackur as to the nature of fused salts, to which the last-named replies that he has found no cause to change his former opinion on the question (*loc. cit.*).

G. S.

**Crystallisation in Ternary Systems. V. Ternary Systems with a Gap of Miscibility in the Liquid and also in the Solid State.** NICOLA PARRAVANO and G. SIROVICH (*Gazzetta*, 1912, 42, i, 577—607. Compare Abstr., 1911, ii, 704, 705).—The process of crystallisation is studied in detail in a single type of ternary system, and rules are given for the determination of the limits of existence of the respective phases. A short account is also given of the remaining possible types.

C. H. D.

**The Formation of a Heat Reversible Gel.** WILLIAM B. HARDY (*Proc. Roy. Soc.*, 1912, A, 87, 29—37).—It has been found that the substance 5-dimethylaminoanilo-3 : 4-diphenylcyclopentane-1 : 2-dione (Ruhemann and Naunton, *Trans.*, 1912, 101, 42) offers special facilities for the study of the relations between the crystalline and colloidal states. Solutions of the crystalline azomethine gelatinise when cooled by a freezing mixture, and gels have been obtained from solution in ethyl alcohol, ethyl ether, acetaldehyde, acetone, carbon tetrachloride, carbon disulphide and acetic acid, and apparently also in chloroform and benzene. The presence of water does not appear to be essential to the gelatinisation, although it lowers the concentration of the solute, which is needed for the change to take place.

All the gels liquefy when kept, with deposition of crystals. At room temperature, this occurs in a few minutes in the case of an ether gel, in a few hours with an alcohol or aldehyde gel, and in some days with a carbon tetrachloride gel. The presence of water retards the liquefaction so that alcohol and aldehyde gels containing water may persist for several days. The spontaneous occurrence of these changes indicates that the gels are labile with reference to the system: saturated solution and crystals.

Above a certain temperature, gelatinisation of the solution does not

take place, but crystals are deposited directly. In the case of solutions in 97·5% alcohol, this temperature is about 35°. Between 35° and 5° the gel is labile, whereas at temperatures below about 5° the gel persists for so long a time as to be sensibly stable.

In regard to the nature of the gelatinisation process, it has been found that nuclei appear to be necessary; the gel formation always starts at distinct points on the walls of the containing vessel. The consequence of this is that a fully formed gel, although it appears to be transparent and homogeneous, has a structure which is determined by the number and nature of the nuclei. It consists of masses more or less imperfectly joined together; these masses are of various sizes in alcohol gels, but very uniform in size in the case of tetrachloride gels. The masses are singly refractive, and when they form in free fluid, the surface is rounded and not at all faceted. Each nucleus in fact forms the centre of a sphere of gelation, which continues as a sphere until it meets neighbouring masses, when the mutual pressure produces a polygon.

The spherical masses appear to be traversed by radiating lines, which are most readily seen in carbon tetrachloride and disulphide gels, which give to the gel a cloudy opaque appearance. When sufficiently magnified each spherical mass of gel is found to be built up of close-packed smaller masses, which are polygonal on account of the close packing and are very uniform in size. In the case of carbon tetrachloride gels, the axis of the smaller spheres measures about  $10\mu$ , and the spheres are arranged in a pattern which radiates outwards from the centre of the larger sphere.

From this it is evident that the gels of the azomethine are built up of two orders of structure, and that the transition from the gel to the crystalline condition is dependent on the intermediate formation of a liquid phase.

The difference in behaviour of the azomethine gels as compared with those of gelatin or agar is probably due to the non-existence in these cases of the intervening region in which the gel melts to a true fluid which is supersaturated with respect to the crystalline form of the solute.

H. M. D.

**General Theory of Colloidal Solutions.** WILLIAM B. HARDY (*Proc. Roy. Soc.*, 1912, A, 86, 601—610).—From the fact that the state of a colloidal solution at any moment is determined, not only by temperature, pressure, and composition, but also by its previous history, it may be inferred that neither the exterior nor the interior fluid masses conform to Gibbs' criterion of stability, and the phase rule is therefore not applicable to such solutions.

An expression is deduced for the osmotic pressure of a heterogeneous solution of this type, and it is shown that the pressure depends on the functions  $dt/dr$  and  $d\sigma/dr$ , which represent respectively the variation of the surface tension at the composite fluid surface and that of the density of the electric charge at the surface with the radius of the globules of the suspended phase. When this radius exceeds the range of molecular action, the globular suspension represents a phase fully formed, and since the pressure and potentials of the transition layer

assumed fixed values in these circumstances,  $dt/dr$  and  $d\sigma/dr$  become equal to zero. The point at which the radius of the globules becomes equal to the range of mutual action of any of the molecules present represents therefore a critical point, and is of great importance in connexion with the theory of colloidal solutions.

The tension at the fluid-fluid interface is also examined, and observations relating to the movement of particles in such composite films under the influence of an electric field are described, which indicate that these films are composed of layers between which there is a constant difference of potential. H. M. D.

**The Tension of Composite Fluid Surfaces and the Mechanical Stability of Films of Fluid.** WILLIAM B. HARDY (*Proc. Roy. Soc.*, 1912, A, 86, 610—635. Compare preceding abstract).—The dependence of the tension and of the mechanical stability of fluid films on the thickness has been examined in detail with special reference to the influence of different substances on the properties of water surfaces. From observations with cymene, paraffin oil, castor oil, and croton oil, it appears that the influence of a substance on the tension of a water surface is remarkably independent of its own tension or viscosity. The influence of all physical factors appears to be insignificant in comparison with that exerted by the chemical nature of the substance. The data obtained for the mechanical stability of the films exhibit very marked variations with changes in the thickness, and in certain definite regions the curves, representing the connexion between the two factors, show very pronounced oscillations. The connexion between the form of these curves and the range of molecular action is examined. H. M. D.

**Action of Water Vapour on Gelatin.** WILDER D. BANCROFT (*J. Physical Chem.*, 1912, 16, 395—406).—A critical discussion of von Schroeder's work (Abstr., 1903, ii, 721), according to which gelatin absorbs more water when immersed in liquid water than when exposed to a saturated atmosphere at the same temperature.

Gelatin and other colloidal gels have a cellular structure. The moisture absorbed in a saturated atmosphere is taken up by the cell walls. In addition, when gelatin is immersed in water, water diffuses into the microscopic cells. It is held to involve no contradiction to the second law of thermodynamics that water should so diffuse into a region where the vapour pressure is higher than that of water on account of the curvature of the cells.

When gelatin swells in a  $N/100,000$  sulphate solution the globules have a lower vapour pressure than water in the mass. From the data with regard to such solutions, it would be possible to calculate the size of the water globules in a gelatin jelly. All conclusions in regard to partial pressures of gels are subject to modification in so far as the colloidal substance forms a true solution under the conditions of the experiment. R. J. C.

**The Law of Mass Action.** PHILIPPE A. GUYE (*Compt. rend.*, 1912, 155, 149—152. Compare Colson, this vol., ii, 631, 632, and Le Chatelier, this vol., ii, 631).—A theoretical paper in which the author discusses

the work and calculations of Washburn (Abstr., 1910, ii, 391, 1044) and their bearing on the law of mass action. He considers that the law applies theoretically only to those systems in which all the substances participating in the reaction obey the laws of Boyle and Avogadro. In other cases the results will be numerically very close to those calculated from the usual formula for the law of mass action.

W. G.

**Enzymic Decomposition of Hydrogen Peroxide. III.** PERCY WAENTIG and OTTO STECHE (*Zeitsch. physiol. Chem.*, 1912, 79, 446—503. Compare Abstr., 1911, i, 759; this vol., i, 228; Senter, 1905, i, 107; ii, 377; 1911, ii, 995).—Further measurements of the velocity of decomposition of hydrogen peroxide in presence of hæmase and other animal extracts have been made in order to ascertain whether the deviations from the normal course of a reaction of the first order can be attributed, as suggested by Senter (*loc. cit.*), to the disturbance of the diffusion in the micro-heterogeneous system by the bubbles of oxygen and by the Brownian movement of the colloidal particles, and to the oxidation of the ferment by the hydrogen peroxide. The data observed in experiments with different concentrations of enzyme and of hydrogen peroxide, with freshly prepared extracts, and extracts which have been allowed to age for different periods, and also the results obtained at different temperatures are inconsistent with this explanation.

It has been found that the course of the reaction varies very considerably in different experiments in which the same enzyme preparation is used. In some cases, the values of the unimolecular velocity-coefficient exhibit a fair degree of constancy from the commencement of the reaction, whilst in others the earlier stages are characterised by a considerable fall in the coefficient, which, however, becomes approximately constant when the reaction has been taking place for some time. This fall in the value of the velocity-coefficient is not more pronounced at 20° than at 0°, a fact which is considered to be incompatible with the oxidation hypothesis. With extracts which have been allowed to age before the hydrogen peroxide solution is added, the values obtained for the velocity-coefficient are in general much smaller than those found for the freshly prepared extracts, the decrease in activity being accompanied by diminished deviation from the normal course of the reaction.

To explain the various observations it is supposed that the progress of the change is to a large extent determined by adsorption phenomena. In this adsorption by the enzyme, both hydrogen peroxide and oxygen, as well as other substances which may be present in the solution, are involved. In support of this view a number of facts have been established, more particularly with reference to the adsorption of oxygen.

If supersaturation with regard to oxygen is prevented by agitation of the solution, the velocity-coefficient increases as the reaction progresses. This effect is very much more pronounced if the agitation is carried out in an exhausted apparatus. On the other hand, if the enzyme solution is saturated with oxygen previous to the reaction, not

only are much smaller values obtained for the velocity-coefficient, but this remains approximately constant during the progress of the change. The disturbing influence of oxygen supersaturation is found to increase as the concentration of the enzyme increases. These facts and others indicate that adsorption effects are of primary importance in connexion with the progress of the enzymic decomposition, and it is shown that a satisfactory explanation of the influence of concentration, of temperature, of the addition of acid and alkali, and of the presence of carbon dioxide in the solution can be obtained on the basis of this adsorption hypothesis. H. M. D.

**Determination of Atomic Weights by Hinrichs' Method.** HENRY LE CHATELIER (*Compt. rend.*, 1912, 155, 110—112).—A theoretical paper in which the author discusses the reasoning employed by Hinrichs in his method of determining atomic weights (compare Abstr., 1909, ii, 653, 723; 1910, ii, 26, 285; 1911, ii, 1080; this vol., ii, 642). W. G.

**A Simple Automatic Mercury Pump.** FREDERICK M. G. JOHNSON (*J. Amer. Chem. Soc.*, 1912, 34, 909—910).—A pump is described which is constructed on the Töpler principle, and has a simple attachment which enables the mercury to be raised and lowered by means of an ordinary water suction-pump. It is claimed that this apparatus is preferable to automatic pumps of the Sprengel type, as the outer air does not pass through the mercury used, and oxidation of the mercury and introduction of dust are thus avoided. E. G.

**Lantern Experiments on Surface Tension.** FRANK B. KENRICK (*J. Physical Chem.*, 1912, 16, 513—518).—1. A shaving of cork floating in water is partly lifted out by a thread passing over a pulley, thereby increasing the area of the surface film. The surface film in contracting to its original area will do work by lifting a small weight.

2. Two capillaries are joined at the bottom by a fine rubber tube so as to form a U-tube, which is entirely filled with water. If a large drop of water is placed on the end of one capillary and a small drop on the other, the larger drop grows at the expense of the smaller.

3a. A solution is saturated in contact with large crystals of gypsum, and a quantity of finely powdered gypsum is added to a part of it. The two saturated solutions are filtered, and 20 c.c. of each are added to equal quantities of sodium phosphate solution, the amount of phosphate being so regulated that the resulting liquid is acidic to phenolphthalein with normally saturated gypsum solution and alkaline with super-saturated gypsum solution.

3b. The same effect is illustrated by suspending a massive crystal of gypsum and a glass scoop containing finely powdered gypsum side by side in a trough of normally saturated solution. The image of the trough being thrown on the screen, a thin stream of super-saturated solution is seen falling from the scoop.

4. The surface concentration of saponin in solution is illustrated by the fact that a freshly formed surface has the same tension as the

surface of pure water. On drawing a saponin solution into a capillary tube and letting it fall, it halts at the pure water level and then sinks slowly to the saponin solution level.

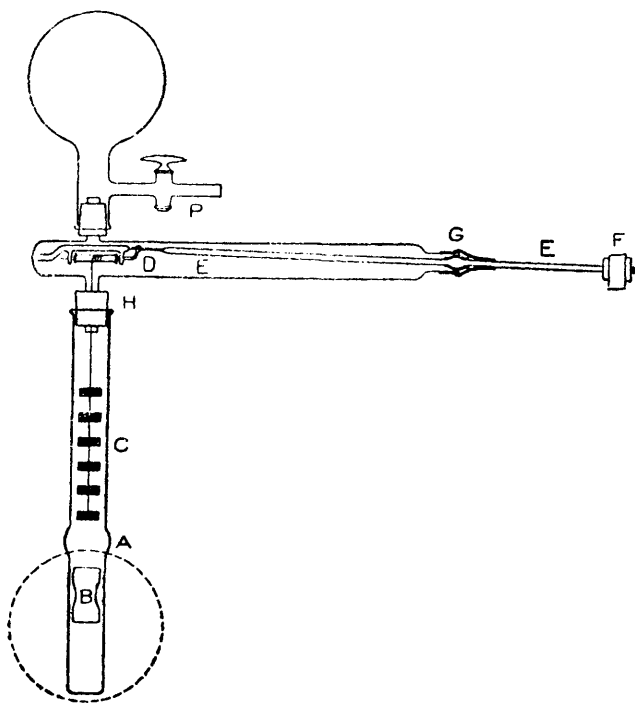
5. The surface concentration in methyl-violet solution is illustrated by shaking it to a foam in a separating bulb. The liquid is quickly drawn off, and when the foam subsides the liquid resulting from it is seen to be of a darker colour.

6. A pad of wire gauze soaked in oil is placed at the bottom of a projection cell and covered with water. The oil remains in the gauze, but on adding a little potassium hydroxide the oil flows up in thin streams to the surface and forms an emulsion.

7. An oily glass rod is immersed in a beaker of water, which is cleaned by passing a stream of tap-water through it until the surface will show camphor movements. A stream of air bubbles stirring up the water has no effect on the camphor movements until the bubbles brush against the oil, when an oil film is immediately formed and carried up to the surface.

R. J. C.

**Lantern Experiments on Reactions in Non-homogeneous Systems.** FRANK B. KENRICK (*J. Physical Chem.*, 1912, 16,



519—526).—A lantern demonstration of Boyle's law is made with an apparatus which consists of a glass piston, *B*, sliding neatly in a glass

tube, *A*. The piston is constricted in the middle, and the space is filled with clean mercury, which acts as a frictionless seal. The maximum pressure the mercury seal will hold is about 11b. per sq. in. The space above the piston is evacuated so that the only pressure on the vapour is the weight of the piston, and any of the superintended weights *C*, of which a number are provided strung on a thread actuated by a little winch worked in the vacuum by the rod *E* passing through the rubber joint *G*. The same apparatus may be used to demonstrate vapour pressure and its variation with temperature, for which purpose the tube *A* may be provided with a hot air jacket and a thermometer.

The crystallisation of a supersaturated solution on nuclei is demonstrated by writing in a clean crystallising dish with a crystal of copper sulphate, and pouring in a supersaturated solution of the same substance, when the writing "develops."

A projection lantern may be used as a lecture room camera by the following expedients. A solid projection of a crystallising dish is thrown on the screen, and a second lantern is focussed to illuminate the same area on the screen. The object to be photographed is placed against the screen and illuminated by the second lantern only whilst it is photographed on a piece of printing-out paper laid in the crystallising dish. When sufficiently exposed, the paper is developed and fixed without removing it from the dish, the whole process being observed on the screen in an orange illumination from the projection lantern.

R. J. C.

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## Inorganic Chemistry.

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**Chlorous Acid.** LASÈGUE (*Compt. rend.*, 1912, 155, 158—160. Compare Bray, Abstr., 1906, ii, 223).—Chlorous acid is obtained in dilute aqueous solution by the action of sulphuric acid on a solution of barium chlorite, the latter being prepared by the interaction of barium carbonate and lead chlorite. The aqueous solution of chlorous acid, which is colourless, soon begins to decompose at the ordinary temperature. On addition of barium hydroxide, after complete decomposition, the chlorine is found to be present as chlorate, chlorite, hypochlorite, and chloride. W. G.

**Action of Thionyl Chloride on Metals and Metalloids.** H. B. NORTH and A. M. HAGEMAN (*J. Amer. Chem. Soc.*, 1912, 34, 890—894).—In an earlier paper (North, Abstr., 1910, ii, 296) an account was given of the action of thionyl chloride on mercury. The investigation has now been extended to several other elements, the experiments being made in sealed tubes at 150—200°.

It has been found that in the case of iron, the reaction proceeds as follows :  $2\text{Fe} + 4\text{SOCl}_2 = 2\text{FeCl}_3 + 2\text{SO}_2 + \text{S}_2\text{Cl}_2$ . When the metal

is present in excess, the reaction takes place thus:  $3\text{Fe} + 2\text{SOCl}_2 = 2\text{FeCl}_2 + \text{FeS} + \text{SO}_2$ . Thionyl chloride reacts with bismuth at  $200^\circ$  in accordance with the equation:  $2\text{Bi} + 4\text{SOCl}_2 = 2\text{BiCl}_3 + \text{S}_2\text{Cl}_2 + 2\text{SO}_2$ . Gold is slowly attacked by thionyl chloride at  $200^\circ$  with formation of auric chloride. The reaction between thionyl chloride and tin results in the production of stannous chloride:  $3\text{Sn} + \text{SOCl}_2 = 2\text{SnCl}_2 + \text{SnS} + \text{SO}_2$ , but in presence of an excess of the reagent, some of the stannous salt is converted into stannic chloride:  $3\text{SnCl}_2 + 4\text{SOCl}_2 = 3\text{SnCl}_4 + 2\text{SO}_2 + \text{S}_2\text{Cl}_2$ . Heumann and Köchlin (Abstr., 1883, 1051) have stated that the action of thionyl chloride on antimony proceeds thus:  $3\text{Sb}_2 + 6\text{SOCl}_2 = 4\text{SbCl}_3 + \text{Sb}_2\text{S}_3 + 3\text{SO}_2$ . This equation has been found to be correct when an excess of antimony is employed. The reaction takes place with violence even at the ordinary temperature. When antimony is heated in a sealed tube with a large excess of the reagent, the trichloride, which is formed at first, becomes converted into the pentachloride:  $3\text{SbCl}_3 + 4\text{SOCl}_2 = 3\text{SbCl}_5 + \text{S}_2\text{Cl}_2 + 2\text{SO}_2$ . In the case of arsenic, the reaction appears to be as follows:  $2\text{As} + 4\text{SOCl}_2 = 2\text{AsCl}_3 + \text{S}_2\text{Cl}_2 + 2\text{SO}_2$ .

Zinc, cadmium, magnesium, lead, chromium, and nickel are not attacked by thionyl chloride at  $200^\circ$ . E. G.

**Density and Compressibility of Nitrosyl Chloride.** EUGÈNE WOURTZEL (*Compt. rend.*, 1912, 155, 152—154).—The author has determined the weight of a litre of nitrosyl chloride at  $0^\circ$  under two different pressures, the nitrosyl chloride being prepared by the direct union of nitric oxide and chlorine, or by the action of nitrosyl hydrogen sulphate on sodium chloride. From his results, he calculates the weight of a normal litre of the gas, assuming that  $p_v$  is a linear function of  $1/v$ . The difference from the theoretical value is within the limits of experimental error. W. G.

**Is Helium Fundamentally an Element of Electro-positive Make-up?** FREDERICK H. LORING (*Chem. News*, 1912, 106, 37).—Helium may be a member of a series including hydrogen and the alkali metals. A formula is given connecting the atomic weights of the members of such a group. C. H. D.

**Some Natural Gases Particularly Rich in Helium.** CHARLES MOUREU and ADOLPHE LEPAPE (*Compt. rend.*, 1912, 155, 197—200. Compare Abstr., 1911, ii, 392, 808).—The authors call attention to the remarkable helium content of the gases eliminated from some French springs, and also to the large amounts (in one case, 17,845 litres) of helium emitted per annum. From this they draw the conclusion that it is "fossil" helium, that is, helium which has for a long time been enclosed in the rocks, and not helium generated year by year from radioactive minerals. They further point out that the five sources with high helium emission lie in a relatively narrow band running S.W.—N.E. W. G.

**Critical Constants and Orthobasic Densities of Xenon.** HUBERT S. PATTERSON, RICHARD S. CRIPPS, and ROBERT WHYTLAW-GRAY (*Proc. Roy. Soc.*, 1912, A, 86, 579—590).—Measurements have

been made of the orthobasic densities of carefully purified xenon between  $16^{\circ}$  and  $-67^{\circ}$ , the substance being contained in a carefully calibrated capillary tube of about 1 mm. diameter, which could be screwed into position on a modified Andrews apparatus. In the actual determination of the densities, Young's method was employed, readings of the liquid and vapour being taken at four different volumes in the case of each temperature. The observed mean densities are found to lie very nearly on the straight line  $D_t = 1.205 - 0.003055t$ , and hence, between the above limits of temperature, xenon follows the law of rectilinear diameters.

Direct measurements gave  $16.6^{\circ}$  as the critical temperature, and 58.2 atmospheres as the critical pressure. From the above equation the critical volume is then found to be 0.866 c.c., which is smaller than that of any substance so far investigated. From the data for the vapour pressure of liquid xenon between  $10^{\circ}$  and  $-20^{\circ}$ , the boiling point, calculated by the method of Ramsay and Young, is found to be  $-106.9^{\circ}$ . Assuming the validity of the law of rectilinear diameters, the density of liquid xenon at its boiling point is 3.063, which corresponds with an atomic volume of 42.7. According to this, the argon series of elements is characterised by a progressive rise in atomic volume with increase in the atomic weight. The variation of the mean density of liquid and saturated vapour is much greater than for the majority of substances, and this appears to be characteristic of the rare gases. The value of the critical coefficient is 3.605, which is considerably greater than the value 2.667 required by van der Waals' equation. In conjunction with the corresponding numbers for the other inert gases, the value of this constant affords no evidence that these substances in the liquid state are different from other normal liquids in respect of their molecular aggregation.

Some measurements of the density of xenon, which had been mixed with oxygen and subjected to the influence of the silent or spark discharge, and then freed from oxygen, seem to show that the two gases become associated in some way which renders the presence of the less condensable gas difficult of detection.

H. M. D.

**Action of Ozone on Alkali Hydroxides.** WILHELM TRAUBE (*Ber.*, 1912, 45, 2201—2211).—The action of ozonised oxygen on potassium hydroxide has been examined as quantitatively as possible. Oxygen is freed from hydrogen and nitrogen by suitable means, and is then ozonised. The product, containing 5—7% of ozone, is passed through an apparatus designed so that the powdered potassium hydroxide (containing about 8% of water and 5% of potassium carbonate) in it can be brought repeatedly and intimately into contact with the gas, and the product can be analysed without any necessity of opening the apparatus. The experiments are performed at about  $-12^{\circ}$ .

The freshly prepared substance has a colour resembling that of potassium dichromate, and, by treatment with water or acid, yields oxygen, but very little hydrogen peroxide. After keeping for a long time at the ordinary temperature or for a short time at  $90-100^{\circ}$ , the

substance becomes yellow, and then yields oxygen and a larger quantity of hydrogen peroxide by decomposition with water or acid.

From the results of a large number of quantitative experiments, it has been found that the ozone is, for the most part, reconverted into oxygen during the reaction, but that a small portion is absorbed by the potassium hydroxide, converting it into a mixture of potassium hydroxide and tetroxide and the yellowish-red substance, which the author, following Baeyer and Villiger, calls potassium ozonate. The potassium ozonate, which is possibly potassium heptoxide, yields only potassium hydroxide and oxygen by decomposition with water; however, by keeping it changes to the tetroxide, the decomposition of which by water produces hydrogen peroxide and oxygen in the molecular proportion of 1 : 1.

C. S.

**Behaviour of Potassium Trinitride [Azoimide] towards Manganese Dioxide at High Temperatures.** HARRY GOLDBERG (*J. Amer. Chem. Soc.*, 1912, 34, 886—890).—Franklin (Abstr., 1905, ii, 581) has pointed out the analogy between liquid ammonia and water, and Browne and Welsh (Abstr., 1911, ii, 1084) have suggested an analogy between the pernitrides (azoimide salts) and the peroxides. The present work was undertaken with the object of ascertaining whether potassium azoimide can effect nitride formation just as the peroxides effect oxidation.

Preliminary experiments on the behaviour of potassium azoimide towards manganese dioxide have shown that when mixtures of these compounds are heated in the air, considerable amounts of potassium manganate are produced. The reaction probably takes place in the following stages: (1) the decomposition of the azoimide with liberation of potassium; (2) the action of the potassium on the manganese dioxide, and (3) the oxidation of the product to potassium manganate by the oxygen of the air. Further work is in progress to ascertain the precise nature of the reaction.

E. G.

**Modifications of Silver. II. Hair-Silver.** VOLKMAR KOHL-SCHÜTTER and E. EYDMANN (*Annalen*, 1912, 390, 340—364. Compare this vol., ii, 253).—The authors are of opinion that the curious, spicular form of native silver, known as hair-silver, must have been produced directly from silver sulphide without any intermediate process of solution or fusion. The production of artificial hair-silver has been accomplished by several investigators, and the authors state that their results contain little new information.

Silver sulphide has been heated in oxygen, hydrogen, air, and steam at suitable, definite, high temperatures; its behaviour when heated with copper, aluminium, or platinum, and also in a vacuum has been examined. In all cases (except in the presence of platinum) at temperatures well below the m. p. of silver sulphide or silver, hair-silver is produced, but the most certain and rapid method of obtaining it is to heat the sulphide in hydrogen at 360° and finally at 400—450°.

There can be little doubt that, in addition to reduction by chemical means, simple dissociation of the silver sulphide is one of the processes

whereby hair-silver is formed, because it is produced by heating a mixture of silver sulphide and silver powder in a vacuum and even by heating silver sulphide alone at  $400^{\circ}$  in a current of carbon dioxide.

The explanation of the formation of hair-silver must take into account the facts that the presence of a gas is not essential, that no process of solution or fusion occurs, and that, in addition to the sulphide, only silver selenide can give rise to hair-silver. Silver sulphide and silver selenide are the only two derivatives of silver which can be changed from an amorphous to a crystalline state at comparatively low temperatures. This transformation, completed so rapidly under such conditions, necessitates the assumption of a considerable vapour pressure, that is, of an appreciable volatilisation of the undecomposed compound. By assuming that by reduction or dissociation of this volatilised portion the silver is obtained in a "pseudo-gaseous" state, the authors are of opinion that they can explain satisfactorily the formation of hair-silver under the various conditions of their experiments.

C. S.

**Rinmann's Green.** A. HEDVALL (*Ber.*, 1912, 45, 2095—2096).—When zinc oxide and cobalt carbonate or oxalate are heated at about  $1100^{\circ}$  and the product is allowed to cool in an atmosphere of carbon dioxide, the Rinmann's green and the excess of either oxide are always obtained in a crystalline condition, whatever the proportions of the constituents of the original mixture. When potassium chloride is used as a flux, Rinmann's green is obtained in comparatively large crystals (2—3 sq. mm.), consisting generally of hexagonal plates, sometimes of long needles or aggregates of small pyramids. The substance has  $D_{17}^{25}$  5.69 and  $n_D$  greater than 2.2. It contains zinc oxide and cobalt oxide in the proportion of about 5 : 1, the cobalt being bivalent. The investigation of the substance and of its individuality is being continued.

C. S.

**The Quaternary Alloys of Lead, Bismuth, Cadmium, and Tin.** NICOLA PARRAVANO and G. SIROVICH (*Gazzetta*, 1912, 42, i, 630—716).—The method of thermal analysis has been applied to quaternary systems by the authors (*Abstr.*, 1911, ii, 704, 705; this vol., ii, 30). As it is possible that a compound may occur in one or both of the binary systems Pb-Sn and Cd-Sn, the theoretical investigation has been extended to include the case of a quaternary system in which one of the binary systems contains a compound, but from which solid solutions are absent, and also the case in which the compound is only formed after complete solidification.

In the system lead-bismuth-cadmium-tin, the solid solutions formed at first are almost completely resolved into their components on cooling, and the observations indicate that the solid phases present at the quaternary eutectic temperature are the almost pure metals. The results are exhibited graphically in the form of projections of the tetrahedral space-model. The quaternary eutectic alloy has m. p.  $70^{\circ}$ , and contains Cd 10.10%, Sn 13.13%, Pb 27.27%, and Bi 49.50%. This composition differs from that assigned to the eutectic by Guthrie (*Phil. Mag.*, 1884, [v], 17, 462), but an examination of Guthrie's alloy

shows that it contains crystals of primary bismuth. It is unlikely that any ternary or quaternary compound is formed, and the development of heat observed in many of the alloys at 95—100°, or 110—115°, is to be attributed entirely to changes in the binary solid solutions, as it always diminishes towards the interior of the tetrahedron. Microscopical examination confirms the thermal results. C. H. D.

**The Density and Coefficient of Linear Expansion of Aluminium.** FRANCIS J. BRISLEE (*Trans. Faraday Soc.*, 1912, 7, 221—228).—Cast aluminium, containing Si 0.25% and Fe 0.25%, has  $D$  2.708, whilst the worked metal has a higher density, reaching 2.72. The coefficient of linear expansion between 0° and 100°, determined on rods 1 metre long, is for hard-drawn aluminium 0.00002432, and for the annealed metal, 0.00002454. C. H. D.

**The Gases in Aluminium.** MARCEL GUICHARD and PIERRE ROGER JOURDAIN (*Compt. rend.*, 1912, 155, 160—163. Compare Abstr., 1911, ii, 803).—The authors have estimated the amounts of different gases given off from samples of aluminium, both clean and well-worn, drawn from varying sources, on heating in a vacuum. The gases come partly from the mass of the metal, and partly from the surface. Of the gases, carbon dioxide exhibits the most remarkable variation in quantity. W. G.

**Alumina as a Drying Agent.** FREDERICK M. G. JOHNSON (*J. Amer. Chem. Soc.*, 1912, 34, 911—912).—During the course of an investigation of phosphonium bromide and iodide (this vol., ii, 833) a drying agent was required for phosphine, hydrogen bromide, and hydrogen iodide, phosphoric oxide having proved useless for the purpose. It has been found that alumina, prepared by igniting the hydroxide at a low temperature, gives very satisfactory results, one gram being capable of absorbing the whole of the moisture from about 10 litres of air, saturated with water vapour at 18°. Alumina is much superior to calcium bromide, zinc bromide, and zinc chloride as a desiccating agent, and is also more efficient than sulphuric acid. A tube filled with alumina can be used for an indefinite period if it is heated from time to time with a smoky flame, while air previously led through sulphuric acid is passed through it. E. G.

**Mixed Crystals of Ammonium Chloride with Nickel, Cobalt, and Copper Chlorides.** HARRY W. FOOTE (*J. Amer. Chem. Soc.*, 1912, 34, 880—886).—Roozeboom (Abstr., 1892, 1384) investigated the mixed crystals of ammonium chloride with ferric chloride, and found that they contained over 7% of the latter salt. The work of others on the mixed crystals of ammonium chloride with other chlorides has been merely of a qualitative nature.

In the present work, determinations have been made of the solubility of various mixtures of ammonium chloride with nickel, cobalt, and copper chlorides at 25°, and both the residues and the solutions have been analysed.

In the case of nickel chloride, a double salt was not found at 25°,

but at a lower temperature the salt,  $\text{NH}_4\text{Cl} \cdot \text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ , was obtained. The experiments indicate that a transition temperature exists, probably slightly below  $20^\circ$ , above which the salt decomposes into a mixture of hydrated nickel chloride and mixed crystals. The maximum amount of nickel chloride which can enter into the composition of the mixed crystals is about 37% at  $25^\circ$ ; the salt seems to be present as the dihydrate.

Ammonium chloride appears capable of taking up more cobalt chloride than nickel chloride, and, like the latter, the cobalt chloride is present in the mixed crystals as the dihydrate. There was no indication of a double salt either at  $25^\circ$  or at any other temperature at which crystallisation occurred.

Cupric chloride yields mixed crystals with ammonium chloride as well as the double salt,  $2\text{NH}_4\text{Cl} \cdot \text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ . The mixed crystals in equilibrium with the double salt contain only about 1.8% of cupric chloride.

Aniline hydrochloride does not form mixed crystals with nickel chloride to an appreciable extent.

E. G.

#### A New Determination of the Atomic Weight of Uranium.

PAUL LEBEAU (*Compt. rend.*, 1912, 155, 163—166).—The present accepted atomic weight of uranium was determined by Richards and Merigold (*Abstr.*, 1902, ii, 506) from the ratio  $\text{UBr}_4 : 4\text{AgBr}$  as 238.53. The author has made a fresh determination starting with uranyl nitrate dihydrate and reducing it at  $1100$ — $1150^\circ$  in a current of hydrogen to uranous oxide, and thus determining the ratio  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O} : \text{UO}_2$ . As the mean of five experiments, he obtains the figure 238.50 for the atomic weight of uranium, thus supporting the previous value (*loc. cit.*).

W. G.

**The Anhydrous Uranyl and Zinc Nitrates.** MARKÉTOS (*Compt. rend.*, 1912, 155, 210—213).—Ditte (*Abstr.*, 1880, 153, 154) endeavoured unsuccessfully to prepare anhydrous nitrates by the action of concentrated nitric acid on the warmed maximum hydrated nitrate. Guntz and Martin (*Abstr.*, 1909, ii, 1019) by distilling nitric anhydride on to a solution of the hydrate in concentrated nitric acid obtained the anhydrous nitrates in the case of copper, manganese, nickel, and cobalt. The method is, however, limited to nitrates only slightly soluble in nitric acid. Anhydrous uranyl and zinc nitrates can be prepared by carefully heating the respective tri- and tetrahydrates in a current of dry nitric anhydride. In the case of the uranyl nitrate the temperature employed is  $170$ — $180^\circ$ , and for zinc nitrate  $130$ — $135^\circ$ . Care must be taken that the temperatures do not rise, as the anhydrous nitrates are decomposed at temperatures slightly higher than the above. The nitric anhydride is generated by the passage of dry carbon dioxide into nitric acid (D 1.4) mixed with one-quarter its volume of sulphuric acid (D 1.84), or in the case of the zinc nitrate into a mixture of phosphoric oxide and nitric acid (D 1.52) kept at  $40^\circ$ .

Uranyl nitrate,  $\text{UO}_2(\text{NO}_3)_2$ , is a yellow, amorphous compound, which reacts violently with ether, and dissolves readily in water with

development of heat. The author has measured the heat of hydration of the anhydrous salt and the di-, tri-, and hexa-hydrates, and finds a decrease with the successive hydrates. Zinc nitrate,  $\text{Zn}(\text{NO}_3)_2$ , is obtained as a pasty substance, which crystallises on cooling, and dissolves in water with great development of heat. W. G.

**Preparation of Colloidal Vanadic Acid.** GUSTAV WEGELIN (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 25—28. Compare Müller, Abstr., 1911, ii, 732).—If the vapour of vanadium oxytrichloride is led into distilled water and the aqueous solution heated to its boiling point, vanadic acid separates out in the form of reddish-brown flakes. If the precipitated acid is filtered and washed, it yields a colloidal solution on further treatment with distilled water. If the solution is evaporated to dryness at low temperatures, a resinous substance is obtained, which redissolves in water, forming a clear colloidal solution. In this respect, the colloidal form of vanadic acid, prepared in this way, differs from the colloidal varieties which have been obtained by other methods of procedure. Differences are also exhibited in respect of the coagulation which occurs on addition of ammonium chloride, and these are probably due to differences in the degree of dispersity of the substance obtained under different conditions. H. M. D.

**Alloys of Platinum with Aluminium.** CHOURIGUINE (*Compt. rend.*, 1912, 155, 156—158).—A study of the solidification curve of alloys of platinum and aluminium, which shows a definite compound  $\text{PtAl}_3$ . A micrographic examination of these alloys showed crystals of this composition in a matrix of aluminium, and they were isolated as octahedral dendrites, violet-black in colour, and analysed, thus proving the correctness of the formula. Microscopic examination of alloys richer in platinum gave evidence of characteristic crystals of another compound, but to this no definite formula could be assigned. In order to protect the aluminium from oxidation during the preparation of the alloys, it was first dipped in a solution of lithium chloride, and dried by warming before being melted in an electric furnace. W. G.

**Isomorphism of Alkali Iridium and Rhodium Chlorides.** ALEXIS DUFFOUR (*Compt. rend.*, 1912, 155, 222—226).—A morphological study of the double chlorides of iridium and rhodium with potassium and ammonium. The author describes a new hydrate of potassium iridohexachloride,  $\text{K}_3\text{IrCl}_6\cdot\text{H}_2\text{O}$ . Having re-analysed the potassium rhodochloride prepared by Leidié (compare Abstr., 1890, 1382), he finds that it only contains one molecule of water, and thus comes into line with the iridium salt. He has measured crystals of potassium and ammonium irido- and rhodo-hexachlorides and dimethylammonium rhodohexachloride and finds that, by suitable choice of orientation and parameters, they are all isomorphous and bear the same relation to the primitive form. W. G.

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## Mineralogical Chemistry.

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**The Origin of Petroleum.** CARL ENGLER and J. BOBRZYNSKI (*Chem. Zeit.*, 1912, 36, 837—838).—Specimens of petroleum from Urycz, Bitkow, and Kleczany, Galicia, formerly described as optically inactive, have been examined, and all prove to contain dextrorotatory substances. It is necessary to carry the distillation under 11—12 mm. pressure beyond 200°, the more volatile fractions being sometimes inactive.

The active constituents are decomposition products of cholesterol, and do not form ozonides. Distillation of cholesterol under 11 mm. pressure yields a dextrorotatory fraction between 260° and 310° which does not react with ozone, or bromine, and closely resembles the similar fraction from Argentine petroleum, the smaller optical activity of the latter being sufficiently accounted for by racemisation.

C. H. D.

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## Physiological Chemistry

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**The Influence of Dry and Moist Air on Gaseous Metabolism.** HANS MURSCHAUSER and HUBERT HIDDING (*Biochem. Zeitsch.*, 1912, 42, 357—371).—The experiments were carried out in Murschhauser's apparatus (following abstract), with additional appliances for either saturating or fully drying the air. Guinea-pigs of varying size were used, and three series of experiments at the temperatures of 20°, 5°, and 35° were carried out. After the experiments the animals were killed, and the body surface measured. It was found that at 5° there was, as compared with the experiment at 21°, an increase of 76.5% carbon dioxide in dry air and 82.8% in moist air. At 35°, as compared with the experiments at 21°, there was a decrease of carbon dioxide in dry air of 18.7%, but an increase in moist air of 7.1%. At 21°, more carbon dioxide is produced in dry air than in moist air. The results do not entirely agree with those carried out by Rubner. The authors suggest an explanation of the observed facts. At low and at medium temperatures, when the air is saturated with moisture, the evaporation from the body is less than in a dry atmosphere, and there is consequently less loss of heat. There must therefore be with increasing moisture at these temperatures a diminution, and with increasing dryness an increase, in the carbon dioxide production. Increase in the moisture up to saturation point at the higher temperature, on the other hand, causes an increased temperature in the body, which shows, as a consequence, an increase in the metabolism. The authors also discuss the influence of the size of the body surface on the results obtained.

S. B. S.

**A Respiration Apparatus.** HANS MURSCHAUSER (*Biochem. Zeitsch.*, 1912, 42, 262—280).—The apparatus, which is specially adapted to investigation of the respiratory exchanges of small animals at constant temperatures, consists of the following essential parts, which are described in detail: (1) An apparatus for maintaining a constant head of water, about 30 metres above the level of the working room, which is fed from the main, and supplies three glass pumps, by means of which a constant stream of air, which can be regulated, is drawn through. (2) An apparatus interpolated just before the pumps, by means of which a small fraction of the air which is sucked through the apparatus can be transferred to one of two gas burettes. One burette is connected at a time, and as this is filled, the gas is transferred to a large collecting bottle, and the other burette is placed in connexion with the apparatus. In this way a sample of the total air which passes through can be obtained. The proportion of the total air drawn off can be regulated so that the gas burette can be filled in any given time. The oxygen in the air thus obtained can be estimated, and in this way the oxygen consumption ascertained. (3) A special apparatus for absorption of carbon dioxide consisting of a battery of specially designed tubes. (4) A thermostat containing the cage of the animal. (5) A combustion furnace connected with a special automatic arrangement for regulating its gas supply, by means of which the aspirated air is warmed to the necessary temperature. (6) A meter for measuring the air drawn through, and wash-bottles for removing the carbon dioxide therefrom. The whole apparatus is figured.

S. B. S.

**Influence of Lack of Oxygen on Tissue Respiration.** FRITZ VERZÁR (*J. Physiol.*, 1912, 45, 39—52).—The submaxillary always uses the same amount of oxygen so long as the blood brings the required quantity, even when the oxygen pressure in the blood decreases to a very low value; this means that the oxygen pressure in the gland must be considerable. Skeletal muscle uses less oxygen if there is less in the blood; this means that the oxygen pressure in muscle is small or zero. The heart follows the same rule, but the result may be influenced by change in the work of the heart. The kidney increases its oxygen-use during lack of oxygen. This is probably caused by some stimulating intermediate metabolic substances. This may in part explain increased oxygen use at high altitudes.

W. D. H.

**Amount of Aliphatic Amino-nitrogen in the Blood of Mammals and its Proteoclastic Power.** EDGARD ZUNZ (*Bull. Soc. chim. Belg.*, 1912, 26, 188—193).—Blood serum of rabbits and dogs, kept at 38°, has a slight proteoclastic power on its own proteins and a greater power in the case of the proteins of the serum of other species. It is probable that blood serum contains, in addition to proteoclastic agents, substances which check their action.

Difibrinated blood and blood of dogs have a higher proteoclastic action with their own proteins than the blood serum of the same animal.

In mixtures of the blood or defibrinated blood of dogs and the

serum of bullocks, the inhibiting substances reduce the proteoclastic action to a much greater extent than is caused by the inhibiting substances of serums in mixtures of dogs' and bullocks' serum.

N. H. J. M.

**The Presence in Blood and Liver of a Ferment Capable of Causing the Hydrolysis of Cholesteryl Esters.** J. H. SCHULTZ (*Biochem. Zeitsch.*, 1912, 42, 255—261).—In the autolysis of human or horse blood, no scission of cholesteryl esters takes place. Horse liver, but not rabbit's liver, causes on autolysis, hydrolysis of cholesteryl esters, which is, however, not complete. On autolysis of a mixture of liver and blood (of horse, and probably of ox), the hydrolysis of cholesteryl esters is complete. It is not complete if plasma or serum is used instead of the whole blood. The technique of estimating free cholesterol in the presence of its esters is given; it depends on the precipitability of the free cholesterol by digitonin according to the Windaus method.

S. B. S.

**Increase in the Number of Red Corpuscles in the Blood Under the Action of Certain Cholesterol Derivatives.** PIERRE THOMAS and (Mlle.) MADELEINE LEBERT (*Compt. rend.*, 1912, 155, 187—190).—Kepinoff (*Abstr.*, 1911, ii, 185) has shown an increase in the number of red corpuscles in the blood of a previously bled rabbit, by the injection of corpuscles from ox blood. It having been shown that these corpuscles always contain a certain quantity of cholesteryl esters, the authors have studied the effect of the subcutaneous injection of such esters on the number of red corpuscles in a rabbit's blood. The ester employed was cholesteryl oleate or one of its oxidation products in the form of an emulsion. By injection of 5 c.c. of such an emulsion, repeated after seven days, an increase of 19% in the number of red corpuscles was found, the effect lasting for several weeks. A similar result was obtained by injection into a bled rabbit, the normal status being attained after three days with an uninjected animal, and in two days with an injected animal, after which time a further increase of 10% on the count was found in the latter case. That the effect is lasting is shown by injection and subsequent bleeding after a lapse of three weeks, after which the normal red-corpuscle content is again attained and passed within two days without any further injection of the cholesteryl oleate.

W. G.

**The Action of Ammonia and Ammonia Derivatives on Oxidation Processes in Cells.** EDUARD GRAFE (*Zeitsch. physiol. Chem.*, 1912, 79, 421—438).—Experiments with blood-corpuscles of the goose as in Warburg's experiments show the influence of ammonia, various amines, and alkaloids. There is increase of oxidation with small, and reversible inhibition with large, doses. The effects are proportional to concentration of hydroxyl ions.

W. D. H.

**Action of Leucocytes on Dextrose.** PHÆBUS A. LEVENE and GUSTAVUS M. MEYER (*J. Biol. Chem.*, 1912, 12, 265—274).—Under the influence of leucocytes, dextrose undergoes dissociation into lactic

acid only, whereas by purely chemical methods the formation of lactic acid from dextrose is always accompanied by numerous side reactions.

W. D. H.

**Protein Metabolism from the Standpoint of Blood and Tissue Analysis. IV. Absorption from the Large Intestine.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1912, 12, 253—258). Compare this vol., ii, 271, 364, 780).—The authors' new methods (this vol., ii, 780) enable them to state positively that absorption of the products of proteolysis occurs from the large intestine, although not so rapidly as from the small intestine. Positive results were obtained with urea, glycine, alanine, Witte's peptone, and creatinine.

W. D. H.

**Protein Metabolism from the Standpoint of Blood and Tissue Analysis. V. Absorption from the Stomach.** OTTO FOLIN and HENRY LYMAN (*J. Biol. Chem.*, 1912, 12, 259—264).—Similar results were obtained in experiments on the stomach of the cat, except in the case of creatinine (see preceding abstract).

W. D. H.

**The Explanation of Chauveau's Experimental Results, from which the Conclusion was Drawn that Fats have Less Value than Carbohydrates as a Source of Energy for Muscular Work.** L. S. FRIDERICIA (*Biochem. Zeitsch.*, 1912, 42, 393—398).—As explanation of Chauveau's result that an animal loses more weight when doing an amount of work on a protein-fat diet than when doing the same amount of work on an isodynamic protein-carbohydrate diet, the author quotes experiments of Benedict and Milner, and others, and shows that the difference between the two results is not due to the fact that fat is not so good a source of energy for muscular work as carbohydrates, but rather to the fact that the body tissues contain more water when the carbohydrate diet is taken than when the fat diet is used.

S. B. S.

**Presence of  $\beta$ -Iminazolyethylamine in the Intestinal Wall; with a Method of Isolating a Bacillus from the Alimentary Canal which Converts Histidine into this Substance.** EDWARD MELLANBY and F. W. TWORT (*J. Physiol.*, 1912, 45, 53—60).—By means of a method previously described for isolating bacilli which destroy creatine, a bacillus of the colon group was isolated from the intestine of the guinea-pig which is capable of producing  $\beta$ -iminazolyethylamine from histidine. The presence of this substance in intestinal extracts is thus accounted for. Acidity prevents the action of this bacillus, and Metchnikoff's idea of the benefit of lactic acid is thus in part supported.

W. D. H.

**Measurement of Tissue Oxidation in vitro (Liver, Central Nervous System).** RYUTA USUI (*Pflüger's Archiv*, 1912, 147, 100—110).—An organ or a part of it is placed in a closed tube, which is then filled up with a suspension of ox-blood in Ringer's solution. The amount of oxidation in the blood so produced is com-

pared with that in a control tube containing the blood suspension only. Oxidation continues and remains constant in liver lobes for some hours, and the oxygen consumption per gram of organ per hour varies between 0.24 and 0.55 c.c. The same constancy is observed in the central nervous system of the frog, the oxygen consumption varying between 63 and 94 c.c. per hour per kilo. of organ.

Oxidation is influenced by various reagents in the same way as Warburg has shown to occur in other cells. W. D. H.

**Glycogen Formation.** GEORG ROSENFELD (*Biochem. Zeitsch.*, 1912, 42, 403—411).—When dextrose is injected into the jugular vein of a starved anaesthetised animal no increase in the percentage of glycogen in the liver could be detected when comparison was made with a sample of the liver extirpated when the animal was anaesthetised and before injection of sugar into the vein. It was found, however, that the liver of dogs after fasting for five days contained less than 1% of glycogen. If meat or sugar is administered to dogs after five days' starvation, increase of glycogen could be detected. In these cases the administration was made without previous operation on the liver, and the sugar was given both *per os* and intravenously. The Kütz method of glycogen estimation was employed. The author suggests a modification of this method, in that the liver, after extirpation, is heated in alcohol instead of water. S. B. S.

**The Liver in Relation to Creatine Metabolism in the Bird.** D. NOEL PATON and W. C. MACKIE (*J. Physiol.*, 1912, 45, 115—118).—Exclusion of the liver in the bird produces a marked change in the distribution of nitrogen in uric acid, and ammonia in the urine, but has no effect on the proportion of creatine. This seems to indicate that in the bird the liver is not connected with creatine metabolism. W. D. H.

**The Significance of the Suprarenal Capsules in the Action of Certain Alkaloids.** HENRY H. DALE and PATRICK P. LAIDLAW (*J. Physiol.*, 1912, 45, 1—26. Compare this vol., ii, 667).—A full account of a research of which a notice has already appeared. The main point is that the investigation of a drug on isolated organs may lead to fallacious results, for the effect on those organs in the intact animal may not be a direct one, but an indirect one by acting on other organs first, such as the suprarenal glands. W. D. H.

**The Action of Ethyl Alcohol and Water on Muscle.** FREDERIC S. LEE and M. LEVINE (*Amer. J. Physiol.*, 1912, 30, 389—394).—Lee and Salant found that alcohol exerted a favourable action on the contraction of frog's muscle; Hough and Ham state that equally favourable results were obtained with Ringer's solution or even water alone. Their experiments were only few in number. The present research confirms the statements of Lee and Salant. W. D. H.

**The Normal Presence of Boron in Animals.** GABRIEL BERTRAND and HENRI AGULHON (*Compt. rend.*, 1912, 155, 248—251).—The authors have examined various organs and tissues of the guinea-

pig, rabbit, sheep, ox, and horse for boron, employing a delicate reaction for the detection of the boron (compare Abstr., 1910, ii, 241, 345). The organs or tissues were collected, dried, and burnt in a platinum boat in a stream of oxygen, or in a muffle furnace. The residue was esterified with methyl alcohol, the ester distilled, and saponified with sodium hydroxide. The alkaline solution was tested with turmeric, and when a reaction occurred, the boron was converted into boron fluoride and examined spectroscopically. The results show that boron is present in the organs of the five animals examined, being most easily detectable in the hair, the horns, the bones, the liver, and the muscles. The amount is, however, always very small. W. G.

**The Non-Enzymatic Character of Oöcytin (Oöcytase).** T. BRAILSFORD ROBERTSON (*J. Biol. Chem.*, 1912, 12, 163—174. Compare this vol., ii, 573, 782).—Oöcytin (called oöcytase in previous papers) is not a proteinase, lipase, or a peroxydase. It does not accelerate the hydrolysis of  $\beta$ -glucosides, neither does it act as a co-enzyme to the lipase of *Ricinus*. It is probably not an enzyme at all. The membrane-forming agent in *Strongylocentrotus purpuratus* spermatozoa is also probably not an enzyme; oöcytin is not a protein.

W. D. H.

**Changes in the Physico-chemical Properties of the Urine and Serum of Dogs after Thyroidectomy.** RAFFAELE PALADINO (*Biochem. Zeitsch.*, 1912, 42, 302—303).—After extirpation of thyroids and parathyroids, the viscosity of serum and urine increases, and their electrical conductivity sinks. There is no marked change in the surface tension.

S. B. S.

**Pathology and Treatment of Severe Diabetes.** E. GRAFE and CHARLES G. L. WOLF (*Deutsch. Arch. klin. Med.*, 1912, 107, 201—235). Full details are given of three cases of severe diabetes, including the estimation of sugar, total nitrogen, various nitrogenous substances, and members of the acetone group in the urine. Particulars of diet and respiratory exchanges are also given. In two cases the acidosis was extreme, and the dextrose nitrogen ratio was often over 5, which points to a formation of sugar from fat. The respiratory quotient was also high, which means that large quantities of glycogen must be oxidised in spite of a diet poor in carbohydrate, or there must be some unknown factor to explain the anomaly. In the third case, a period of lessened sugar excretion occurred without changing the diet; the acidosis and the creatine output also diminished, and the respiratory quotient rose. The amount of creatine is a good index of the severity of the case.

Therapeutically the best results both on the sugar and the acidosis were obtained by the use of alcohol (100—160 grams of absolute alcohol a day) combined with large amounts of sodium citrate and sodium hydrogen carbonates (70—100 grams per week).

W. D. H.

**Inhibition of Glycosuria. I. The Influence of Hirudin on Glycosuria Produced by Adrenaline and by Diuretin.** MIROSLAV MICULICICH (*Arch. exp. Path. Pharm.*, 1912, 69, 128—132).—The

glycosuria produced by adrenaline is inhibited by intravenous injection of hirudin, owing to its effect on blood-pressure and diuresis. Excretion of sodium chloride is not inhibited. Hirudin has no such action on the glycosuria which is produced by the central stimulation of diuretin.

W. D. H.

**Inhibition of Glycosuria. II. The Influence of Ergotoxin on Glycosuria Produced by Adrenaline and Diuretin.** MIROSLAV MICULICICH (*Arch. exp. Path. Pharm.*, 1912, 69, 133—148).—Ergotoxin, subcutaneously or intravenously administered, inhibits adrenaline glycosuria, or if this glycosuria already exists, it cuts it short. This is due to inhibition of hyperglycæmia and a specific impermeability to sugar in the kidney. The output of sodium chloride is not affected, but diuresis is inhibited. The hyperglycæmia and glycosuria (but not the diuresis) produced by diuretin are also inhibited by ergotoxin.

W. D. H.

**The Influence of Glutaric Acid on Phloridzin Glycosuria.** A. I. RINGER (*J. Biol. Chem.*, 1912, 12, 223—226).—A criticism of the methods and results of Baer and Blum. Contrary to what they state, glutaric acid has no inhibitory effect on the action of phloridzin.

W. D. H.

**Is Œdema Determined by the Acid Content of the Tissues?** A. R. MOORE (*Pflüger's Archiv*, 1912, 147, 28—34).—Martin H. Fischer (Abstr., 1910, ii, 329) holds that dropsy is mainly produced by the acidity of the tissues attracting water from the blood. The present experiments lend no support to this view.

W. D. H.

**The Colloid-chemical Theory of Water Absorption by Proto-plasm.** MARTIN H. FISCHER (*Biochem. Bull.*, 1912, 1, 444—460).—A defence of the author's view on the cause of œdema.

W. D. H.

**Enzymes as Possible Factors in the Development of Œdema.** WILLIAM J. GIES (*Biochem. Bull.*, 1912, 1, 461—482).—A discussion of Martin H. Fischer's views on the cause of œdema, and suggestions that enzymes of the nature of hydrolases or proteases may be factors in the tissue changes which increase the affinity of the tissues for water. The results obtained so far do not, however, demonstrate that enzymes are involved.

W. D. H.

**Preparation from Yeast and Certain Foodstuffs of the Substance the Deficiency of which in Diet Occasions Polyneuritis in Birds.** CASIMIR FUNK (*J. Physiol.*, 1912, 45, 75—81).—The substance which prevents beri-beri was isolated from yeast, milk, or brain, and possibly from lime juice. For curing pigeons of polyneuritis, 0.02 to 0.04 gram by the mouth was used. Its chemical properties suggest that it is a pyrimidine base forming a constituent of nucleic acid (compare Edie and others, this vol., ii, 794).

W. D. H.

**A Case of Bence-Jones Proteinuria.** FRANCIS W. LAMB (*Proc. physiol. Soc.*, 1912, iii—iv; *J. Physiol.*, 45).—The properties of the protein in this case closely resemble those described by Hopkins and Savory. By means of a microscope with a hot stage, the microscopic changes were observed; at 45—47° a cloud of minute spherule appeared which decomposed at 50—60°, and between 80° and 95° melted to oily droplets. On cooling, opacity reappeared. The same occurred with dialysed solutions of the protein (precipitated by ammonium sulphate), but less markedly. The clearing of the fluid at high temperatures is not due to solution, but in great measure to this "melting" phenomenon. W. D. H.

**The Partition of Iodine in Syphilitic Tissues.** OSWALD LOEB (*Arch. exp. Path. Pharm.*, 1912, 69, 108—113).—The greater part of the iodine given as a drug in syphilis is organically united to the syphilitic tissues, the proportion of this to inorganic iodine being 1·6 : 1. Figures are given for blood and glandular tissues to show the great increase in iodine in syphilitic as compared with normal tissues under the same conditions. W. D. H.

**Experimental Changes in Arteries in Rabbits Produced by Aliphatic Aldehydes.** OSWALD LOEB (*Arch. exp. Path. Pharm.*, 1912, 69, 114—127).—Aliphatic aldehydes produced in rabbits typical arterial necrosis. This does not occur with furfuraldehyde, aromatic aldehydes, alcohols, ketones, and sodium acetate. The effect was not obtained in cats, rats, or dogs. W. D. H.

**The Pharmacological Action of Harmine.** JAMES A. GUNN (*Trans. Roy. Soc. Edin.*, 1912, 48, i, 83—96).—The minimal lethal dose of harmine hydrochloride per kilogram of body-weight by subcutaneous injection is: for the frog, 0·6 gram; for the guinea pig, 0·12 gram; for the rabbit, 0·23 gram; for the rat, 0·2 gram, and for the pigeon, 0·15 gram. In frogs the drug produces a paralytic effect on the central nervous system; excitability and rigor on the isolated muscle and in strong solutions, when perfused through the heart, arrest in the position of almost complete diastole; weaker solutions diminish the completeness of systolic contraction. The drug has also a slight peripheral constricting action on the blood-vessels.

In mammals, the drug produces a fall of blood-pressure due to the weakening of the heart contractions, and cardiac failure is the chief cause of death. In sub-lethal doses it stimulates respiration, but in larger doses it paralyzes respiration. It produces also a fall of temperature, and even in small doses it stimulates the contractions and augments the tone of the uterus.

The author compares and contrasts the actions of harmine and harmaline. There is a great similarity between the two.

S. B. S.

**Quantitative Investigations on the Change of Toxicity of Morphine when in Presence of other Opium Alkaloids.** HEINRICH CESAR (*Biochem. Zeitsch.*, 1912, 42, 316—324).—In con-

tinuation of the other investigations on this subject in Straub's laboratory, the author now estimates the effect of the addition of narcotine alone, papaverine alone, and the two alkaloids together on the toxicity of morphine, determining in each case the minimal lethal dose for mice. In the case of narcotine-morphine mixtures the results are somewhat complex, there being two optimal points of maximum toxicity, one being in the mixture of 1 part of morphine and 0.2 part of narcotine, and the other, 1 part of morphine and 1 part of narcotine. Mixtures between these limits are less toxic. Owing to the toxicity of pavaverine, the results of the action of the mixture are not easy to interpret. Its effect is, however, in certain cases, not a purely additive one. S. B. S.

**The Action of Bases and Basic Salts on Alkaloid Salts.** ISIDOR TRAUBE (*Biochem. Zeitsch.*, 1912, 42, 470—495).—In confirmation of the results obtained by other investigators, the author finds that the addition of alkalis and alkali salts largely increases the pharmacological and toxic action of numerous alkaloidal salts. These results have been obtained by quantitative experiments on tadpoles. The magnitude of the increase of action is a function of the strength of the base employed and of the nature of the alkaloid. By this method of investigation a very simple and exact way is indicated for ascertaining the strength of bases, for not only can the pharmacological method be employed, but also, in accordance with the authors cohesion pressure theory of osmosis, the increase of toxicity is parallel with the diminution of surface tension of the alkaloidal salt solution produced by the addition of alkali. Instead, therefore, of animal experiments, a stalagmometric method can be employed. In the case of alkaloids, such as morphine, where the addition of alkalis to their salts does not produce a marked lowering of surface tension of the solution, it does not produce an increased toxic action. On these results, the author suggests a theory of the local action of alkaloids, whereby their action at different points in the organism is a function of the alkalinity of the tissues at these points, and he suggests various therapeutic experiments, whereby the action of drugs may be increased by the addition of alkalis. S. B. S.

**The Influence of Sodium Carbonate on the Toxicity of Basic Dyes.** ISIDOR TRAUBE (*Biochem. Zeitsch.*, 1912, 42, 496—499).—The majority of dyes which lower the surface tension of water are more toxic to tadpoles than those which do not. Certain substances which are relatively non-toxic, however, have their toxic action increased by the addition of sodium carbonate (methylene-blue, toluidine-blue, and methyl-green), whereas the toxicity of other more toxic dyes (night-blue, Nile-blue, malachite-green, and magenta) are not rendered more toxic by the addition of alkalis. The results here are different to those obtained with alkaloids (see preceding abstract), and this is apparently due to the alterations in the size of the particles which undergo change on addition of alkalis. The surface-tension rule does not, therefore, strictly hold in this case. S. B. S.

**Selective Tissue Colouring and Chemico-therapeutics. II. Sources of Experimental Errors.** WERNER SCHULEMANN (*Arch. Pharm.*, 1912, 250, 389—395. Compare this vol., ii, 791).—In experiments on the dyeing of living tissues, errors are so easily and unconsciously made that the author thinks it desirable to record the sources of some in his experience.

The dyes employed must be chemically pure, or at all events the impurities in them must be known. The impurities may have toxic properties; inorganic adulterants such as sodium chloride or sulphate introduce complications through "salting out"; in many cases the amount of actual dye in a given quantity of the commercial preparation cannot be ascertained. Mixtures of dyes can generally be detected by strewing the powdered substance on filter-paper moistened with water or alcohol; the components of the mixture produce each its spot of characteristic colour. Mixtures of dyes of similar colour are detected in the same way on the surface of concentrated sulphuric acid.

Solutions for the dyeing of living tissues should be 0.5% solutions prepared in the cold; heating may produce a different colloidal state of the dye, with possibly a greater tendency to gel-formation, and in this state the solution may be useless. Clear solutions only are permissible. The number of injections must be noted, and the tissues of the animal should be examined twenty-four hours after the last injection. Frequently it is extremely difficult to distinguish cells dyed orange or yellow from the surrounding fresh cells. The age of the animal under examination must be stated.

C. S.

**Distribution of Chlorate in a Woman Fatally Poisoned by Potassium Chlorate.** JACOB ROSENBLUM (*Biochem. Bull.*, 1912, 1, 482).—Fifty grams of potassium chlorate were taken, and the analyses were made within twelve hours of death. Small quantities were recovered from various organs, but the total only amounts to 0.34 gram. The salt is therefore rapidly excreted, or reduced to chloride.

W. D. H.

**The Significance of Hydrocyanic Acid in the Production of Toxic Effects by Tobacco Smoke.** KARL B. LEHMANN and KARL GUNDERMANN (*Arch. Hygiene*, 1912, 76, 98—115).—There is no reason for assuming the presence of dicyanogen in tobacco smoke. Hydrocyanic acid in smoke is best estimated by absorption in acid silver nitrate solution and the amount calculated from the silver content in the purified precipitate. The amount of hydrocyanic acid in the tobacco smoke depends on the rate at which the air is drawn through a cigar; the less rapid the rate, the smaller the amount of acid. Under no conditions could enough hydrocyanic acid be detected to cause toxic effects.

S. B. S.

## Chemistry of Vegetable Physiology and Agriculture.

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**Bacterial Metabolism. III.** ARTHUR I. KENDALL and CHARLES J. FARMER (*J. Biol. Chem.*, 1912, 12, 215—218. Compare this vol., ii, 793).—The sparing action of carbohydrate for protein is again brought out in relation to other micro-organisms. Certain bacteria are able to appropriate certain definite constituents of the protein molecule, especially that part which contains a carbohydrate radicle, leaving the remainder but little acted on until the more desirable portion is largely exhausted. W. D. H.

**Bacterial Metabolism. IV.** ARTHUR I. KENDALL, CHESTER J. FARMER, EDWARD P. BAGG, jun., and ALEXANDER A. DAY (*J. Biol. Chem.*, 1912, 12, 219—222).—All the streptococci studied, with one exception, which scarcely grew in a medium free from dextrose, produce acid in a sugar-free medium. W. D. H.

**Influence of Uranium Salts on Alcoholic Ferments.** E. KAYSER (*Compt. rend.*, 1912, 155, 246—248).—Uranium salts, in minute quantities, exert a stimulating effect on cider yeast, whilst larger quantities, 0.2 gram per litre, diminish the quantity of alcohol formed. The same toxic action is exerted on sucrase and zymase, sucrase being more sensitive than zymase. After a number of generations, yeasts can be accustomed to support the presence of uranium salts. Uranates of potassium and ammonium have a greater toxic effect than uranyl nitrate or phosphate. W. G.

**Alcoholic Fermentation II. The Conversion of Acetaldehyde into Ethyl Alcohol by Living and Dead Yeast.** S. KOSTYTSCHEFF and E. HÜBENET (*Zeitsch. physiol. Chem.*, 1912, 79, 359—374).—Acetaldehyde is reduced to ethyl alcohol when incubated with pressed yeast, air-dried yeast, hefanol, zymin, or the juice prepared by macerating air-dried yeast. These experiments lend support to the hypothesis that acetaldehyde is an intermediate stage in the alcoholic fermentation of sugar. The fact that this formation of alcohol takes place equally well in the absence as in the presence of formic acid, is not in agreement with Schade's theory that lactic acid is first formed from the sugar, and is further converted into acetaldehyde and formic acid, which react to form carbon dioxide and alcohol.

An alternative hypothesis consists in supposing that the sugar is converted into pyruvic acid with formation of atomic hydrogen. The pyruvic acid is then converted into carbon dioxide and acetaldehyde, and the latter reduced by the hydrogen to alcohol (compare Neuberg and Kerb, *Zeitsch. Gärungsphysiol.*, 1912, 1, 114). W. J. Y.

**The Formation of Volatile Acids by Yeast During the Process of Re-fermentation of Wine.** C. VON DER HEIDE and E. SCHWENK (*Biochem. Zeitsch.*, 1912, 42, 281—288).—By re-fermentation

is understood the addition of sugar solution to wines poor in alcohol, and the further fermentation of this mixture by yeast. During this process, volatile acids are sometimes formed, the production of which has been ascribed to the inoculation of the mixture with two small quantities of yeast. The authors have experimentally tested this hypothesis, determining the amounts of volatile acids formed when re-fermentation mixtures containing varying initial quantities of alcohol and sugar are inoculated with varying numbers of yeast cells. The experiments were all carried out with carefully sterilised materials, and no relationship could be determined between the amounts of volatile acids formed and the number of yeast cells used for inoculation. In the case of inoculations with small numbers of yeast cells, there were relatively large amounts of unfermented sugar present at the end of the experiment. In actual practice the amount of volatile acid is larger when small amounts of yeast are used for inoculation than when large amounts are used, and the difference between this fact and the above laboratory experimental facts, the authors explain to be due to the differences in conditions, in that the laboratory materials were all sterile, a condition impossible in practice. In the latter case, unless alcoholic fermentation is rapid from the start, which is only possible when sufficient yeast is used for inoculation, the bacteria have a chance of development and thus cause the presence of the acids.

S. B. S.

**Influence of Nitrogenous Matter on the Production of Ethyl Acetate in Alcoholic Fermentation.** E. KAYSER (*Compt. rend.*, 1912, 155, 185—187).—The yeasts employed were obtained from sugar cane and pine apples. The nitrogenous matter was furnished in the form of malt dust, peptone, asparagine, leucine, carbamide, glycine, and ammonium sulphate. The yeasts were sown in media containing 150 grams of sucrose, 1 gram of potassium hydrogen phosphate, traces of magnesium sulphate, and 0.5 gram of nitrogen, in one of the different forms, per litre. The protein nitrogen gave a higher yield of ethyl acetate with both yeasts. The yeast from sugar cane preferred peptone and ammoniacal nitrogen, whilst that from pine apple preferred amino- and amide-nitrogen.

W. G.

**Action of Different Salts on the Development of *Aspergillus niger*.** ALEXANDER KIESEL (*Compt. rend.*, 1912, 155, 193—196. Compare Clark, *Abstr.*, 1899, ii, 627).—A study of the effect of some twenty-seven acids and acid salts on the growth of *Aspergillus niger* with an endeavour to determine the limiting doses which inhibit certain vegetative phenomena, such as germination, development of mycelium, and fructification. The results, which are given in tabular form, show that the physiological activity of the acids and salts does not, in general, correspond with their chemical activity, the action of the fatty acids and also of chloroacetic acid being much more powerful physiologically than chemically.

W. G.

**Influence of Zinc on the Consumption of its Hydrocarbon, Nitrogenous and Mineral Food by *Aspergillus niger*.** MAURICE JAVILLIER (*Compt. rend.*, 1912, 155, 190—193. Compare *Abstr.*, 1908, ii, 124; 1911, ii, 222, 421, 644; this vol., ii, 377).—The presence

or absence of zinc has a marked effect on the consumption of all the substances necessary to the growth of *Aspergillus niger*. Under certain conditions, zinc regulates the consumption of sugar, giving a larger crop, when present, with a smaller sugar consumption per gram-weight of dry matter. In itself it is incapable of rendering nitric nitrogen assimilable, but it greatly influences the results with ammoniacal nitrogen. Presence of zinc produces a much greater dry weight of crop and a smaller nitrogen consumption. Finally, in the ashes of *Aspergillus niger*, grown on a zinc-containing medium, there is more silicon and phosphorus, but less sulphur, whilst the potassium content remains about constant.

W. G.

**Autolysis of Mould Cultures.** ARTHUR W. DOX and LEONARD MAYNARD (*J. Biol. Chem.*, 1912, 12, 227—232).—Common saprophytic moulds allowed to grow in suitable media form a dense mycelium, which after several weeks disintegrates; the change is attributed to autolysis. During the first week or two, the mould assimilates most of the nitrogen of the medium, and subsequently restores to it a large portion. Nitrogen was not assimilated from the atmosphere.

W. D. H.

**Influence of Phytin on the Growth of Lupine Seedlings.** A. R. ROSE (*Biochem. Bull.*, 1912, 1, 428—438).—Phytin added to soil does not cause any stimulation of growth that can be attributed to the phytic acid. It acts just as inorganic phosphates do.

W. D. H.

**Rôle of Metallic Salts in the Assimilation of Nitrates by Green Plants.** OCTAVE DONY-HÉNAULT (*Bull. Soc. chim. Belg.*, 1912, 26, 266—276).—The photochemical reduction of nitrates to nitrites is greatly increased by the presence of manganese salts. Slight alkalinity is favourable to the reduction. A precipitate of the composition represented by the formula  $Mn_2O_3 \cdot H_2O$  is formed, indicating simultaneous oxidation and reduction. Addition of dextrose further increases the reduction, and, at the same time, prevents precipitation of the manganese.

Iron salts act similarly to manganese salts, but in slightly acid solutions. For this reason, iron and manganese together have less rather than more action than each alone.

The results of experiments with cress invariably showed that nitrogen in the form of nitrates is more rapidly mobilised in presence of manganese or iron salts than in their absence.

The conclusion is drawn that the catalytic function of a mineral element will depend chiefly on the conditions of the medium, and that the least variation in alkalinity or acidity may suspend the activity of one catalyst and revive that of another; and that the conception of enzymes specifically adapted to each phenomenon of oxidation or reduction is irrational. Manganese salts may cause both reduction and oxidation according to the conditions.

N. H. J. M.

The Biochemical Behaviour of Perchlorates, Chlorates, Nitrates, and Nitrites, and the Reducing Power of the Root Nodules of Leguminosæ, especially of *Vicia faba*. UGO ALVISI and M. ORABONA (*Gazzetta*, 1912, 42, i, 565—575).—Chlorates, but not perchlorates, are reduced by enzymes, whilst *Penicillium glaucum* reduces ammonium perchlorate, but not the potassium salt. Perchlorates are more harmful to bean plants than chlorates, and ammonium perchlorate is reduced to chloride. The ammonium salt is also less stable than the potassium salt towards the root-nodules of the bean. Experiments with nitrates and nitrites are inconclusive.

C. H. D.

The Passage of Salts through Protoplasm. I. The Influence of Salts on the Absorption of Dyestuffs by the Living Cell. JOSEF ENDLER (*Biochem. Zeitsch.*, 1912, 42, 440—469).—As a result of experiments on different varieties of plant cells, the author draws the following conclusions. Neutral salts in low concentrations favour the entrance of dyestuffs into cells, whereas in higher concentrations they inhibit the entrance. The inhibitory action of various anions is in the following order: nitrate < chloride < sulphate < tartrate, citrate < aluminate < salicylate. The difference in the action of the cations is less marked, aluminium having a slightly stronger inhibitory action than the others. The exit of dyestuffs from cells in the presence of salts was also investigated. The exit is favoured by various ions in the following order: sodium < potassium < magnesium < [calcium] < aluminium, and nitrate < chloride < sulphate < tartrate < citrate. S. B. S.

The Interdependence of Protein Degradation in Plants, and their Respiratory Processes. II. The Action of Carbohydrates, Phosphates, and Oxidising Reagents on the Formation and Assimilation of Ammonia in Killed Plants. WLADIMIR PALLADIN and NICOLAUS IWANOFF (*Biochem. Zeitsch.*, 1912, 42, 325—346. Compare this vol., ii, 477).—The experiments were carried out with various killed yeast preparations. It was found that autolysis in water is accompanied by the formation of ammonia, or substances which readily yield ammonia on hydrolysis. The addition of phosphates inhibits this ammonia formation, the monopotassium salt acting in this respect more vigorously than the dipotassium salt. Dextrose inhibits the ammonia formation more strongly than the phosphates; if it is added to an autolysing mixture, further formation of ammonia ceases, and if phosphate is added in addition to the dextrose, the ammonia already formed commences to disappear. An explanation of these facts is offered by the authors, who assume that in addition to processes by means of which ammonia is set free from proteins, processes also exist by means of which ammonia can be assimilated. They suggest that methylation of intermediary degradation products can take place, in which process either dextrose or its intermediary degradation products can take part, for it is known that betaines are widely distributed in plants. Under the conditions of the experiments, ammonium pyruvate or acid

ammonium malate are not assimilated. Lactose has but little effect in inhibiting ammonia formation. No very definite solution of the question as to the part played by oxygen in processes discussed could be obtained. S. B. S.

**Importance of Hydrogen Cyanide and Glucosides Producing Hydrogen Cyanide in Plant Chemistry.** ARMAND JORISSEN (*Bull. Soc. chim. Belg.*, 1912, 26, 199—205).—A summary of results obtained by the author (*Bull. Acad. Roy. Belg.*, 1884, [iii], 8; 1887, 14; 1891, 21) and by Dunstan, Greshoff, Treub, and by Laurent and Marchal. N. H. J. M.

**Fruit of Diervilla Florida.** LOWELL E. DAWSON (*Chem. News*, 1912, 106, 18—20).—The ripe fruit of the bush honeysuckle, *Diervilla Florida*, is dark red in colour, resembling large currants. The dry fruit contains 38% of sugar, part of which is lævulose, 3.5% of ash, of which a full analysis is given, 3.75% of an oil which seems to belong to the castor oil group, and 2.86% of nitrogen. Tartaric and citric acids are present, and probably narceine, which was not identified with certainty. E. F. A.

**The Glucoside in the Seeds of Hevea brasiliensis, Müll. Arg.** K. GORTER (*Rec. trav. chim.*, 1912, 31, 264—266).—By repeated extraction with boiling alcohol (96%) a glucoside has been isolated from the seeds of *Hevea brasiliensis*, which is found to be identical in every respect with the phaseolunatin isolated by Dunstan and Henry from the beans of *Phaseolus lunatus* (*Abstr.*, 1904, ii, 71) and from the roots of the bitter cassava (*Abstr.*, 1906, ii, 795). W. G.

**Biochemical Studies on Soils Subjected to Dry Heat.** FRED J. SEAVER and ERNEST D. CLARK (*Biochem. Bull.*, 1912, 1, 413—427).—Extracts of heated soils have a deeper colour than those of unheated soils. This serves as an index of increase of soluble matter. Heated soils retard the growth of green plants, but increase that of fungi. W. D. H.

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### Analytical Chemistry.

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**Preparation of Normal Solutions.** WILLEM STORTENBEKER (*Chem. Weekblad*, 1912, 9, 565—570).—The author discusses the errors usually characteristic of volumetric analysis, and the precautions adopted to eliminate them. A. J. W.

**Estimation of Iodine in Presence of Other Halogens and Organic Matter.** E. C. KENDALL (*J. Amer. Chem. Soc.*, 1912, 34, 894—909).—During an investigation of the thyroid gland, a method was devised by Hunter (*Abstr.*, 1910, ii, 650) for estimating small

quantities of iodine in organic substances. This method was based on the oxidation of the iodine to iodic acid and the subsequent estimation of the latter. It has been found that the reactions involved in this process are quantitative when larger amounts of iodine are present, and the conditions have therefore been determined under which the method can be applied to the estimation of iodine in presence of bromides, chlorides, and organic matter.

When the iodine is present in the free state or as an iodide, the solution to be tested is rendered neutral or slightly alkaline and is treated with phosphoric acid and sodium hypochlorite. The solution is left for two to three minutes after it has become colourless, and 5% solution of phenol is then added. The phenol combines with the free chlorine in solution to form chlorophenol. A few drops of phenolphthalein are added, and the solution made slightly alkaline with sodium hydroxide. It is then acidified with phosphoric acid and excess of potassium iodide introduced. Iodine is liberated and is titrated with sodium thiosulphate. The method is not affected by the presence of chlorides.

When bromine is present, benzene is added to the solution before it is treated with sodium hypochlorite. After the iodine has been oxidised to iodic acid, the solution is boiled. The benzene reacts with the hypochlorite and hypobromite to form chloro- and bromobenzene, whilst the free bromine is expelled during the boiling.

If iodine is to be estimated in material containing organic matter, nitrites, copper, iron, mercury, or silver, such substances must be removed and the iodine obtained in the form of iodide. This can be accomplished by fusing the substance with sodium hydroxide, and, after cooling, adding a little potassium nitrate and repeating the fusion. The contents of the crucible are dissolved in water and the solution is filtered if necessary. The solution is then acidified, sodium hydrogen sulphite having been previously added to prevent loss of iodine with the carbon dioxide evolved. The iodine is now present as hydriodic acid, and can be estimated by the method already described. A modification of this process has been devised for estimating iodine when present in small quantities, and especially with reference to the iodine of the thyroid gland. It is also recommended as a qualitative test, and is said to be capable of detecting 0.005 mg. of iodine.

Full details of these methods are given, as well as of the precautions to be observed in their application. E. G.

**Estimation of Inorganic Phosphorus in Plant Substances.**  
R. C. COLLISON (*J. Biol. Chem.*, 1912, 12, 65—72).—The finely ground sample is extracted with 94—96% ethyl alcohol containing 0.2% of hydrochloric acid; this prevents enzyme and bacterial decomposition of organic phosphorus compounds, and, further, the latter are practically insoluble in this solvent. The extract is filtered after three hours' shaking, a procedure which is usually very rapid even with extracts of leguminous seeds which are otherwise difficult to filter. An aliquot portion of the filtrate is made just alkaline with ammonia, and after remaining all night it is filtered. The precipitate is carefully transferred to the filter, washed with ammoniacal alcohol, and allowed to

dry. It is next dissolved in 0.5% nitric acid, and the phosphorus precipitated with acid molybdate solution.

E. F. A.

**Estimation of Arsenic.** ERWIN RUPP and FRANZ LEHMANN (*Arch. Pharm.*, 1912, 250, 382—389).—Arsenic in organic matter can be rapidly estimated as follows. The substance under examination, 5—20 grams, is intimately mixed with 10 grams of powdered potassium permanganate and 10 c.c. of dilute sulphuric acid in a porcelain dish. The mixture is heated, with frequent shaking, on the water-bath for fifteen minutes. The almost powdery product, while still warm, is slowly treated with 25 c.c. of concentrated sulphuric acid, and soon afterwards, with 30 c.c. of 3% hydrogen peroxide. When the effervescence has ceased, the liquid is washed into a Kjeldahl flask with 30 c.c. of concentrated sulphuric acid, and 10 grams of hydrated ferrous sulphate are added. After cooling the flask and adding 50 grams of sodium chloride, the contents are distilled on a sand-bath. The distillate, which must pass through a Kjeldahl safety-bulb, is collected in 100 c.c. of water and 40 grams of sodium hydrogen carbonate in a large Erlenmeyer flask. The distillation is stopped as soon as the sodium hydrogen carbonate has disappeared, and the contents of the receiver are cooled, basified with sodium hydrogen carbonate, and filtered if necessary, and titrated with  $N/10$ - or  $N/100$ -iodine solution; 0.5 c.c. of  $N/100$ -iodine must be subtracted from the titre.

The organic matter can be destroyed by potassium persulphate and dilute sulphuric acid, but the method is less satisfactory than that described above.

C. S.

**Estimation of Arsenious Acid with Potassium Permanganate in Presence of Hydrochloric Acid.** LUDWIG MOSER and F. PERJATEL (*Monatsh.*, 1912, 33, 751—758).—The estimation of arsenious acid with permanganate in acid solution requires certain precautions. If the oxidising agent is added too rapidly to a fairly concentrated solution of arsenious acid, a yellow or brown coloration is produced, and it is impossible to fix the end point of the reaction. Good results are obtained by the following process:

0.1 to 0.3 Gram of arsenious acid is dissolved in a little concentrated sodium hydroxide containing 1 gram of solid sodium hydroxide, and diluted to 100 or 200 c.c. About 10—15 c.c. of concentrated hydrochloric acid are added, and permanganate run in at the ordinary temperature drop by drop with good stirring. The end point is denoted by a rose coloration, which persists for two to three minutes.

E. F. A.

**Separation of Arsenic from Antimony and Other Metals by means of Methyl Alcohol in a Current of Air.** LUDWIG MOSER and F. PERJATEL (*Monatsh.*, 1912, 33, 797—820).—The solution containing arsenic in concentrated hydrochloric acid solution, to which methyl alcohol has been added, is heated in a boiling-water bath, and a current of dry air passed through. Part of the arsenic volatilises as trichloride, the rest distils as methyl arsenite, and becomes hydrolysed on passing into water placed in the receiver.

When the arsenic is present in the trivalent state, the operation can be carried out directly, but when arsenic acid is present, it must first be reduced by means of a ferrous salt. Under the experimental conditions, methyl alcohol has no reducing action on the quinquivalent arsenic.

The usual process of oxidising arsenious acid with concentrated sulphuric acid and potassium chlorate leads to loss of arsenic, and should be abandoned. The velocity of oxidation is small, and in spite of an excess of chlorine, arsenic trichloride remains unattacked, and volatilises when the solution is heated. Oxidation of arsenic derivatives by chlorine in alkaline solution is complete.

Arsenic acid is only reduced in traces when acted on by concentrated hydrochloric acid.

The chief advantage of the new process is its simplicity, and the avoidance of a stream of hydrogen chloride. The distillation is complete in one and a-half hours.

Examples are quoted to show the separation of arsenious acid from antimony, which is estimated in the residue, the estimation of arsenic in ores, and its separation from other metals.

The arsenic in the distillate is titrated in sodium hydrogen carbonate solution with iodine, the presence of methyl alcohol being without effect.

E. F. A.

**The Technical Analysis of Cement.** G. HENTSCHEL (*Chem. Zeit.*, 1912, 36, 821—822).—Silica may be rapidly and accurately estimated in cement by grinding 1 gram with 20—30 c.c. of 80% acetic acid and heating on the water-bath until decomposed. It is then heated to boiling, 20 c.c. of hot water are added, followed by dilute nitric acid until the red colour due to iron disappears. After again boiling, the solution is decanted from the silica, which is washed on the filter with water containing a little nitric acid, dried, and ignited.

Sulphates are estimated in the filtrate by heating to boiling and precipitating with crystallised barium chloride. After five to ten minutes, hydrochloric acid is added, and the solution is boiled for a further five to ten minutes. The barium sulphate may then be collected after five minutes.

C. H. D.

**Rapid Estimation of the Impurities Contained in Paints Made with Zinc Oxide.** ÉMILE KOHN-ABREST (*Ann. Chim. anal.*, 1912, 17, 249—254).—A technical process for the approximate estimation of lead carbonate, zinc sulphide, barium sulphate, etc., in commercial zinc-white, or the paint made thereof.

In the case of paint, 0.4 gram of the sample is burned after adding a few c.c. of 15% ammonium nitrate, when a white ash is obtained readily; of the dry material, 0.2 gram is taken. The mass is treated in a tube with 12 c.c. of a liquid made by mixing 100 c.c. of ammonia with 100 c.c. of 20% ammonium chloride and 100 c.c. of 20% ammonium carbonate.

The zinc oxide dissolves completely, whereas the impurities are left

undissolved. By comparison with mixtures of known composition, a fair idea may be obtained as to the amount of admixture present (lead carbonate for instance). To make sure, the ammoniacal liquid may be decanted and the precipitate tested rapidly; for instance, if completely soluble in dilute hydrochloric acid, barium sulphate is absent, and lead or zinc should be tested for. The process does not work well for the detection of zinc sulphide in paints. L. DE K.

**Analysis of White Metals Containing Copper, Antimony, Tin, Lead, Iron, and Zinc.** R. KOPENHAGUE (*Ann. Chim. anal.*, 1912, 17, 241—243).—Two grams of the alloy are boiled with nitric acid (800 c.c. diluted to a litre). After evaporating to dryness, the mass is dissolved in 20 c.c. of nitric acid, 25 c.c. of ammonium nitrate (120 grams per litre) are added, and the whole is heated to boiling. When cold, the deposit is collected and washed with a liquid composed of 40 c.c. of nitric acid, 30 c.c. of ammonia, and water up to a litre. The filtrate contains copper, lead, iron, and zinc, whilst the precipitate contains tin and antimony more or less contaminated with copper, lead, and iron. The latter is then rinsed off the filter, a large excess of ammonia is added, and a current of hydrogen sulphide is passed, which causes the tin and antimony to dissolve, leaving behind traces of the other sulphides which are dissolved in nitric acid and a drop of bromine, and after boiling united with the main solution.

The ammoniacal sulphide solution is evaporated to dryness, 100 c.c. of solution of potassium chlorate (50 grams per litre) are added, and then 35 c.c. of hydrochloric acid. After evaporating to dryness, the residue is dissolved in 8 c.c. of hydrochloric acid, 150 c.c. of water, and 25 grams of ammonium oxalate are added. After heating to boiling, the antimony, with a trace of copper, is precipitated by passing a current of hydrogen sulphide for two hours; the tin is not precipitated. After adding a little ammonium sulphate to the almost boiling liquid, the precipitate is collected and washed with a strong solution of oxalic acid to which has been added a little ammonium sulphate and hydrochloric acid. The precipitate is next heated with 20 c.c. of a 15% solution of potassium hydroxide until the sulphides become black; the antimony is then reprecipitated from the filtrate by adding a slight excess of hydrochloric acid, and after redissolving the precipitate in hydrochloric acid and potassium chlorate, the residue obtained on evaporation is dissolved in dilute hydrochloric acid, potassium iodide is added, and the iodine liberated (which represents the antimony) is titrated with thiosulphate.

The tin is recovered from its solution by electrolysis. The lead is separated as usual by evaporation with sulphuric acid. The filtrate is freed from copper by means of hydrogen sulphide, and the zinc and iron, after being separated by means of a double precipitation with ammonia, are found by a volumetric estimation of the iron and precipitation of the zinc as sulphide, which is then heated to oxide. The copper is determined separately. Two grams are dissolved in 30 c.c. of nitric acid (1:1), diluted to 300 c.c., and electrolysed without paying attention to the tin-antimony precipitate. The deposit

obtained must be redissolved in 10 c.c. of sulphuric acid and 20 c.c. of nitric acid, and, after diluting to 300 c.c., electrolysed again.

L. DE K.

**Electrolytic Estimation of Manganese and its Separation from Iron.** HENRI GOLBLUM and [Mlle.] HÉLÈNE GUNTHER (*Compt. rend.*, 1912, 155, 166—168).—Working at 80° with 100 c.c. of solution containing variable quantities of iron and manganese and 10 grams of ammonium oxalate, using a platinum dish as anode and a rotating cathode consisting of a small platinum capsule with holes in it, the authors obtained complete deposition of 0.1 gram of manganese as manganese dioxide, in an adherent form, in one and a-half hours. The deposit contained not more than five parts of iron per 1000. The success of the operation depends on the density of the current and the rate of revolution of the cathode, the best results being obtained with 2 amperes at 3 volts and a rotation of 700 turns per minute. Under these conditions most of the iron remains in solution, and can be deposited by further electrolysis.

W. G.

**The Electrolytic Estimation of Molybdenum.** I. ARTHUR FISCHER and J. WEISE (*Zeitsch. anal. Chem.*, 1912, 51, 537—550).—A critical investigation of the electrolytic estimation of molybdenum.

In order to accelerate the electrolysis, a small quantity of sulphuric acid has hitherto been employed, but the authors have substituted for this hydrochloric acid (about 0.25 c.c. of fuming acid to 120 c.c. of liquid).

The molybdenum sesquioxide deposited may be converted into molybdenum trioxide, without the use of nitric acid, by simply heating for some time at 400° by means of an electric arrangement.

L. DE K.

**The Estimation of Thorium, Especially in Monazite Sand, by means of Sodium Hypophosphate.** ARTHUR ROSENHEIM (*Chem. Zeit.*, 1912, 36, 821. Compare Koss, this vol., ii, 809).—In the analysis of monazite sand, 100 grams are converted into sulphates, dissolved in cold water, and diluted to a litre. After cooling, 100 c.c. of the clear solution are taken, mixed with 50 c.c. of concentrated hydrochloric acid and 180 c.c. of water, heated to boiling, and precipitated by means of a cold saturated solution of sodium hypophosphate. The precipitate is filtered hot, and washed with slightly acid, hot water until free from other earths. The precipitate contains thorium, zirconium, and titanium. In order to separate from these impurities, it is heated with the filter paper with 50 c.c. of concentrated sulphuric acid, gradually adding crystals of potassium nitrate. After removal of most of the acid by evaporation, the residue is boiled with dilute ammonia, and then with hydrochloric acid. Thorium is precipitated from the filtrate as oxalate.

The thorium hypophosphate is converted into pyrophosphate by ignition without the filter, but the weight is always slightly low.

Sodium hypophosphate is conveniently prepared by the anodic

oxidation of phosphides (Rosenheim and Pinsker, Abstr., 1910, ii, 708).  
C. H. D.

**The Testing of Enamels containing Antimony.** RUD. RICKMANN (*Zeitsch. angew. Chem.*, 1912, 25, 1518—1519).—The enamel (cleansed from any adhering iron) is boiled for half an hour with 4% acetic or 2% tartaric acid solution, and the filtrate is divided into halves. One portion is tested for antimony with hydrogen sulphide, and should this be present, the other portion is titrated with standard permanganate. Should, however, no permanganate be consumed, this proves that the metal was present in its higher state of oxidation (sodium metantimoniate), which, according to the author, is harmless.

L. DE K.

**Analysis of Platinum Alloys.** H. ARNOLD (*Zeitsch. anal. Chem.*, 1912, 51, 550—554).—One gram of the alloy is dissolved in *aqua regia*, the solution is evaporated to dryness, and the residue evaporated three times with a little hydrochloric acid. The mass is then dissolved in 10 c.c. of hydrochloric acid, and 1 gram of potassium hydroxide dissolved in a little water is added. After evaporating just to dryness, the mass is treated with 50 c.c. of alcohol, and the potassium platinichloride is washed by decantation with alcohol until this runs off colourless. The compound is then dried, and to it is added the ash of the filter used, when it is gradually heated until the potassium chloride begins to melt. A complete reduction of the compound to platinum and potassium chloride is readily effected by heating in a current of hydrogen. The whole is then heated gently, first with dilute nitric acid and then with dilute ammonia, to dissolve any silver chloride. The residual platinum is then ignited and weighed; it is advisable to evaporate it with a little hydrofluoric acid should it be contaminated with silica. In the alcoholic filtrate the metals (copper, nickel, iron, etc.) are separated by the usual methods. The ether process for separating iron from nickel is recommended.

L. DE K.

**Some Tests for the Determination of the Purity of Turpentine Oils.** RÉNE MARCILLE (*Bull. Soc. chim.*, 1912, [iv], 11, 762—766).—A description of tests for the detection of adulteration in turpentine oils; the tests described are based on (1) the solubility in 98% acetic acid; (2) the thermal effect of mixing with sulphuric acid; (3) the solubility in sulphuric acid.

D. F. T.

**Indirect Estimation of Alcohol in Beer.** WILHELM FRESenius and LEO GRÜNHUT (*Zeitsch. anal. Chem.*, 1912, 51, 554—561).—A new formula is proposed, namely,  $1/\Delta_{e/c}^{(a)} = 1 + 1/D_{e/c} - 1/\Delta_{e/c}^{(e)}$ , in which  $\Delta_{e/c}^{(a)}$  = the (calculated) density of the beer distillate made up with water to the original weight,  $D_{e/c}$  the density of the beer fully deprived of carbon dioxide, and  $\Delta_{e/c}^{(e)}$ , the density of the alcohol-free residue made up to its original weight. Reference is then made to the usual alcohol tables (alcohol by weight).

If the density is required with regard to water at 4°, the formula

becomes :  $1/\Delta_{e/4}^{(a)} = 1/\delta_{e/4} + 1/D_{e/4} - 1/\Delta_{e/4}^e$ , in which  $\delta_{e/4}$  = the density of water at  $t^\circ$  in regard to water at  $4^\circ$ .  
L. DE K.

**A Colour Reaction of Alcohols and Alcoholic Hydroxyl Groups.** LEOPOLD ROSENTHALER (*Chem. Zeit.*, 1912, 36, 830).—A red coloration is obtained when an alcohol is heated in presence of sodium or potassium hydroxides with a mixture consisting of 1 part of a 0.7% sodium nitrite solution and 4 parts of a 0.5 sulphanic acid solution (in dilute hydrochloric acid). The reaction is not very sensitive, but may be obtained with 2.5 mg. of ethyl alcohol or 10 mg. of glycerol. The higher alcohols and certain carbohydrates give the coloration, as do also hydroxy-acids, such as lactic, malic, tartaric, and citric acids. The coloration develops slowly at the ordinary temperature, except in the case of malic acid, this acid giving a reaction almost immediately.  
W. P. S.

**Estimation of Phenol and *p*-Cresol in Mixtures.** HUGO DITZ and FRIEDRICH BARDACH (*Biochem. Zeitsch.*, 1912, 42, 347—356).—Polemical. A reply to Siegfried and Zimmermann (*Abstr.*, 1910, i, 72, 941).  
S. B. S.

**A Modification of Ritter's Method for the Estimation of Cholesterol.** HARRY J. CORPER (*J. Biol. Chem.*, 1912, 12, 197—204).—The error in Ritter's method occasioned by the use of an excess of sodium ethoxide in saponification (compare this vol., ii, 302) can be overcome by neutralising this substance with carbon dioxide. The method is then accurate within milligrams.  
W. D. H.

**Critical Study of Sugar Analysis by Copper Reduction Methods.** AMOS W. PETERS (*J. Amer. Chem. Soc.*, 1912, 34, 928—954).—A study has been made of the various processes for estimating sugar by copper reduction with the object of finding a rapid and accurate method suitable for use in urine analysis. The conditions of the reduction and of the volumetric estimation of copper in alkaline tartrate solutions by the iodide method have been carefully investigated and standardised. All the conditions have been controlled by means of dextrose of known purity, and a series of values has been tabulated which enables the probable limits of error to be estimated. The method thus elaborated has yielded good results.  
E. G.

**Detection of Adulteration by Colloido-chemical Methods.** ERNST MARRIAGE (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 1—5).—It has been found that the form in which lead iodide is precipitated, when a jelly containing potassium iodide is brought into contact with an aqueous solution of lead nitrate, varies according to the nature of the colloidal medium. If the jellies and superposed aqueous solutions are contained in test-tubes, slow diffusion and precipitation occur, and after some days or weeks, differences are shown by different jellies which are directly visible by the naked eye. The conditions of the interaction can, however, be so arranged that, with the aid of a microscope, differences are exhibited after a few hours.

The variation in the character of the precipitated lead salt may in certain cases be utilised for the detection of adulteration in fruit jellies. The possibility of this is demonstrated by a comparison of the results obtained with gelatin, agar, and various fruit jellies, and with jellies containing mixtures of these in different proportions.

H. M. D.

**Detection and Estimation of Volatile Fatty Acids by Steam Distillation in Vacuum.** F. EDELSTEIN and F. VON CSONKA (*Biochem. Zeitsch.*, 1912, 42, 372—392).—The authors give the manipulative details for the method indicated in the title, and examples of the application to various physiological and pathological materials.

S. B. S.

**Estimation of Fat by the Method of Direct Hydrolysis.** S. SZÉKELY (*Biochem. Zeitsch.*, 1912, 42, 412—413).—In view of the fact that the principle of this method of fat estimation was introduced by Liebermann and Székely, the author suggests that it should be designated as the "direct hydrolysis method" rather than the "Kumagawa-Suto method."

S. B. S.

**Detection of Adulteration of Butter.** LUCIEN ROBIN (*Ann. Chim. anal.*, 1912, 17, 254—256).—A slight modification of the author's process for the detection of margarine and cocoanut oil in butter (*Abstr.*, 1907, ii, 239).

It is now recommended that the fatty acids soluble in water should be determined instead of the insoluble acids, and the latter then obtained by difference, by subtracting the first from those soluble in alcohol (56·5° French).

This is carried out by placing 60 c.c. of the filtrate at 15° (which contains besides the acids soluble in water also those soluble in the 56·5° alcohol) in a 120 c.c. flask, and after adding a spoonful of talc, the whole is made up to the mark with water. After thorough shaking, 100 c.c. of the filtrate are titrated with *N*/10-potassium hydroxide and phenolphthalein. The volume of alkaline liquid added  $\times 0.6 =$  water-soluble portion. Multiplied by 4.8 a close approximation to the Reichert number is obtained.

In judging the amount of cocoanut oil, the relation insoluble in water/soluble in water  $\times 10$  must be reduced from 13 to 12.

L. DE K.

**Modifications of the Robin Process for Butter Analysis.** MARION (*Ann. Chim. anal.*, 1912, 17, 256—258).—It is pointed out how essential it is that in Robin's process (see preceding abstract) the temperature should be constant at 15°. Moreover, the strength of the alcohol (56·5° French) must be maintained all through the operation.

Starting from absolute alcohol is very inconvenient, but the author gives instructions how to employ such alcohols as are kept in any laboratory and are of a known strength.

L. DE K.

## General and Physical Chemistry.

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**Refraction and Magnetic Rotation of Mixtures.** FREDERIC SCHWERS (*Compt. rend.*, 1912, 155, 398—400).—In connexion with the results recorded by Muller and Guerdjikoff (this vol., ii, 325) it is pointed out that since magnetic rotation and refractive index are both dependent on co-volume, it is unlikely that one should be a linear function of concentration, whilst the other should show a "break" in the curve at a definite concentration (compare Abstr., 1910, ii, 913, 1039; 1911, ii, 92, 949). Further, the figures found for the refractive indices of (1) aniline, and (2) some of the alcohol-aniline mixtures, do not agree with the fairly concordant figures recorded by previous workers. T. A. H.

**The Refractive Indices of Solutions of the Cadmium Haloids.** FREDERICK H. GETMAN and HELEN T. GILROY (*Amer. Chem. J.*, 1912, 48, 138—145).—The molecular refractivities of aqueous solutions of cadmium chloride, bromide, and iodide, varying in concentration from approximately 1% to 40%, are nearly constant over the entire range of concentrations. Using the values of the atomic refractivities of the halogens given by Baxter (Abstr., 1911, ii, 557), the atomic refractivity of cadmium is calculated to be 5.30, 5.52, and 5.05 in the solutions of the chloride, bromide, and iodide respectively, giving a mean value of 5.29. T. S. P.

**Dispersion of Cinnabar.** HERMANN ROSE (*Centr. Min.*, 1912, 527—531).—The refractive indices of cinnabar have been determined for light of different wave-lengths with a prism cut from a crystal from New Almaden. L. J. S.

**Variation of the Abiotic Power of the Ultra-violet Rays with their Wave-length.** MME. VICTOR HENRI and VICTOR HENRI (*Compt. rend.*, 1912, 155, 315—318).—A study of the abiotic power of ultra-violet rays below  $\lambda = 3000\mu$ . The sources used for the rays were (1) a condensed spark from magnesium; (2) a mercury arc in quartz; (3) a condensed spark from cadmium. Screens were employed to arrest certain portions of the ultra-violet spectrum. A table is given showing the ultra-violet rays from the three sources employed, and the amount of energy transmitted by the following screens: viscose, 0.06 mm.; a glass plate, 0.14 mm.; cellulose acetate, 0.05 mm.; a solution of acetone (5%), 5.0 mm.; and (10%) 5.0 mm., and a glass plate, 0.7 mm. in thickness. The last column in the table gives the coefficient of extinction by egg-white as a type of protoplasm. The results show that the abiotic power of the ultra-violet rays increases continuously as the wave-length diminishes, and that it is proportional to the coefficient of absorption by protoplasm. W. G.

**Ultra-red Emission Spectra.** HANS LEHMANN (*Ann. Physik*, 1912, [iv], 39, 53—79).—The extinction of phosphorescence by ultra-red

rays has been made use of in the investigation of the ultra-red emission spectra of various elements. The phosphorescent plates were covered with a layer of active zinc sulphide, prepared by precipitation of an ammoniacal zinc chloride solution with unpurified hydrogen sulphide and heating the dry precipitate to a moderate white heat, and this was caused to phosphoresce by exposure for one or two minutes to the light from an arc lamp, which had passed through a saturated solution of cupric ammonia sulphate. The plates were then subjected to the action of the ultra-red radiation for a period of two to eight minutes, removed as quickly as possible, and brought into contact with a photographic plate sensitised for the ultra-red portion of the spectrum.

The spectra were produced by means of a carbon arc, the poles of which were impregnated with calcined salts of the various metals investigated, and the optical apparatus, consisting of a prism spectrograph, was suitably adjusted for observations in the ultra-red region. Wave-length data, extending from  $\lambda = 700$  to  $\lambda = 1500\mu\mu$ , are recorded for copper, silver, gold, magnesium, strontium, zinc, cadmium, mercury, aluminium, thallium, lead, antimony, and bismuth. For comparison, the results obtained by Paschen and by Randall by different methods are also recorded in the tables of wave-lengths. H. M. D.

**Magnetic Resolution of Fine Spectral Lines in the Vacuum Arc Light.** CH. WALI-MOHAMMAD (*Ann. Physik*, 1912, [iv], 39, 225—250).—The effect of a magnetic field on various lines in the spectra of zinc, cadmium, thallium, and bismuth has been examined. The data show that the sharp lined satellites are in many cases highly complex in character, the resolving action of the magnetic field giving rise to triplets, quadruplets, quintriplets, sextriplets, and nonets. In general, the separation of the resolved lines increases in proportion to the strength of the applied field. When the lines are sufficiently sharp, the resolution can be measured in very weak fields (about 300 Gauss).

In reference to the cadmium line  $\lambda = 4678$ , it is found that satellites, which cannot be seen in ordinary circumstances, become visible when a magnetic field is applied.

The bismuth line  $\lambda = 4722$  is of very complex character, and two of its satellites are displaced by a magnetic field, the displacement being proportional to the square of the strength of the field.

H. M. D.

**Influence of Density on the Position of the Emission and Absorption Lines in a Gas Spectrum.** G. H. LIVENS (*Phil. Mag.*, 1912, [vi], 24, 268—293).—An interpretation is given of the change of position of the lines in the emission and absorption spectra of a gas with change in its density. The theory, which attributes the effect to a density change in the actual incandescent vapour, is based on the electron theory of optical effects as developed by Lorentz and Drude, and consists mathematically in the introduction into the equations of motion of the single typical electron of a term which expresses the effect due to the polarisation of the surrounding medium.

It is shown that the magnitude of the displacements calculated on the basis of this theory is in agreement with those which have been found experimentally by different observers. It seems probable that the shift of the lines observed by Humphreys in his experiments on the arc spectra of metals in air at pressures ranging from 1 to 100 atmospheres can also be accounted for on the basis of this theory.

H. M. D.

**Changes in Certain Absorption Spectra in Different Solvents.** THOMAS R. MERTON (*Proc. Roy. Soc.*, 1912, *A*, 87, 138—147).—Photometric measurements of the absorption of uranous chloride have been made for a number of different solvents. The results obtained for solutions in water, methyl acetate, formamide, methyl alcohol, and ethyl alcohol show that the differences in the absorption spectra cannot be ascribed to a shift in the position of the bands, for the entire character and the intensity of the absorption vary considerably according to the nature of the solvent.

Whilst the spectra furnished by the above solutions consist of more or less diffuse bands without sharply defined maxima, those given by solvents containing a ketone group show well defined absorption lines in addition to the bands. On addition of hydrochloric acid, the general absorption is diminished, whilst the intensity of the line absorption is increased. Other chlorides exert a similar, although smaller, effect, and the same influence appears to be exerted by hydrochloric acid in other solutions.

From experiments with uranous chloride and sulphate and with uranyl chloride and nitrate, it is found that the absorption is the same whether the solutions are mixed or placed in separate cells. The shift in the absorption maxima which is observed when an acid radicle is partly replaced by another is therefore not due to the formation of intermediate compounds, since it can be readily explained by the superposition of the two absorption curves.

Up to a pressure of 750 atmospheres, no influence of pressure on the absorption spectra of solutions could be detected. H. M. D.

**Ultimate Rays and the Great Sensitiveness of Chromium, Manganese, Iron, Nickel, and Cobalt.** ANTOINE DE GRAMONT (*Compt. rend.*, 1912, 155, 276—278. Compare *Abstr.*, 1907, ii, 517, 788; 1908, ii, 645; 1910, ii, 85, 811).—The author has determined for the above metals the lines which persist in the spectra even when only very small traces of the metal are present. The measurements and order of dilution are given for each of the metals, and note is also made of certain errors which must be avoided or compensated for in making the measurements. By this method it is claimed that it is possible to detect the presence of one ten-thousandth part of any one of the metals, and in some cases even higher orders of dilution can be detected.

W. G.

**Absorption Spectra of Hydrogen Peroxide.** N. ROSANOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1146—1152).—Various authors have observed the presence of hydrogen peroxide in solutions of

radioactive salts, but, in considering the absorption of ultra-violet light by radioactive elements and their degradation products, Zelinsky (this vol., ii, 524) regarded the part played by the hydrogen peroxide formed under the influence of radium as small. The author has investigated the absorption spectra of ultra-violet light by solutions of hydrogen peroxide of various concentrations, and draws the conclusion that it is highly probable that the absorption of short waves by radioactive substances is conditioned by two factors: by the emanation developed, and, to a considerable extent, by the hydrogen peroxide formed under the influence of this emanation. As these two factors exist together, it is difficult to decide which of them plays the larger part in the absorption. The magnitude of the absorption may be taken as a measure of the degree of activity of the substance only when this is used in the solid state.

Usher (this vol., ii, 6) states that hydrogen, oxygen, and ozone are formed in solutions of radioactive salts. The author finds that saturation of water with hydrogen, oxygen, or nitrogen is without effect on its absorption curve. Although it has not been shown experimentally, it is assumed that ozone is also without influence, since unpublished investigations by Zelinsky indicate that alcoholic solutions of acetylene, propylene, and *cyclopropane* have no absorptive influence.

T. H. P.

**Spectrum of Argon.** G. STEAD (*Proc. Camb. Phil. Soc.*, 1912, 16, 607—609).—The conditions under which the red and blue spectra of argon are produced have been examined by experiments with a special form of discharge tube containing a calcium oxide cathode.

If the pressure is greater than about 0.02 mm., a fairly bright positive column is produced, which shows the red without any trace of the blue spectrum. At lower pressures, the positive column ceases to exist. If, however, the cathode beam is deflected by application of a magnetic field, it is possible to obtain a positive column at pressures which are much too low for its production in ordinary circumstances. The positive column produced in this way also gives the pure red spectrum.

The cathode beam is always blue in colour, and with a large difference of potential, the spectrum of this is practically identical with that yielded by the gas discharge through an ordinary vacuum tube, that is, almost pure blue. When the potential difference, and in consequence the temperature, is reduced, the red spectrum begins to appear, and when the beam is very faint, the spectrum presents much the same appearance as the spectrum of the negative glow in an ordinary discharge.

From these experimental results, it would appear to be impossible to obtain the red or the blue spectrum in the same portion of the tube by simply altering the conditions of discharge.

H. M. D.

**Spectra of Silicon and Fluorine in a Geissler Tube.** C. PORLEZZA (*Gazzetta*, 1912, 42, ii, 42—54).—The author has compared the spectra given in a Geissler tube by silicon tetrachloride and tetrafluoride, all the lines corresponding with silicon and fluorine being

carefully measured. New lines have been observed for silicon and, in considerable number, for fluorine. Photographs are given of the different spectra, and the numerical results are given in tables containing also the results of previous investigators. T. H. P.

**Measurements in the Antimony Spectrum.** HEINRICH SCHIPPERS (*Zeitsch. wiss. Photochem.*, 1912, 11, 235—253).—Wave-length measurements of the lines in the arc and spark spectra of antimony are recorded, the data being referred to the international normal lines. The spectral region covered extends from  $\lambda = 6648$  to  $\lambda = 2054$ . As already indicated by Kayser and Runge, constant differences are shown between the frequencies of lines belonging to the different groups. H. M. D.

**Measurements in the Barium Spectrum.** KARL SCHMITZ (*Zeitsch. wiss. Photochem.*, 1912, 11, 209—235).—Accurate wave-length measurements have been made of the lines in the arc and spark spectra of barium, the data being referred to the normal lines recommended by the International Union for Co-operation in Solar Research. The wave-length numbers, which extend from  $\lambda = 2214$  to  $\lambda = 7060$ , are discussed in detail with special reference to the various series formulæ which have been put forward. H. M. D.

**Changes in the Absorption Spectra of "Didymium" Salts.** WALTER C. BALL (*Proc. Roy. Soc.*, 1912, A, 87, 121—137).—A comparison has been made of the absorption spectra of "didymium" under widely varying conditions. From the results it would appear that there are two distinct classes of didymium spectra: (a) the ionic spectrum, and (b) the non-ionised spectrum. The ionic spectrum is given by aqueous solutions of the didymium salts of strong acids, especially at small concentrations. The non-ionised spectrum, being in every case the spectrum of a compound, shows slight variations from one compound to another, but has a definite character. Such spectra are those given by didymium salts of weak acids, those produced by addition of an alkali metal salt of a weak acid to the didymium salt of a strong acid, those given by solutions of didymium salts in non-aqueous solvents, such as ethyl alcohol, glycerol, acetone, and pyridine, and those given by the crystalline or melted nitrate.

In presence of sucrose, it is possible to obtain alkaline solutions of didymium, and the spectrum given by such a solution is quite exceptional, some of the lines being displaced to a very large extent.

The variation occurring in the didymium spectrum on passing from highly concentrated to very dilute aqueous solutions is almost entirely confined to the first stage of the dilution process, although the electric conductivity data indicate that considerable changes in the degree of ionisation occur during the later stages of the dilution process.

H. M. D.

**The Arc Spectrum of Mercury in the Visible and Red Regions.** GEBHARD WIEDMANN (*Ann. Physik*, 1912, [iv], 38, 1041—1055. Compare Paschen, *Abstr.*, 1910, ii, 3).—The wave-

lengths and relative intensities of the lines in the visible and red regions of the arc spectrum of mercury have been measured. The spectrum is analysed with reference to the occurrence of principal and subsidiary series.

H. M. D.

**Dispersion and Absorption of Mercury and Tin for the Visible and Ultra-violet Spectrum.** PETER EROCHIN (*Ann. Physik*, 1912, [iv], 39, 213—224).—The optical constants of mercury and tin have been measured by Voigt's reflexion method. Curves are plotted which show the dependence of the refractive index, the index of absorption, and the absorption coefficient on the wave-length of the incident light. The results are discussed in reference to the electron theory.

H. M. D.

**Measurements in the Spectrum of Molybdenum from  $\lambda = 4647$  to  $\lambda = 7134$ .** CHRISTIAN WEIGAND (*Zeitsch. wiss. Photochem.*, 1912, 11, 261—276).—Accurate measurements of wave-lengths have been made for the lines in both the arc and spark spectra. In the case of the sharpest lines, the wave-lengths of corresponding lines in the two spectra do not differ by more than a few thousandths of an Ångström unit. The values obtained by the author agree in general more closely with those of Exner and Haschek than with those obtained by Eder and Valenta. A considerable number of new lines have been obtained, especially in the green portion of the spectrum.

H. M. D.

**Anomalous Dispersion of Certain Organic Colouring Matters.** W. ROHN (*Ann. Physik*, 1912, [iv], 38, 987—1013).—The determination of the constants of the elliptical polarisation of the strongly absorbed rays has been applied in the investigation of the dispersive and absorptive power of pararosaniline, brilliant-green, rhodamine-6G extra, and sodium fluorescein (uranine). All four substances exhibit anomalous dispersion, and the curves obtained by plotting the refractive index, coefficient of absorption, and index of absorption against the wave-length are found to be of a somewhat complex character. The theoretical discussion of the experimental results is reserved.

H. M. D.

**Fluorescent Properties of Sodium Fluorescein in Solution.** W. ROHN (*Ann. Physik*, 1912, [iv], 38, 1014—1017).—A comparison has been made of the fluorescence spectra of ethyl-alcoholic and aqueous solutions of sodium fluorescein (uranine). For exciting light of wave-length  $\lambda = 5300$ , the spectrum of the 0.001*N*-aqueous solution extends from  $\lambda = 5780$  to  $\lambda = 5160$ , and that of the corresponding alcoholic solution from  $\lambda = 5850$  to  $\lambda = 5190$ . The maxima are at  $\lambda = 5390$  and  $\lambda = 5460$  respectively. The displacement of the spectrum on passing from one solution to the other is in accordance with Kundt's rule, and the deviation from Stokes' rule is appreciably greater in the case of the alcoholic solution.

H. M. D.

**Luminescence Analysis.** OTTOMAR WOLFF (*Chem. Zeit.*, 1912, 36, 1039. Compare this vol., ii, 388).—The fluorescence of impure potassium carbonate previously observed is due to the presence of

potassium sulphide. A fluorescence microscope has now been constructed, by means of which the particles may be investigated. The orange fluorescence of some specimens of mercuric chloride is due to mercurous chloride, and the formation of this compound during the sublimation of the mercuric salt may always be observed. Of other mercury salts, only mercurous bromide has been found to fluoresce.

C. H. D.

**Temperature-coefficients of Phototropic Transformations.** MAURICE PADOA and G. TABELLINI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 188—192).—Photochemical reactions being distinguished by their comparatively slight sensitiveness to rise of temperature, the authors have investigated the temperature relations of the phototropic changes occurring in piperyl-*o*-tolylsazone, in order to ascertain if the change is physical or chemical in nature. Previous experiments have shown that the velocity of decoloration of a phototropic substance gradually diminishes as the process advances, this indicating that phototropic transformations follow the law of mass action and are, therefore, homogeneous reactions.

Measurements of the times occupied by darkened piperyl-*o*-tolylsazone in returning to its original pale yellow colour when placed in a feebly illuminated chamber at 10°, 0°, and -10° show that the velocity of the change is very approximately doubled by a rise of temperature of 10°. Calculation on this basis of the duration of the retrocession at -100° gives a result in agreement with that obtained experimentally.

The mean times in seconds for the reverse change to occur in sunlight were found to be: 39 at 10°, 24 at 0°, 28 at -10°, and 30 at -20°. Measurements of the velocity of coloration at -10° and -90° gave the relative values 1.6 and 1 respectively, the temperature-coefficient being hence 1.06 per 10°.

With benzaldehydephenylhydrazone a rise of temperature of 10° increases the velocity of decolorisation from 1 to 1.7, whilst the velocity of the reverse change is almost independent of the temperature.

The conclusion is drawn that phototropic changes are true chemical reactions.

T. H. P.

**Relations between Phototropy and Constitution.** MAURICE PADOA and L. SANTI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 192—196).—According to Stobbe's observations (*Abstr.*, 1908, ii, 339), the fulgides,  $\begin{matrix} \text{CR}^1\text{R}^2\text{:C}\cdot\text{CO} \\ \text{CR}^3\text{R}^4\text{:C}\cdot\text{CO} \end{matrix} > \text{O}$ , exhibit phototropic properties only when one or two of the four radicles are hydrogen atoms. Of the osazones, those obtained from disubstituted hydrazines correspond with completely substituted fulgides, and the authors have prepared various phenylmethyl- and diphenyl-osazones, none of which is found to be phototropic.

Hydrazones of the type  $\text{NH}_2\cdot\text{N}\cdot\text{CHR}$  exhibit phototropy, but only when the aromatic radicle R is not substituted in the ortho-position, whilst no hydrazone of the form  $\text{NRR}^1\cdot\text{N}\cdot\text{CHR}^2$  is a phototropic

substance (compare Padoa and Santi, Abstr., 1910, i, 779; 1911, i, 693; Padoa and Bovini, this vol., i, 223).

$\beta$ -Benzilphenylmethylosazone,  $C_2Ph_2(:N \cdot NMePh)_2$ , m. p.  $183^\circ$ , is non-phototropic.

$\beta$ -Anisilphenylmethylosazone,  $C_2(C_6H_4 \cdot OMe)_2(:N \cdot NMePh)_2$ , forms dark yellow needles, m. p.  $151-152^\circ$ , and is non-phototropic.

$\beta$ -Piperilphenylmethylosazone,  $C_2(C_6H_3 \cdot O_2 \cdot CH_2)_2(:N \cdot NMePh)_2$ , crystallises in yellow, non-phototropic needles, m. p.  $91-92^\circ$ .

$\beta$ -Benzildiphenylosazone,  $C_2Ph_2(:N \cdot NPh_2)_2$ , forms yellow needles, m. p.  $203^\circ$ .

$\beta$ -Anisildiphenylhydrazone,  $C_2(C_6H_4 \cdot OMe)_2(:N \cdot NPh_2)_2$ , crystallises in yellow needles, m. p.  $135-136^\circ$ .

Unsuccessful attempts were made to prepare  $\beta$ -piperildiphenylosazone.  
T. H. P.

**Kinetics of Photochemical Reactions.** FRITZ WEIGERT (*Zeitsch. Elektrochem.*, 1912, 18, 654-656).—The paper deals mainly with the photochemical decomposition of ozone; the results of the investigation have already been published (this vol., ii, 715). A method is described by which the sensitiveness of the reaction in ultra-violet light can be compared with that in visible light. The sensitiveness, as measured by the amount of decomposition under conditions otherwise comparable, is  $2.3 \times 10^{-8}$  mol. per cal. in ultra-violet light, and  $4.8 \times 10^{-10}$  mol. per cal. in ordinary light in the presence of chlorine as sensitiser  
G. S.

**Photo-electric Effect of Some Compounds.** A. LL. HUGHES (*Phil. Mag.*, 1912, [vi], 24, 380-390. Compare Abstr., 1911, ii, 572; this vol., ii, 5).—The emission of electrons by various solid compounds subjected to the action of ultra-violet light has been investigated. Mercurous and mercuric iodide, mercurous and mercuric chloride, antimony tri-iodide, and bismuth trichloride show well-marked effects after exposure for some time to the ultra-violet rays, but dry zinc chloride and phosphoric oxide appear to be inactive. The action is very small in the case of lead iodide and almost negligible for ferric chloride. Although large and gradually increasing effects are obtained with the above-mentioned halogen salts, the initial photo-electric activity of these substances is either zero or very small, except in the case of antimony tri-iodide. From the observed behaviour, it appears that the salts themselves are not photo-electric for light of the wavelength employed, and that the emission of electrons is due to the primary decomposition of the halogen salt by the light and the subsequent action of the rays on the separated metal. The more stable the salt, the less is the effect produced.

Although zinc chloride and phosphoric oxide are inactive when dry, they show a distinct effect in contact with moist air. This cannot be accounted for by the photo-electric activity of water.

Experiments with anthracene show that the photo-electric activity of this substance is produced entirely by light of wave-length shorter than  $\lambda = 2002$ . The maximum emission velocity for  $\lambda = 1849$  is 0.87 volt.  
H. M. D.

**Photochemical Reactions in Aqueous Solutions.** ALFRED BENRATH (*J. pr. Chem.*, 1912, [ii], 86, 336—344. Compare Abstr., 1905, i, 730; 1911, ii, 535).—When dissolved in an aqueous solution of ferric chloride and exposed to sunlight during the summer, formaldehyde is oxidised to glyoxal. The formation of the latter compound is preceded by the polymerisation of formaldehyde to glycollaldehyde (compare Pribram and Franke, Abstr., 1911, i, 420).

*tert.*-Amyl alcohol is oxidised under similar conditions to acetone and acetaldehyde, whilst fatty acids either remain unattacked or are oxidised very slowly. Succinic acid yields carbon dioxide, propionic acid, and ethyl chloride, which is partly hydrolysed to alcohol and then undergoes oxidation to acetaldehyde.

Methylsuccinic acid loses carbon dioxide, yielding butyric acid, and is also oxidised to carbon dioxide and propyl chloride:  $C_2H_3Me(CO_2H)_2 + 2FeCl_3 = 2CO_2 + 2FeCl_2 + C_3H_7Cl + HCl$ . Part of the propyl chloride is hydrolysed to propyl alcohol, which is then oxidised to propaldehyde.

On exposure to light in a 2*N*-solution of nitric acid containing ferric nitrate, organic acids are oxidised to aldehydes and ketones, which undergo further oxidation with the formation of acids. It is probable that ketonic acids are formed as intermediate products, and that aldehydes and ketones are produced from these by loss of carbon dioxide; thus citric acid yields acetone, acetic acid, formaldehyde, and hydrocyanic acid. Malonic acid is oxidised to formaldehyde, malic acid to glyoxal, tartaric acid to oxalic acid, and succinic acid to formaldehyde and hydrocyanic and oxalic acids.

When oxidised with ferric nitrate in nitric acid solution, ethyl alcohol yields acetaldehyde, formaldehyde, acetic acid, and glyoxal, together with glyoxylic and acethydroxamic acids. Acetone is oxidised to acetic acid, formaldehyde, and hydrocyanic acid.

In all the above-mentioned oxidations with ferric nitrate, carbon dioxide is evolved, which is accompanied by nitrous oxide, produced by reduction of the nitric acid. In some cases the nitric acid is reduced to nitrogen or even ammonia; thus, both formic and oxalic acids yield carbon dioxide, the nitric acid being reduced to nitrogen and ammonia. Mandelic acid gives rise to nitrogen, carbon dioxide, and benzaldehyde; aminoacetic acid yields the same two gases, together with formaldehyde and glyoxylic acid.

Similar results have also been obtained by the use of potassium dichromate in place of nitric acid and ferric nitrate. A dilute solution of acetic acid and potassium dichromate, on exposure to light, yields carbon dioxide, formaldehyde, and glyoxal. F. B.

**Action of Sunlight and of Radium Compounds on Glass.** W. A. DOUGLAS RUDGE (*Proc. Camb. Phil. Soc.*, 1912, 16, 571—573).—Observations relating to the coloration of glass-tubing under the influence of sunlight are recorded. The action of radio-active material is very similar to that of sunlight, but the coloration ultimately attained is much more intense. The production of an amethyst colour is supposed to be due to the presence of manganese in the glass.

H. M. D.

**Quantitative Investigation of the Absorption of Ultra-violet Rays by Aliphatic Alcohols, Acids, Esters, Aldehydes, and Ketones.** JEAN BIELECKI and VICTOR HENRI (*Compt. rend.*, 1912, 155, 456—458\*).—The absorption was measured photometrically, and the results calculated from the formula  $I = I' \cdot 10^{\epsilon \cdot c \cdot d}$ , where  $\epsilon$  is the molecular coefficient of extinction,  $c$  the concentration in gram-molecules per litre, and  $d$  the thickness (in cms.) of the layer of solution. The values of  $\epsilon$  for various wave-lengths for the several classes of substances mentioned are quoted.

The alcohols show a continuous and increasing absorption from  $\lambda = 3000$  to  $\lambda = 2144$ , which augments rapidly with the number of  $\cdot\text{CH}_2\cdot$  groups in the molecule. The monobasic acids show an absorption about 2000 times as great as that due to methyl alcohol. Oxalic acid produces an absorption 30,000 times as great as that of methyl alcohol, but when the two  $\cdot\text{CO}_2\text{H}$  groups are separated by one or more  $\cdot\text{CH}_2\cdot$  groups, the absorption is about fifteen times as great as that of the monobasic acids. Esters show less absorption than the acids from which they are derived. The absorption due to formaldehyde is about twelve times that shown by methyl alcohol, but the three next homologues show a definite absorption band near  $\lambda = 2800$ , beyond which the absorption falls to a minimum at  $\lambda = 2350$  to  $2470$ , and then increases again strongly. The ketones have an absorption band at  $\lambda = 2680$ , after which the absorption diminishes steadily for the shorter wave-lengths.

In general, the absorption augments with increasing molecular complexity.

T. A. H.

**Photochemical Action of Resins.** FERDINANDO VIGNOLO-LUTATI (*Atti R. Accad. Sci. Torino*, 1912, 47, 841—854).—From the results of a series of preliminary investigations, the author draws the conclusion that the photochemical action of resins is both chemical and physico-chemical in character. Either the formation of ozone or peroxide during the auto-oxidation of resins, or some other modification in their chemical equilibrium, is apparently accompanied by the emission of rays of very short wave-length, to which the photochemical effects are due.

T. H. P.

**Solubility of Coloured Resinates Submitted to the Action of Light.** J. LARGUIER DES BANCELS (*Compt. rend.*, 1912, 155, 280—282).—Coloured resinates are prepared by treating resin with aqueous solutions of alkali hydroxides, adding a suitable colouring matter (safranine, rhodamine, etc.), and then precipitating with a salt of zinc or magnesium. These substances when dissolved in terebene, spread in a thin layer on glass plates, dried, and exposed to the light of the sun or of a mercury vapour lamp, became, at the end of a certain time, insoluble in such solvents as benzene, but soluble in solvents such as methyl or ethyl alcohol. This effect on the solubility is produced essentially by radiations of short wave-length. It depends also on the drying, since, if this is pushed too far, the resinates dissolve in alcohol whether submitted to light or not.

W. G.

\* and *Ber.*, 1912, 45, 2819—2825.

**The Law of Photochemical Absorption for the Reaction Products by Means of Ultra-violet Rays.** VICTOR HENRI and RENÉ WURMSER (*Compt. rend.*, 1912, 155, 503—505).—The authors have studied the variation in photochemical action with the wave-length for ultra-violet rays. They worked with an aqueous solution of acetone, submitted to rays of wave-length  $\lambda = 2981 - 2144$ , measuring the rate of acid formation. Their results show that there is a striking similarity between the absorption curve of acetone in the ultra-violet portion of the spectrum and the chemical activity of the different rays. The law of photochemical absorption applies to the action of ultra-violet rays on acetone in aqueous solution, and the reaction is an example where the extreme ultra-violet rays are less active than those of greater wave-length. W. G.

**The Absence of Penetrating Radiations during Chemical Reactions.** MAURICE DE BROGLIE and L. BRIZARD (*Le Radium*, 1912, 9, 249).—About a litre of detonating mixture retained in soap-suds on a plate of aluminium 1 mm. thick was exploded. The plate formed one side of a completely-closed and mechanically-strong condenser. Ionisation in the condenser, by penetrating rays capable of penetrating the aluminium plate, was looked for by means of an electrometer connected to the condenser. In these experiments, and also when a strong charge of fulminate of mercury was exploded, the results were entirely negative. F. S.

**Emission Velocities of Photo-Electrons.** A. LL. HUGHES (*Phil. Trans.*, 1912, A, 212, 205—226).—Measurements have been made of the maximum velocity with which photo-electrons are emitted from the surface of various metals subjected to the action of monochromatic ultra-violet light. The surfaces were prepared by distillation of the metals in a liquid-air vacuum. The data obtained for calcium, magnesium, cadmium, zinc, lead, antimony, bismuth, and arsenic show that the energy of the fastest electrons is proportional to the frequency of the incident light. If  $V$  represents the velocity measured in volts, then the variation of  $V$  with the frequency  $n$  can be satisfactorily represented by the equation  $V = kn - V_0$ .  $V_0$  is identified with the energy required to separate an electron from the molecule.

In the case of related elements of the same valency, the values of  $k$  and  $V_0$  increase in a regular manner as the atomic volume decreases.

By an indirect method, values of  $V_0$  have also been obtained for selenium and oxygen, and it is further shown that the maximum emission velocity of the photo-electrons from a continually forming mercury surface is identical with the velocity of the electrons from a surface prepared by distillation in a vacuum. H. M. D.

**The Ionisation Produced by the Collision of Positive Ions in Gaseous Mixtures.** RICHARD D. KLEEMAN (*Proc. Camb. Phil. Soc.*, 1912, 16, 621—630. Compare this vol., ii, 8).—A new method is described by means of which the ionisation produced by the collision

of ions with neutral molecules has been examined. The form of the apparatus is such as to facilitate the investigation of the question whether the addition of a small quantity of a foreign gas to the gas already present in the ionisation chamber introduces a new simple ion. Ionisation curves have accordingly been obtained for both positive and negative ions for various simple gases and gaseous mixtures.

The ionisation curves, which are obtained by plotting the current against the applied potential difference, consist roughly of horizontal and vertical lines, the commencement of the vertical line indicating at what point the ionisation by collision begins to have an effect. In the case of the ionisation produced by the collision of negative ions, the effect of the addition of a small quantity of a foreign gas is in all cases to displace the vertical part of the curve away from the zero, this being due to a decrease in the mean free path of the simple ion. The same result is obtained for the positive ions if the molecules of the foreign gas consist of atoms, each of which has approximately the same weight as the atoms contained in the molecules of the gas already present in the chamber. If, however, hydrogen is added in small quantity to oxygen, nitrogen, carbon dioxide, or nitrous oxide, the vertical part of the curve is shifted towards the zero, and at the same time the curve usually becomes more steep. The same result is obtained if the molecules of the added gas contain hydrogen atoms.

From these results it would appear that the mass of the simple positive ion is not independent of the nature of the gas in which it is generated, but that the ion is characteristic of the atomic constituents of the gas molecules.

H. M. D.

**Ionisation by Collision in Gases and Vapours.** W. R. BARSS (*Amer. J. Sci.*, 1912, [iv], 34, 229—241).—The ionisation due to collision between ions and molecules has been examined, the  $\alpha$ -rays emitted by uranium oxide being employed as the ionising agent. From the results obtained in air and hydrogen, it follows that the negative ions generated by collision with  $\alpha$ -particles are identical with those produced by the action of Röntgen rays and ultra-violet light, for the collision constants are the same in all three cases.

Experiments made with sulphur dioxide, ethyl alcohol, ethyl chloride, ethyl ether, and methyl iodide show that the phenomenon is the same in vapours as in gases, provided the pressure is not too great. At higher pressures, a difference in behaviour is observed, this being shown by the crossing of the ionisation curves obtained for different distances of separation of the electrodes. It is suggested that this may be due to the formation of molecular aggregates in the vapours.

Until the sparking potential is approached, the negative ion only is effective in producing new ions by collision both in vapours and in gases.

H. M. D.

**Mobility of Radioactive Atom-Ions in Gases.** S. RATNER (*Compt. rend.*, 1912, 155, 453—455).—The mobility in air of recoil-atoms of radium-*B* from radium-*A* has been determined by two methods, including that of Franck (*Abstr.*, 1909, ii, 953), and the values

found were 1.28 and 1.35. For hydrogen the value was 5.65. In air for pressures up to 10 cm. the mobility is inversely proportional to the pressure.

T. A. H.

**A Comparison of the Ionisation Within Closed Vessels Due to Röntgen and  $\gamma$ -Rays.** ARTHUR S. EVE (*Phil. Mag.*, 1912, [vi], 24, 432—436).—When the ionisation, in similar closed cylindrical vessels with walls 0.5 mm. thick made of different materials, produced by  $X$ -rays and the  $\gamma$ -rays of radium-*C* are compared, the  $X$ -ray ionisation diminishes as the density of the material is reduced from that of lead to that of cardboard, whereas the  $X$ -ray ionisation increases. This is shown to support Bragg's view that  $X$ -rays ionise mainly or wholly by generating electrons in the air and walls of the vessel with velocities of the same order as cathode-rays, whereas the  $\gamma$ -rays ionise by virtue of  $\beta$ -rays with velocities of the same order as those of radium-*C* generated mainly at the inside walls of the vessels. Experiments with 0.5 mm. thick iron and zinc electroscopes indicated that with  $X$ -rays the ionisation is only about 15%, but with  $\gamma$ -rays it is 140% of that in the free air.

F. S.

**Positive Rays.** SIR JOSEPH J. THOMSON (*Phil. Mag.*, 1912, [vi], 24, 209—254. Compare Abstr., 1911, ii, 457).—Further results are given by the method of simultaneously deviating the positive rays, passing through a fine hole in the cathode, by a magnetic and electric field and recording the deviation on a photographic plate sealed inside the discharge tube. From the lines traced by the rays, the value of the ratio  $m/e$  of the ray can be deduced, that of the hydrogen atom being reckoned as unity. Much experience is necessary to distinguish the "primary lines" from the "secondary lines," and it is only the former which can be used in the analysis of the gases carrying the discharge. These enter the electric and magnetic fields charged, and retain their charge unaltered in their passage through the fields, whereas the secondary lines are due to atoms or molecules which experience a change in the number of charges carried while in the fields. Both positively and negatively charged particles occur with hydrogen, carbon, oxygen, sulphur, and chlorine, but with helium, argon, nitrogen, and mercury no negatively charged particles have been observed. In very pure oxygen, dried by liquid air, the only negative line is due to atomic oxygen, but in presence of 1 to 3 volume % of hydrogen, a negatively charged particle with a value 33 for  $m/e$ , appears which may be due to  $O_2$ , but is more probably due to  $HO_2$  or  $H_2O_2$ . In these circumstances the other line is probably due to OH and not to O. The line 33 disappears if the proportion of hydrogen is increased, but in mixtures of ethylene and oxygen it is seen when only a small quantity of oxygen is present. In vapours of hydrocarbons containing one atom of carbon in the molecule, the line 12 is the only negative line, but in ethylene and acetylene another of value 24, and in benzene of 36 also, are observed. One of the most striking results is the extent to which the gas molecules are dissociated by the discharge, and all photographs show positive lines indicating atoms as well as molecules. In benzene there are 17 different types of positive

carrier, and the results for methyl and ethyl alcohol, ethyl and methyl ethers are all identical.

The relative brightness of the lines is misleading as to the number of carriers producing them, the lighter and more quickly moving atoms of hydrogen and helium producing enormously greater effect on the photographic plate than the slower and heavier, but equally energetic, carriers. This followed from experiments in which the relative number of each type of carrier having a different value of  $m/e$  was determined by allowing them to fall separately into a Faraday cylinder and determining the charge transported, a method which is capable of results of great accuracy. With photographic and fluorescent screen methods the brightest lines are always due to hydrogen atoms and molecules, but Faraday cylinder measurements showed that often their numbers were but a fraction of one per cent. of the heavier carriers, such as oxygen, carbon monoxide, and carbon dioxide.

Atoms with double charges have been observed in all cases except hydrogen. Several lines, obeying the tests for primaries so far as can be seen, do not correspond with any known substance, for example, one in a mixture of hydrogen and helium corresponding with the value 6. In hydrogen one of value 3 corresponding with  $H_3$  is seen under certain conditions, but not in absence of oxygen or air. In nitrogen at not too low pressure, there is a line 43 which is probably  $N_3$ . In addition, lines corresponding with the single atom with 1, 2, and even 3 positive charges, and to the molecule  $N_2$  with single positive charge have been observed, but never negative lines. In mixtures of hydrogen and oxygen a line of value about 50 may be due to ozone, but is not observed in absence of hydrogen, and is probably  $H_2O_3$ . In addition to water, 18, a line of value 20, corresponding with  $H_4O$ , is observed. In carbon disulphide a line 44, which may be  $CS$ , and in mixtures of hydrogen and nitrogen the ammonia line, are seen.

By the Faraday cylinder method the true ratios of the numbers of the various carriers in the discharge through carbon monoxide, hydrogen and oxygen, carbonyl chloride, and carbon dioxide have been determined, which reveal the enormous discrepancy between the sensitiveness of the photographic plate and of fluorescent screens to the light and heavy carriers respectively.

The true nature of ionisation is discussed from the point of view of the photographs obtained. The evidence is held to be contrary to the view that the atoms in the molecule are oppositely charged. Each atom appears to act as a neutral doublet, in which the disposition of the positive and negative charges in the atom condition its attraction of the adjacent atoms.

F. S.

**The Secondary Rays Excited by the  $\alpha$ -Rays of Polonium. II.** V. E. POUND (*Phil. Mag.*, 1912, [vi], 24, 401—414. Compare this vol., ii, 514).—The secondary rays excited by the  $\alpha$ -rays of polonium from carbon surfaces increase as the temperature of the carbon is reduced to that of liquid air, in atmospheres of air, oxygen, and hydrogen, which is attributed to the increase in the amount of gas condensed on the surface of the carbon. In the case of brass surfaces the secondary radiation is about 25% higher at room tempera-

ture than it is in liquid air. This is ascribed to the gas condensed on brass being partly liberated as it is cooled, and the explanation is supported by the fact observed, that it is easier to exhaust a brass vessel at the ordinary temperature than at liquid-air temperature, gas being generated in the latter case. F. S.

**The  $\beta$ -Particles Reflected by Sheets of Matter of Different Thicknesses.** W. WILSON (*Proc. Roy. Soc.*, 1912, A, 87, 100—108).—A strong preparation of uranium-*X* was placed by the side of an electroscope, the direct rays being stopped by a block of lead, and reflectors were brought into a position to reflect the  $\beta$ -rays into the electroscope, the absorption coefficient,  $\mu$ , of the reflected radiation being determined in aluminium. The proportion of the radiation reflected from a thick plate was greatest for lead and least for aluminium, and the absorption coefficient of the reflected rays was greatest for aluminium and least for lead. Two types of reflected rays were produced from the group of hard  $\beta$ -rays of uranium-*X*, the value of  $\mu$  for the softer being about 300 ( $\text{cm.}^{-1}$ ), and for the harder from 20 to 44 for the various metal reflectors of varying thickness. The results agreed well with Schmidt's theory. From thick sheets the values for  $\mu$  for aluminium, copper, and lead were respectively 33.7, 26.6, and 20.2 ( $\text{cm.}^{-1}$ ) for the harder type of reflected rays. F. S.

**The Absorption of Radioactive Projections (Recoil Products) and the Ionisation Produced by Them.** LOUIS WERTENSTEIN (*Compt. rend.*, 1912, 155, 450—453).—The results of an investigation of the absorption by air and hydrogen at pressures of 1 mm. and 6 mm. respectively of the radiation constituted by radioactive projections of radium-*B* from radium-*A* are given.

The method consists in directing a narrow column of projected atoms of radium-*B* from a disk covered with radium-*A* by means of a diaphragm on reception disks maintained at a positive potential and placed at various distances from the active disk.

The results show that for the pressures mentioned the absorptive powers of the two gases are practically identical. The diminution in number of particles in both cases is small up to distances of 5 cm., but beyond that the number diminishes rapidly until at 10 cm. it is only a few hundredths of the initial value, after which it falls slowly and then appears to be due to diffusion of uncharged or negatively charged atoms. For the two gases at the pressures mentioned the range is about 10.5 cm.

Using the method already described (this vol., ii, 222), it was found that in an ionisation chamber 4 mm. deep, placed 25 mm. from the active disk, the recoil atoms of radium-*B* produced in air at 1 mm. pressure 3.7 times as many ions as  $\alpha$ -rays; at 45 mm. distance the ionisation fell in the ratio 1.6 : 1, whilst in hydrogen at 6 mm. pressure for the same change in distance it fell in the ratio 3 : 1. T. A. H.

**An Ionising Radiation Due to Radioactive Recoil, Emitted by Polonium.** B. BIANU and LOUIS WERTENSTEIN (*Compt. rend.*, 1912, 155, 475—477).—An extension of the mode of investigation described

already (this vol., ii, 222) to polonium, shows that the latter emits an easily absorbable ionising radiation, similar to that afforded by radium-*C*.

Some difficulty was experienced in obtaining a layer of polonium sufficiently thin to permit recoil to take place (compare Abstr., 1910, ii, 816), but eventually a satisfactory surface was prepared. The ionisation produced was only proportional to the pressure when the latter was nearly high enough to cut off the radiation. The product of the minimum pressure, *p*, necessary to effect this at various distances, *d*, was about 70 as compared with 120 for radium under like conditions. The ratio of these two numbers is very near that between the ranges of  $\alpha$ -rays of polonium and radium. At a pressure of 2 mm. and a distance of 6.5 mm., the ionising power of the radiation was 2.5 times that of polonium  $\alpha$ -rays, and was completely stopped by aluminium leaf  $0.5\mu$  thick. The magnetic field suppresses a part of the radiation at low pressures, indicating the existence of a second radiation, easily deviable in a magnetic field, and having the characters of a secondary radiation excited by  $\alpha$ -rays. At pressures below 1 mm., negative secondary rays are produced, which tend to predominate when the pressure is still further reduced.

T. A. H.

**The Electrical Charges Carried by the  $\alpha$ - and  $\beta$ -Rays.** JEAN DANYSZ and WILLIAM DUANE (*Compt. rend.*, 1912, 155, 500—503. Compare Rutherford, Abstr., 1905, ii, 621).—The authors have determined the electrical charges carried by the  $\alpha$ - and  $\beta$ -rays from 1 curie of emanation in equilibrium with radium-*A*, -*B*, and -*C*. The radioactive source employed was a bubble of emanation about 0.5 cu. mm. in volume, repelled by a thin glass sphere coated with mercury. They limited the measurement to a pencil of rays (a known fraction of all the rays emitted) by means of screens, pierced with circular openings. The charge was received on a Faraday cylinder, and measured by a quartz piezo-electric. The source of the rays and the Faraday cylinder was enclosed in a metallic box, in which a good vacuum was maintained, which was placed between the poles of an electro-magnet. The charges received by the cylinder were found not to be modified by interposition of leaves of aluminium 0.004 mm. in thickness. From their results the authors find that the electrical charge carried by the  $\alpha$ -rays from 1 curie of emanation is 90.8 electrostatic units, from which they deduce (1) the value 0.595 cu. mm. at  $15^\circ$  for the volume of 1 curie of emanation (compare Rutherford, Abstr., 1908, ii, 791); (2) that the volume of helium given off by 1 gram of radium in equilibrium with its emanation and radium-*A*, -*B*, and -*C* is 156 cu. mm. per year. Admitting that the charge on a  $\beta$ -particle is half that on an  $\alpha$ -particle, the number of  $\beta$ -particles produced by the emanation under the stated conditions is 3 to 4 for every 3  $\alpha$ -particles.  $\beta$ -Rays do not produce, to any appreciable extent, slow secondary rays of the nature of  $\delta$ -rays.

W. G.

**The Determination of the Ionisation Curve for the  $\alpha$ -Rays from Polonium in Mercury Vapour.** T. SMITH TAYLOR (*Phil. Mag.*, 1912, [vi], 24, 296—301).—By means of a special apparatus the Bragg

ionisation-range curve of the  $\alpha$ -rays of polonium was determined in mercury vapour at 330° and 451 mm. The curve was found to be of the general type found for other gases and vapours, departing somewhat more from the theoretical form (that the ionisation is inversely proportional to the cube-root of the range still to be traversed) than in other cases. From the curves in mercury vapour and in air at the same temperature, the pressure in the latter case being adjusted to make the ranges the same, it was deduced that the energy required to produce an ion in mercury vapour is 0.72 times that required in air. F. S.

**The Diffusion of Actinium Emanation and the Active Deposit Produced by it.** JOHN C. McLENNAN (*Phil. Mag.*, 1912, [vi], 24, 370—379).—The experiments of Kennedy (*Abstr.*, 1909, ii, 955) are discussed theoretically, and further experiments are suggested.

F. S.

**Determination of the Quantity of Emanation in Spring Waters.** G. BERNDT (*Ann. Physik*, 1912, [iv], 38, 958—985).—The corrections which must be applied to the results obtained by the various methods used in the estimation of the emanation content of spring waters are discussed, and formulæ are deduced which enable the magnitude of the correction to be calculated for each of the different methods of estimation.

H. M. D.

**Radioactivity of the Thermal Mineral Waters of Usson (Ariège).** GUSTAVE MASSOL (*Compt. rend.*, 1912, 155, 373—375).—The waters of Usson are divided into three groups of springs: des Plaïes, Condamy, and Soumain. The author has measured the radioactivity of the gases dissolved in the waters of the two first and of the waters themselves, and also of the gas spontaneously liberated at des Plaïes. The two sources have practically the same radioactivity. The gases dissolved or spontaneously liberated consist almost entirely of nitrogen and the rare gases, with a trace of hydrogen sulphide and carbon dioxide, and their radioactivity is due to radium emanation.

W. G.

**Influence of Pressure and Temperature on the Electrolytic Conductivity of Solutions.** FRIEDRICH KÖRBER (*Zeitsch. physikal. Chem.*, 1912, 80, 478—480. Compare *Abstr.*, 1911, ii, 863).—Polemical against Lussana (*Abstr.*, 1911, ii, 462).

G. S.

**Conductivity of *pseudo*-Acids and of the True Acids in Mixtures of Acetone and Water.** C. H. SLUITER (*Chem. Weekblad*, 1912, 9, 668—673).—An investigation of the electric conductivity of mono- and di-nitroso-orninol, monochloroacetic acid, and succinic acid at 25° has yielded the following results: (1) addition of acetone to aqueous solutions of the true acids produces a greater fall in the electrical conductivity than that resulting from a similar addition to the corresponding solution of the *pseudo*-acids; (2) the form of the *pseudo*-acid chiefly present in aqueous solution has a lower ionisation constant than the form present in acetone solution; (3) the influence

exerted by acetone on the isomerisation of a *pseudo*-acid is similar to that exerted by alcohol. A. J. W.

**Behaviour of Ionised Liquid Dielectrics on the Passage of Electric Currents.** H. J. VAN DER BIJL (*Ann. Physik*, 1912, [iv], 39, 170—212).—The rate of recombination of the ions produced by the action of the  $\gamma$ -rays of radium on liquid insulators has been determined by a method in which the disturbing effects of ionic diffusion are more or less completely eliminated. The results obtained in experiments with carefully purified hexane, carbon tetrachloride, and carbon disulphide show that recombination takes place in accordance with Thomson's formula,  $dn/dt = -an^2$ , in which  $n$  is the number of positive or negative ions per c.c., and  $a$  the coefficient of recombination. The deviations from this formula, which are exhibited by Jaffé's results (compare Abstr., 1909, ii, 208), are probably due to the special character of the experimental method employed.

By means of an indirect method (compare Jaffé, Abstr., 1910, ii, 481) involving the determination of the conductivity for small potential differences and of the saturation current, the values of the recombination coefficient furnished by the direct method have been confirmed. The values of  $a$  obtained by the direct method are 2.19, 0.78, and 1.90, and by the indirect method, 2.26, 0.802, and 1.74 for hexane, carbon tetrachloride, and carbon disulphide respectively.

The direct method for the determination of the ionic recombination coefficient can also be utilised for the measurement of the diffusion coefficients of the positive and negative ions, and these values, as well as the thermal velocities, the mean free paths, the masses, and the radii of the ions, have been calculated for each of the three liquid insulators. It is further shown that the electric charge on the ions generated by  $\gamma$ -rays in hexane is equal to the charge of the ordinary type of univalent ion. H. M. D.

**The Electrical Properties of Copper-Zinc Alloys.** LUIGI NORSI (*Compt. rend.*, 1912, 155, 348—351).—A determination of the electrical conductivity, the thermal coefficient, the thermoelectric power, and its variation with temperature of alloys of copper and zinc containing from 0 to 100% by volume of zinc. A table of results is given and the curves are plotted, showing maxima corresponding with the formulæ  $\text{CuZn}$ ,  $\text{CuZn}_2$ , and  $\text{CuZn}_3$ . W. G.

**Effect of Tempering on the Electrical Resistance of Bronze and Brass.** A. PORTEVIN (*Compt. rend.*, 1912, 155, 459—460).—It has been suggested that the increase in electrical resistance shown both by steels and by aluminium-bronzes after tempering is due to the partial maintenance in solid solution of the constituents of the eutectoid. This explanation finds support in the results now recorded, which show that tempering effected at temperatures above those at which eutectoids are formed increases the electrical resistance of bronze and brass. T. A. H.

**Electrical Conductivity of Alloys in Relation to the Electron Theory.** N. I. STÉPANOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 910—1000).—The first part of this paper contains an account of

previous work on the constitution of alloys by the author and other investigators.

In the second part, methods of preparing alloys applicable to brittle and readily oxidisable metals and of measuring their conductivities are described. These methods have been employed in the investigation of alloys of magnesium and lead, magnesium and tin, magnesium and copper, magnesium and zinc, and magnesium and bismuth. The results of the measurements of electrical conductivity are in agreement with those given by other methods. The conductivity method proves especially sensitive as regards solid solutions, which were detected in four of the five above cases, although they were not indicated by other metallographic methods. The formation of a definite compound or of a solid solution of the metals is accompanied by a considerable fall in the conductivity. The temperature-coefficients of the conductivities of definite intermetallic compounds are of approximately the same magnitudes as those of pure metals, but with solid solutions they are decidedly less.

In the third part the author discusses the various theories of the electrical conductivity of alloys and of the nature of solid metallic solutions, and advances a view in explanation of the different temperature-coefficients shown by the conductivities of definite compounds and those of solid solutions.

T. H. P.

**The Disruptive Charge Through Pure Sodium Vapour.** LOUIS DUNOYER (*Compt. rend.*, 1912, 155, 270—273).—The author has studied the discharge between two stout nickel electrodes in a vapour of pure sodium, in a tube heated to various temperatures. The potential difference was gradually increased until the tube became luminous. Working at 350°, it was found that the discharge could take two distinct forms, and that by further increasing the tension by a few volts after luminosity had commenced, it became very brilliant and the current traversing the vapour rose considerably in quantity, the electrodes becoming red hot. By plotting the curve showing the relationship between the disruptive tension and the temperature of the saturating vapour, a Paschen's curve is obtained, which shows a minimum at about 250°. The minimum tension at this temperature is 335 volts. The value of the expression  $ap$  (where  $a$  is the distance between the electrodes and  $p$  the pressure) is very low indeed, being only 0.04, as against 0.55 for air and 1.55 for hydrogen. This the author explains by the theory of ionisation by shocks.

W. G.

**The Polarisation of Electrodes.** ANDRÉ BROCHET (*Compt. rend.*, 1912, 155, 340—343).—A theoretical paper in which the author discusses the distribution of the equipotential lines in a coulombmeter with a plate of copper placed between the electrodes either parallel or perpendicular to them.

W. G.

**Periodic Phenomena at Electrodes which can be made Passive.** ALFRED ADLER (*Zeitsch. physikal. Chem.*, 1912, 80, 385—411. Compare Grave, *Abstr.*, 1911, ii, 896; Ostwald, *Abstr.*, 1900, ii, 730; 1901, ii, 24).—The periodic evolution of gas which

occurs when certain metals are treated with acid has been investigated, more particularly in the case of iron. In most cases the metal was brought into the periodic condition by electrolytic polarisation.

Impurities in the iron have no influence on the periodic phenomena. With increase of temperature the oscillations become more rapid, and at still higher temperatures iron becomes permanently active. When the periodic condition, in the case of iron, is brought about at a definite potential, the duration of the periods is proportional to the amount of oxygen liberated, in other words, to the current density. When iron has become passive, it can be restored to the periodic condition by treatment with hydrogen at a suitable potential. Charging with oxygen destroys the oscillating condition. The periodic condition is produced only at certain definite potentials, which lie between those at which iron remains active and at which it goes immediately into the passive condition.

Pure chromium, copper, and nickel do not show periodic phenomena, but alloys of these metals with iron show the effect, which is therefore due to the presence of iron.

In explanation of this phenomenon the author adopts Grave's theory (*loc. cit.*), that pure iron is inactive and is rendered active by acids. The cause of the oscillations is to be found in local currents formed between active and passive portions of the iron electrode, whereby the passive iron is rendered active by the liberated hydrogen ions.

G. S.

**Internal (Total) and Free Energy in Certain Cases of Electrolytic Dissociation.** HARALD LUNDÉN and D. GARDNER (*Med. K. Vetensk. Nobelinst.*, 1912, 2, No. 16, 1—7).—The formulæ of Arrhenius (compare this vol., ii, 131) for the relationship between total and free energy in electrolytic dissociation are tested by means of the data for succinic acid, phenol, *m*-nitrophenol, and tropine with satisfactory results.

G. S.

**Determination of the Degrees of Dissociation of Electrolytes in Mixtures.** N. ANDREEFF and A. SAPOSHNIKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 895—905).—As is well known, it is possible, from a knowledge of the specific conductivities of various electrolytes with a common ion, to prepare a solution of these having a definite concentration of the common ion. The authors show that, knowing the concentration and the conductivity of a mixture of two such electrolytes, the concentration of the common ion and the degrees of dissociation of the electrolytes can be calculated.

Since  $\alpha = \lambda_v/\lambda_\infty$  and  $\lambda_v = \eta \cdot 1000v$ ,  $\alpha/v = \eta \cdot 1000/\lambda_\infty(1)$ , and  $\eta = \alpha\lambda_\infty/v \cdot 1000(2)$ . For the more simple case, where 1 mol. of each of *n* electrolytes is present,  $\lambda_{0\infty} = \lambda_{1\infty} + \lambda_{2\infty} + \dots$  and  $\eta_0 = (\eta_1 + \eta_2 + \dots)/n$ , where  $\lambda_{0\infty}$  and  $\eta_0$  are respectively the molecular conductivity at infinite dilution and the specific conductivity of the mixture, and  $\lambda_{1\infty}$ ,  $\lambda_{2\infty} \dots$  and  $\eta_1$ ,  $\eta_2 \dots$  the corresponding magnitudes for the separate components. As the mixture must be isohydric,  $\alpha_1/v_1 = \alpha_2/v_2 = \dots$ , and hence, from equation (1),  $\alpha_0/v_0 = n\eta_0 \cdot 1000/(\lambda_{1\infty} + \lambda_{2\infty} + \dots)$ ; measurement of  $\eta_0$  gives, therefore, the concentration of the common ion of the

mixture. Introduction of the value of  $\alpha_0$  into equation (2) then gives the specific conductivities of the components.

This method of calculation can be applied to the determination of (1) the form of the dissociation of polyionic electrolytes, (2) the quantities and forms of complex ions in mixtures, and (3) the extents of dissociation of electrolytes unknown in the free state, and also (4) to the investigation of the cause of the deviation of mixtures from the isohydric state.

The results are given of an investigation in this way of mixtures of: hydrochloric and acetic acids; hydrochloric, acetic and nitric acids; potassium chloride and nitrate. The values obtained are in accord with the calculations.

T. H. P.

**The Dissociation of Ternary Electrolytes.** JAMES W. McBAIN (*J. Amer. Chem. Soc.*, 1912, 34, 1134—1137).—In criticising the reference of Noyes and Falk (this vol., ii, 527) to the divergences in apparent dissociation of ternary electrolytes when the results of conductivity and freezing-point measurements are compared, the author points out that the two phenomena occur in different ranges of concentration, and can be explained by assuming intermediate ions (for example,  $\text{BaCl}^+$ ) in the more dilute, and complex anions (for example,  $\text{BaCl}_3^-$ ) in the more concentrated solutions. Whilst commending Noyes and Falk's series of compilations of smoothed results, it is suggested that in many cases they should be supplemented by more detailed studies of all the related data available.

J. C. W.

**Weak and Strong Binary Electrolytes.** C. VAN ROSSEM (*Chem. Weekblad*, 1912, 9, 714—719).—The author gives tables showing the degree of dissociation of succinic acid and benzylidenemalononic acid in solutions of various normalities at 25°, and of hydrochloric acid and potassium chloride at 18°.

A. J. W.

**The Ionisation Constant of Phenolphthalein and the Effect on it of Neutral Salts.** LUDWIG ROSENSTEIN (*J. Amer. Chem. Soc.*, 1912, 34, 1117—1128).—The fraction of phenolphthalein transformed from the colourless to the coloured form in solutions of various hydrogen-ion concentrations and of various neutral-salt concentrations has been determined by comparing the colour with that of a completely transformed solution of the indicator having the same total indicator concentration. The hydrogen-ion concentration was fixed by means of solutions of ammonium hydroxide and ammonium chloride, whilst potassium chloride was the neutral salt employed.

The observed fraction is a measure of the relation between the change in colour of the indicator and the concentration of the hydrogen-ion, that is, of the apparent ionisation constant, which has received widely-differing values in the literature. It is now found that, assuming the indicator to be a monobasic acid, the calculated constant increases with the alkalinity of the solution, even when the amount of neutral salt is kept constant, and it is further shown that this can be explained, as does Wegscheider (*Abstr.*, 1908, ii, 806), by considering that the indicator acts as a dibasic acid. Taking into

account the tautomeric relationships involved, it is then necessary to assume that the coloured form of the indicator is produced in appreciable quantity only when the second hydrogen of the acid has been replaced.

Neutral salts are shown to have a great effect on the fraction of the indicator transformed, the ionisation-constant being doubled by increasing the salt-concentration from 0.03 to 0.40 *N*. The change of the constant  $K_1$ , regarding the indicator as a monobasic acid, with the total salt-concentration  $C_s$ , can be expressed by  $K_1 = 0.77 \times 10^{-10} [1 + 2.8(C_s \gamma)^{0.5}]$ , which function is analogous to the expression for the deviations shown by strong electrolytes. J. C. W.

**Conductivity of Rosaniline Hydrochloride in Water and in Certain Organic Solvents.** HAROLD S. DAVIS (*Trans. Nova Scotia Inst. Sci.*, 1912, 13, 40—51).—The electrical conductivity of rosaniline hydrochloride in water, methyl and ethyl alcohols has been measured at 0° and 25° in different dilutions, and in acetic acid at 18° and 25°. The results correspond closely with those obtained for tetraethyl-ammonium iodide by Walder, so that the presence of the benzene nucleus has no characteristic influence on the electrical conductivity. In a dilution of 100 litres, the degrees of dissociation are as follows: water 95%, methyl alcohol 84%, ethyl alcohol 81%, acetic acid 53%. Ostwald's dilution law holds fairly well for the more concentrated solutions in the organic solvents, but not for the aqueous solutions.

G. S.

**Determination of Small Hydrogen Ion Concentrations from the Intensity of the Residual Current.** LUDWIG R. FRESSENIUS (*Zeitsch. physikal. Chem.*, 1912, 80, 481—508).—It is shown, on the basis of the principles already given by Nernst and Merriam (*Abstr.*, 1905, ii, 674) and by Eucken (*Abstr.*, 1907, ii, 425), that under certain conditions the  $H^+$  ion concentration in solutions can be calculated from the intensity of the residual current. The method is particularly suitable for solutions of strong acids and bases in the presence of excess of a neutral salt, a change in the  $H^+$  ion concentration from  $10^{-6}$  to  $4.10^{-6}$  mols. per litre corresponding with a difference in the intensity of the residual current to the extent of about  $10^{-7}$  ampere. The method does not give such accurate results for solutions of weak acids and bases, and is inapplicable when the neutral salts are hydrolysed in solution.

The method has been applied to the determination of the dissociation constants of phenolphthalein, and it is shown, in agreement with Wegscheider (compare *Abstr.*, 1908, ii, 806), that the results can be interpreted on the assumption that phenolphthalein is a dibasic acid.

G. S.

**Potentials of Zinc in Alcoholic Solutions of Zinc Chloride.** FREDERICK H. GETMAN and VERNETTE L. GIBBONS (*Amer. Chem. J.*, 1912, 48, 124—138).—The authors have measured the electrical conductivities of solutions of zinc chloride in water, methyl alcohol, and ethyl alcohol as solvents. The conductivities in aqueous solutions

are normal, whilst those in alcoholic solutions give evidence of association of the solute, and also of possible complex formation between solute and solvent. In methyl-alcoholic solution the curves showing the relation between the molecular conductivity and the dilution at 0° and 25° respectively intersect each other, the molecular conductivity at 25° being less than at 0° for high concentrations and greater than at 0° for low concentrations (compare Getman, Abstr., 1911, ii, 888).

Molecular-weight measurements by the ebullioscopic method show that in both alcohols zinc chloride is associated, the association in methyl alcohol being greater than in ethyl alcohol.

Measurements of the potentials of zinc in aqueous and alcoholic solutions of zinc chloride show that the potential follows Nernst's law in aqueous solutions of greater concentration than 0.1 molecular; in diluter solutions the potentials determined experimentally are much smaller than the calculated (compare Denham, Trans., 1908, 93, 41). In methyl-alcoholic solutions the potentials oscillate over a range of more than ten millivolts. In ethyl-alcoholic solutions the potential diminishes uniformly with decreasing concentration, this behaviour being the reverse of that which holds in aqueous solutions (compare Getman, *loc. cit.*).

From the potential measurements in aqueous solutions the heat of ionisation of zinc is calculated to be 32,120 cal. T. S. P.

**Influence of Current Density on the Formation of Persulphuric Acid and the Changes in Concentration of Persulphuric Acid and Caro's Acid.** ERICH MÜLLER and R. EMSLANDER (*Zeitsch. Elektrochem.*, 1912, 18, 752—756. Compare Müller and Schellhaas, Abstr., 1907, ii, 539).—In the prolonged electrolysis of sulphuric acid the final concentration of persulphuric acid is the greater the greater the current density, but the final concentration of Caro's acid is independent of the current density. The total concentration in active oxygen (persulphuric acid + Caro's acid) increases in course of the electrolysis to a maximum. Whilst, however, the concentration of Caro's acid increases continuously up to the stationary condition, the concentration of persulphuric acid attains a maximum, and then falls to a constant value. G. S.

**Electrochemical Reduction of Condensation Products of Aldehydes with Amines.** KURT BRAND and A. HÖING (*Zeitsch. Elektrochem.*, 1912, 18, 745—752. Compare Abstr., 1909, i, 784; Knudsen, *ibid.*, i, 890; Law, Trans., 1912, 101, 154).—The statement of Knudsen (*loc. cit.*) that ethylideneimine is not reduced to ethylamine either in alkaline or almost neutral solution is confirmed, the explanation being that the former substance is changed in solution to aldehyde-ammonia. The hydrogen used up at the cathode is probably employed in reducing the aldehyde formed from aldehyde-ammonia.

In alkaline solution hydrobenzamide is reduced at a lead cathode to benzylamine and dibenzylamine; in the same circumstances benzylidenemethylamine is reduced quantitatively to benzylmethylamine, and benzylidene-*p*-aminophenol yields benzyl-*p*-aminophenol. Even with a

large current no decomposition into toluene and aminophenol occurs. Benzylidene-*o*-aminophenol on solution in sodium hydroxide decomposes into benzaldehyde and *o*-aminophenol, and can therefore not be electrolytically reduced to benzyl-*o*-aminophenol in alkaline solution. G. S.

**Formation of Hydrogen Cyanide in the High Tension Electric Flame.** A. V. LIPINSKI (*Zeitsch. Elektrochem.*, 1912, 18, 229—230); J. MOSCICKI (*ibid.*, 730—731. Compare Abstr., 1911, ii, 1057).—Polemical. G. S.

**Realisation of the Thomson-van der Waals *p-T-v*-Surface.** JULIUS MEYER (*Zeitsch. Elektrochem.*, 1912, 18, 709—710).—The surface in question corresponds with the temperature to which a liquid can be superheated without the formation of vapour, and has been investigated experimentally for a number of organic liquids. The air-free liquid was confined in a capillary over mercury under pressure, raised to a definite temperature, and the pressure then gradually diminished to zero. For ethyl ether the pressure could be diminished to zero only for temperatures below 115°. The corresponding temperatures for other liquids are as follows: methyl ethyl ether, 58°;  $\beta$ -methylbutane, 95°; benzene, 168°; ethyl alcohol, 155°. These results are in good agreement with those calculated from the critical temperatures by the rule of van der Waals. The temperature for water could not be satisfactorily determined, owing to its action on the material of the capillary tube at high temperatures. G. S.

**Compressibilities of Certain Hydrocarbons, Alcohols, Esters, Amines, and Organic Haloids.** THEODORE W. RICHARDS, W. N. STULL, JOSEPH H. MATHEWS, and CLARENCE L. SPEYERS (*J. Amer. Chem. Soc.*, 1912, 34, 971—993. Compare Abstr., 1909, ii, 214).—The compressibilities of forty-seven liquid hydrocarbons, alcohols, amines, esters, and organic haloids have been determined. The results, taken in connexion with several others previously published, bear out the rule that, in general, the greater the compressibility of a substance, the greater is its decrease with increasing pressure. It is pointed out that this rule may be predicted from the theory of compressible atoms.

For similar compounds, even of widely differing molecular weight, the quotient  $10^4\Delta/(\beta \times 10^6)^{2.05}$  is approximately constant;  $\beta$  is the compressibility at 20° in terms of megabars between 100 and 300 megabars, and  $\Delta$  is the difference between the compressibilities over the ranges 100—300 and 300—500 megabars. The value of the constant is about 15 for the hydrocarbons and esters, and about 18 for monohydric alcohols and amino-compounds containing more than three atoms of carbon; for the organic haloids the value is about 15.

The full discussion of the results, especially in relation to the theory of compressible atoms, is reserved for a later paper.

T. S. P.

**Thermal Expansion of Alloys of Aluminium and Zinc.** WLADIMIR SMIRNOFF (*Compt. rend.*, 1912, 155, 351—352).—A measure-

ment of the mean linear expansion of rods of alloys of aluminium and zinc, varying in composition, between 25° and 250°. A table and curve are given showing a minimum corresponding with a compound  $\text{Al}_2\text{Zn}_3$ . The expansion curves of all alloys containing the crystals of  $\text{Al}_2\text{Zn}_3$  show a deviation at a temperature of 260—270°, indicating a sudden change in the dimensions of the alloy due to a transformation of the crystals of this definite compound. W. G.

The History of Distillation and of Alcohol. EDMUND O. VON LIPPMANN (*Zeitsch. angew. Chem.*, 1912, 25, 1680—1682).—The process of distillation was quite unknown in the time of Aristotle, but was employed by the hellenistic alchemists. C. H. D.

A Hygrometric Method of Vapour-pressure Determination. W. R. FORBES (*Chem. News*, 1912, 106, 88).—A copper test-tube, immersed in a water-bath, is provided with an upper glass vessel, through a side-arm of which passes a glass rod carrying a black glass disk, crossed by a silver band. The dew-point is observed by means of the disk, and the vapour pressure is then obtained from tables. C. H. D.

Specific Heats. I. J. N. BRÖNSTED (*Zeitsch. Elektrochem.*, 1912, 18, 714—717).—The specific heats of a number of substances have been determined from 0° to 19° in a well-insulated calorimeter made of a block of copper, the temperatures being measured with a platinum thermometer. Some of the results are as follows: White tin, 0.05382; grey tin, 0.04962; potassium hydrogen tartrate, 0.2314; potassium hydrogen racemate, 0.2348; aragonite, 0.1899; calc-spar, 0.1887; thallous picrate, yellow, 0.134; red, 0.137; silver, 0.05535, and mercury, 0.03325.

The van't Hoff-Thomsen rule, according to which the modification stable at high temperature has the higher specific heat, is valid in the case of tin, but the rule, supported more particularly by Richarz (compare Abstr., 1893, ii, 404), that the substance with the higher specific heat has the smaller density, is not valid in the case of tin. The two tartrate modifications also follow the van't Hoff-Thomsen rule, but the differences in the specific heats of the two forms of calcium carbonate and of thallous picrate are too small to admit of definite conclusions being drawn.

In order to determine the energy relations in the two reactions:  $\text{NH}_4\text{Cl} + 2\text{PbCl}_2 \rightarrow \text{NH}_4\text{Cl}, 2\text{PbCl}_2$  and  $\text{HgCl} + \text{Ag} \rightarrow \text{AgCl} + \text{Hg}$ , the specific heats of the substances concerned have been determined. The free energy of the first reaction at room temperature is 2780 cal.; for the second reaction, 1050 cal. G. S.

A Summary of the Specific Heats of Gases. GILBERT N. LEWIS and MERLE RANDALL (*J. Amer. Chem. Soc.*, 1912, 34, 1128—1134).—Since most of the chemical equilibria which have been studied at high temperatures involve gases, and as specific heats play an important part in the subsequent calculations, the authors have reviewed the various values assigned to the common gases, in order

to select the most probable formulæ for further reference. The older measurements, which may be classed under the direct calorific, the adiabatic, and the explosion methods, have been supported by much recent work.

For any monatomic gas the round value  $C_p = 5.0$  is adopted. For diatomic gases, the practice of Le Chatelier and of Nernst in taking 6.50 for the molecular heat at absolute zero is confirmed, and the following formulæ are suggested: for nitrogen, oxygen, carbon monoxide, nitric oxide, hydrogen chloride, bromide and iodide,  $C_p = 6.50 + 0.0010T$ ; for hydrogen,  $C_p = 6.50 + 0.0009T$ ; for chlorine, bromine, and iodine,  $C_p = 6.50 + 0.004T$ .

The values recently assigned to water by Holborn and Henning (Abstr., 1907, ii, 844) and by Pier (Abstr., 1909, ii, 789; 1910, ii, 1031) lead to the formula  $C_p = 8.81 - 0.0019T + 0.0000222T^2$ , which is also adopted for hydrogen sulphide. From the work of these same experimenters the formula  $C_p = 7.0 + 0.0071T - 0.00000186T^2$  is calculated for carbon dioxide, and this formula is also given to sulphur dioxide, Fürstenau and also Pier having found that this gas behaves exactly like carbon dioxide.

The various figures obtained in the case of ammonia fall on a straight line given by the equation  $C_p = 7.5 + 0.0042T$ . J. C. W.

**Experimental Determination of the Ratio of the Specific Heats  $C_p/C_v$  for Potassium and Sodium Vapours, and the Conclusions to be Drawn Therefrom.** MAX ROBITZSCH (*Ann. Physik*, 1912, [iv], 38, 1027—1032).—By means of the apparatus described by Wenz (Abstr., 1910, ii, 1061) the author has measured the velocity of sound in potassium vapour at temperatures between 680° and 1000°, and in sodium vapour between 750° and 920°. The data give for the mean probable value of the specific heat ratio,  $1.64 \pm 0.007$  for potassium, and  $1.68 \pm 0.03$  for sodium. These results show conclusively that the molecules are monatomic. H. M. D.

**Mean Specific Heat of Quartz and of Fused Quartz.** KARL SCHULZ (*Centr. Min.*, 1912, 481—491. Compare Abstr., 1911, ii, 1059).—The following determinations were made for three ranges of temperature:

	20—100°.	20—250°.	20—410°.
Quartz from Marmarosch, Hungary ...	0.1875	—	—
„ „ Minas Geraes.....	0.1871	0.2086	0.2253
Fused quartz (from Minas Geraes)* ...	0.1855	0.2054	0.2204
„ „ † .....	0.1860	—	—

\* Ref. index  $n_D = 1.4584$ ,  $D^{20}_D = 2.21$ .

†  $n_D = 1.4589$ ,  $D^{20}_D = 2.21$ .

The differences between the specific heats of the glass and of the crystallised material increase with the temperature; and at lower temperatures the glass would consequently have a higher specific heat than the crystal, as already found experimentally by Nernst (Abstr., 1911, ii, 964). L. J. S.

**Influence of a Third Component on the Freezing Point of a Binary Mixture.** G. MUCHIN (*Zeitsch. Elektrochem.*, 1912, 18, 757—761).—The influence of cadmium iodide, mercuric chloride, and

resorcinol on the freezing point of mixtures of benzene with methyl, ethyl, and propyl alcohols, and of resorcinol on the freezing point of a mixture of benzene and pyridine has been determined. In all cases the freezing points were raised by the addition of the third component, and the extent of the elevation appears to be connected with the heat of solution of the third component in the non-freezing liquid (alcohol, pyridine). Different explanations of the elevation in question are considered, but no definite conclusions are reached. G. S.

**Heats of Formation of Solid Solutions.** GIUSEPPE BRUNI and MARIO AMADORI (*Atti R. Inst. Veneto Sci.*, 1911, '71, 251—259).—The three binary mixtures, in equimolecular proportions, of potassium chloride, bromide and iodide were fused and rapidly cooled, the heats of solution in water of the solid solutions thus obtained being compared with those of the corresponding mechanical mixtures of the salts. The following table gives the heats of formation of the mixed crystals, together with the gaps in the miscibility at low temperatures (crystallisation from water) and at high temperatures (fusion) (compare Amadori and Pampanini, this vol., ii, 48, 154):

	KCl + KBr.	KBr + KI,	KCl + KI.
Gap in miscibility { at high temp.	0	0	9—51 mol. % KI
{ at low temp...	0	7—76 mol. % KI	1—93 mol. % KI
Heat of formation of mixed crystals	- 250	- 392	- 551 cal.

Hence, the amount of heat absorbed in the formation of the solid solutions increases with the gap in the miscibility in the cold.

The above results differ numerically from those obtained by Schemtschuschny and Rambach (*Abstr.*, 1910, ii, 204). T. H. P.

#### Heat of Combination of Acidic Oxides with Sodium Oxide.

**VIII. Heat of Formation of the Oxides of Vanadium and Uranium.** WILLIAM G. MIXTER (*Amer. J. Sci.*, 1912, [iv], 34, 141—156. Compare *Abstr.*, 1911, ii, 966).—The following is a summary of the results obtained, those denoted with an asterisk being calculated from the experimental results:  $V_2O_5 + 3Na_2O = 3Na_2VO_4$ , 165,800 cal.;  $V_2O_3 + 2Na_2O_2 + Na_2O = 3Na_2VO_4$ , 214,800 cal.;  $V_2O_4 + Na_2O_2 + 2Na_2O = 3Na_2VO_4$ , 174,600 cal.;  $V_2O_2 + 3Na_2O_2 = 3Na_2VO_4$ , 340,000 cal.;  $2V + 5O = V_2O_5 + >441,000^*$  cal.;  $V_2O_3 + 2O = V_2O_5 + 87,800^*$  cal.;  $V_2O_4 + O = V_2O_5 + 28,200^*$  cal.;  $V_2O_2 + 3O = V_2O_5 + 232,400^*$  cal.;  $V_2O_2 + 2O = V_2O_4 + 204,200^*$  cal.;  $V_2O_3 + O = V_2O_4 + 59,600^*$  cal. The value obtained by Ruff and Martin (this vol., ii, 166) for the heat of formation of vanadium pentoxide is probably much too low.

$3U + 4O = U_3O_8 + 845,200$  cal.;  $U + 3Na_2O_2 = Na_2UO_4 + 2Na_2O + 341,800$  cal.;  $UO_3 + Na_2O = Na_2UO_4 + 96,100$  cal.;  $UO_2 + Na_2O_2 = Na_2UO_4 + 110,900$  cal.;  $UO_3 + Na_2O = Na_2UO_4 + 96,100$  cal.;  $3UO_2 + 2O = U_3O_8 + 75,300$  cal.;  $U_3O_8 + Na_2O_2 + 2Na_2O = 3Na_2UO_4 + 285,100$  cal.;  $U + 3O = UO_3 + 303,900^*$  cal.;  $UO_2 + O = UO_3 + 34,200^*$  cal.;  $U_3O_8 + O = 3UO_3 + 16,200^*$  cal. T. S. P.

**Isotherms of Monatomic Substances and of their Binary Mixtures XIII.** The Empirical Reduced Equation of State for Argon. H. KAMERLINGH ONNES and C. A. CROMMELIN (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 273—280. Compare Abstr., 1911, ii, 203).—The coefficients of the equation of state for argon have been calculated.  
C. H. D.

**Thermo-Osmosis.** AUBERT (*Ann. Chim. Phys.*, 1912, [viii], 26, 145—208, 551—582. Compare Abstr., 1909, ii, 543).—An extension of the results already published (*loc. cit.*). It is shown that all membranes do not set up thermo-osmosis, and those which are active fall into two classes: *positive*, causing a flow from the cooler to the warmer side; or *negative*, inducing a flow in the opposite direction. Thermo-osmosis is intimately connected with the presence of soluble substances in the membrane (compare Flusin, Abstr., 1908, ii, 359), and inactive membranes may be made active by impregnating them with soluble salts, and, conversely, active membranes may be rendered inactive by washing. It is suggested that the phenomenon has much in common with electrical osmosis (Perrin, Abstr., 1905, ii, 138), and is due to a difference of potential set up on either side of the membrane, chiefly as the result of difference in the concentrations of the solutions formed on the colder and warmer sides.

An account is first given of Lippman's work on this subject (Abstr., 1907, ii, 668), and it is shown that the possibility of thermo-osmosis can be deduced from van't Hoff's law. The explanations of osmosis advanced by Magnus, Poisson, Battelli and Stefanini (Abstr., 1907, ii, 233) are considered, and it is shown that these fail to account for the fact that in thermo-osmosis the flow takes place in different directions depending on the membrane.

The principle of the apparatus used in the investigation has been described already (*loc. cit.*), and in this memoir its construction and working are given in detail.

The positive membranes investigated were gelatin slightly hardened by formaldehyde, tannin or potassium dichromate, goldbeaters' skin, pigskin, and parchment. Porous clay, pipeclay, and collodion proved inactive, but the third substance was rendered active for water and ethyl alcohol by slightly impregnating it with potassium acetate or ammonium nitrate. The negative membranes examined were parchment paper and viscose.

The following new general conclusions are drawn. Thermo-osmosis may take place with various liquids (water, salt solutions, methyl, ethyl, isobutyl or amyl alcohol) so long as the membrane used has some imbibing power for the liquid used. No diosmosis occurs. For given differences in pressure and temperature the rate of flow is not constant; in general, it falls from its initial value, then rises to a maximum, and finally falls steadily.  
T. A. H.

**Influence of Temperature, Specific Gravity, and Chemical Nature of Liquids on the Turbulence Viscosity.** WALTHER SOBKAU (*Physikal. Zeitsch.*, 1912, 13, 805—820. Compare Abstr., 1911, ii, 793).—Further experiments have been made on the influence

of pressure and temperature on the viscosity of liquids in a condition of turbulent flow. In the case of ethyl acetate, which has been examined in detail at temperatures between  $7^{\circ}$  and  $40^{\circ}$ , it is found that the viscosity, as measured by the time of flow of a given volume of liquid through the capillary, does not vary in a uniform manner with changing pressure, but that it changes more or less abruptly at two points, whereby three distinct regions, conditioned by differences in the mode of flow, are indicated. These points of transition are dependent on the temperature, the pressures, at which the discontinuities occur, falling as the temperature rises. This effect is more marked in the case of the discontinuity corresponding with the smaller pressure.

Similar relationships are exhibited by amylene, acetone and chloroform, and from the data obtained for these four liquids, it appears that the primary stage in the turbulent flow is regulated by a general law, which may be expressed in the form  $\sqrt[3]{p^2 \cdot t \cdot e^{\theta/273}} = C$ , in which  $p$  is the driving pressure,  $t$  the time of flow,  $\theta$  the absolute temperature, and  $C$  a constant.

In this type of turbulent flow, the influence of temperature on the velocity with which the liquid passes through the capillary is independent of the specific nature of the substance.

In the third stage, the time of flow is given by  $t = 36.05 \sqrt{D} / \sqrt{p}$ , where  $D$  is the density of the liquid. From this it would appear that, in this type of flow, a column of the liquid is projected through the capillary as if it were a frictionless solid rod, whilst the liquid in the neighbourhood of the walls of the capillary remains stationary.

In the second (transition) stage, which is observed when the rate of flow is greater than in the first and smaller than in the third stage, the mode of flow represents a more or less unstable combination of the types which are characteristic of the first and third stages of turbulent flow.

H. M. D.

**Properties of Substances Connected with the Kinetic Properties of the Molecules. I.** RICHARD D. KLEEMAN (*Proc. Camb. Phil. Soc.*, 1912, 16, 631—642. Compare this vol., ii, 734).—The general formulæ obtained in a previous paper (*loc. cit.*) are considered in greater detail, and new expressions are obtained for the partial pressures exerted by the molecules in a mixture.

H. M. D.

**The Different Kinds of Internal Energies of a Substance. II.** RICHARD D. KLEEMAN (*Proc. Camb. Phil. Soc.*, 1912, 16, 584—599. Compare this vol., ii, 535).—A theoretical paper in which the radius of the sphere of action of a molecule, the average velocity of a molecule, the viscosity and diffusion of gases, and the form of the function ( $\phi$ ) in the author's equation for the attraction between two molecules (compare *Abstr.*, 1910, ii, 492) are discussed. A formula is also deduced for the internal heat of vaporisation of a liquid, and on the assumption that ( $\phi$ ) in the law of molecular attraction is a function of the temperature only, the author calculates from the data for ethyl ether that ( $\phi$ ) =  $2.97 \times 10^{-45}$  (gram) (cm.) (sec.)<sup>-2</sup>.

The gravitational attraction between two molecules of a liquid,

which are averagely situated, is vanishingly small in comparison with the chemical attraction. According to the above value of  $(\phi)$ , the chemical attraction is greater than the gravitational for distances of separation of the molecules of the order of 10 cm., and this shows that the attraction decreases more rapidly with the separation for large distances than that expressed by the inverse fifth power law.

H. M. D.

**Some Applications of the Law of the Rectilinear Diameter.**  
H. DAVIES (*Phil. Mag.*, 1912, [vi], 24, 415—424. Compare this vol., ii, 426).—By making use of the law of rectilinear diameters, certain general relationships have been deduced for substances in the liquid state of aggregation.

The ratio  $(k)$  of the volume at absolute zero to the real volume occupied by the molecules is given by  $k = (K + 2)/(K - 1)2\alpha T'_c$ , in which  $K$  is the specific inductive capacity,  $\alpha$  the coefficient of expansion, and  $T_c$  the critical temperature of the liquids. The data for a number of organic compounds are shown to afford concordant values for  $k$ , the mean being equal to 2.5.

The expression  $(K - 1)/(K + 2)d$  is termed the inductive power of the liquid, and this is shown to be equal to  $V_c/10$ , where  $V_c$  is the critical volume. This relationship is also in satisfactory agreement with the experimental data for different liquids.

Although Guye has already pointed out the existence of a connexion between the molecular refractive power and the critical coefficient,  $T_c/P_c$ , such a relationship has not been deduced theoretically. It is now found, however, that the molecular inductive power and the above critical ratio are connected by the equation  $(K - 1)M/(K + 2)d = 2.3T_c/P_c$ . The actual values of the ratio of the molecular inductive power to the critical coefficient are in approximate agreement with this relation.

The co-volume is shown to be given by the expression  $\phi = (v - b) = V_c\alpha T/4$ , and the intrinsic pressure  $\pi$  by the equation  $\pi = 4R/\alpha V_c = 4R(2T_c - T)/V_c$ . From these, the temperature variation of  $\pi$  is obtained in the form  $d\pi/dT = -4R/V_c$ , which may be written  $1/\pi \cdot d\pi/dT = -\alpha$ . These equations afford a means of calculating the intrinsic pressure and its temperature-coefficient for any liquid for which the critical data are available. The values thus obtained, as well as those for the co-volume, are tabulated for some twenty non associated organic compounds.

H. M. D.

**The Protoplasmic Membrane and the Significance of Surface Tension in the Action of Water Soluble Substances on the Organism.** JACOB BÖESEKEN and K. J. WATERMAN (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 58—61).—In connexion with previous experiments on the growth of *Penicillium glaucum* in contact with aqueous solutions of various organic substances, measurements have been made of the influence of narcotically active substances on the surface tension of olive oil. This influence is very small, and the results are, therefore, consistent with the view that the protoplasmic membrane consists of fat-like substances.

Other measurements show that the narcotic action of salicylic acid and the inactivity of *m*- and *p*-hydroxybenzoic acids cannot be referred to differences in the surface tension of their aqueous solutions. The difference in the action of the three isomerides is probably connected with the value of the ratio of distribution (oil-water), which is very much greater for salicylic than for the other two acids. H. M. D.

**Mechanism of the Arrest of Diastases by Filtration.** MAURICE HOLDERER (*Compt. rend.*, 1912, 155, 318—319).—Diastase is retained on a porcelain filter when filtered in acid or neutral solution, but not in an alkaline solution (compare Abstr., 1910, i, 212, 345). If to the solution, before filtering, 10% of white of egg or 1% of peptone is added, practically the whole of the diastase passes through, even in an acid solution. The same effect is produced by filtering the albumin solution prior to the diastase solution instead of mixing them. The author puts forward the explanation that the albumin is fixed on the porcelain, saturating its affinity, and thus preventing the diastase from being fixed in its turn by the same mechanism. W. G.

**Experimental Determination of the Surface Tension of Alcohol-Water Mixtures by the Method of Capillary Waves.** LEO GRUNMACH (*Ann. Physik*, 1912, [iv], 38, 1018—1026. Compare Abstr., 1909, ii, 215).—Measurements have been made of the surface tension of a complete series of mixtures of water and ethyl alcohol by the method of capillary waves. On comparing the results with those furnished by the method of capillary rise, it is found that the surface tension values yielded by the capillary wave method are smaller for pure alcohol and all alcohol-water mixtures, whereas a higher value is obtained in the case of pure water.

This result is in agreement with previous observations (*loc. cit.*), and it appears that the capillary wave method yields higher values for pure liquids of high surface tension and lower values for liquids of small surface tension than those which are given by the method of capillary rise. These differences may be explained by the influence of traces of impurities, by the absorption of air, and the adsorption of water vapour, all of which tend to introduce errors into the measurement of the surface tension by the method of capillary rise, whereas the effect is very much smaller in the case of the wave method, in which the capillary surfaces are regenerated in a continuous manner.

H. M. D.

**Adsorption of Gases by Carbon and other Porous Substances.** WALTHER HEMPEL and GEORG VATER (*Zeitsch. Elektrochem.*, 1912, 18, 724—727).—The adsorptive power of different varieties of charcoal and other porous materials for gases, more particularly hydrogen and nitrogen, has been measured at 20°, -78°, and -185°. The results show that the adsorptive power of animal charcoal for all gases is considerably greater than that of cocoa-nut charcoal. The best results were obtained with charcoal prepared at 600°. The diatomic gases cannot be satisfactorily separated for analytical purposes

by means of charcoal. The volumes of a number of gases adsorbed by 1 gram of charcoal at 20° and at -78° are given in tabular form.

G. S.

**Dissociation of Certain Oxides, Carbonates, and Sulphides.** WALTHER HEMPEL and CARL SCHUBERT (*Zeitsch. Elektrochem.*, 1912, 18, 229).—The dissociation of a number of natural ores and chemical compounds, such as pyrolusite, lead peroxide, and potassium permanganate, has been investigated by heating the substances in an electric furnace and observing the temperatures at which dissociation commences and is complete. No details as to the duration of heating are given.

G. S.

**Osmotic Pressure of Concentrated Solutions of Carbon Dioxide.** OTTO SACKUR [with O. STERN] (*Zeitsch. Elektrochem.*, 1912, 18, 641—644).—In cases where Henry's law does not hold, the osmotic pressure,  $\pi$ , of a solution of a gas saturated under the pressure,  $P$ , can be calculated by means of the expression  $\pi = \int_0^P k dP(1)$ , when  $k$ , the absorption coefficient, or solubility, is known for a series of pressures from zero upwards. The solubility of carbon dioxide in methyl and ethyl alcohols and in methyl and ethyl acetate has been determined at -59° and -78° and at pressures from 50 to 700 mm. mercury, and the results are expressed in terms of the absorption coefficient (Bunsen) and in terms of "solubility" (Ostwald). It is shown that Henry's law is the more nearly obeyed when the results are expressed in the latter form.

Above a certain pressure,  $P_0$ , the solubility,  $k$ , can be represented satisfactorily by the expression  $k = k_0 + a(P - P_0)$ . By means of this expression the osmotic pressures are calculated according to equation (1) and the results are tabulated. It is shown that even up to 100 atmospheres the osmotic pressures thus obtained are in very close agreement with the simple van't Hoff law, although carbon dioxide in the gaseous form deviates greatly from the simple gas laws under corresponding conditions. A rather complicated expression for the osmotic pressure of concentrated solutions is quoted (the deduction of this expression is not given), and it is shown that the above result is in accordance with the kinetic theory of the osmotic pressure of concentrated solutions.

G. S.

**Calculation of Diffusion Experiments.** OSCARRE ARPA (*Gazzetta*, 1912, 42, ii, 172—183).—The author has previously (1911, ii, 472) given results calculated for the diffusion phenomena occurring in Buscaglioni and Purgotti's and Vanzetti's apparatus on the assumption that precipitation begins when the concentration of the product of the reaction (formed in the colloidal state) reaches the stability limit of the suspensoid.

As it might be thought that the concordance between the values thus obtained and Vanzetti's experimental numbers is due to the particular values of the diffusion coefficients employed in the calculations, the author examines this and other factors influencing the results, such as the imperfect applicability of the theoretical laws of

diffusion to the concentrated solutions employed by Vanzetti. Allowance for all sources of error, however, in no way impairs the agreement between theory and experiment.

T. H. P.

**New Method for Determining the Diffusion of Dissolved Substances.** L. WILLIAM ÖHOLM (*Medd. K. Vetensk. Nobelinst.*, 1912, 2, No. 22, 1—23).—The apparatus consists of four round brass slabs each having in the middle a hole of about 2 cm. diameter, of a plain bottom slab, and a lid, all of brass. In an experiment the slabs are placed one above the other, so that the central openings exactly coincide, and then the central cylinder so formed is filled with the solvent, for example, water, up to the top of the third slab. The solution containing the diffusing substance is then put in from below by means of a pipette connected to a small tube which passes through the centre of the bottom slab, sufficient of the liquid being drawn in to fill the hole in the second slab; the brass cover is then put on, and the arrangement allowed to remain. The three lower slabs are provided with grooves, into which the liquid from the slab above it runs when the latter is pushed to the side. It is shown by experiments with potassium chloride that the arrangement gives good results. It is particularly useful for viscous solutions.

With this apparatus it is shown that the diffusion resistance to potassium chloride is greatly increased by the addition of sucrose or glycerol to the solution. The diffusion-coefficient of the salt in water is about 1.326 at 18°, in 1.5*N*-sucrose solution it falls to 0.42, in a 2*N*-solution to 0.220, and in a 7.48*N*-glycerol solution to 0.175.

G. S.

**Solubility and Electro-affinity.** FILIPPO CALZOLARI (*Gazzetta*, 1912, 42, ii, 85—92).—At 20°, caesium chlorate and perchlorate are somewhat less soluble than the corresponding potassium salts, but are more soluble than those of rubidium. These results are not in accord with the predictions of the theory of electro-affinity. Further, the order of these salts as regards their solubilities varies with the temperature.

T. H. P.

**Solubility of Certain Salts.** HERMANN EHLERT and WALTHER HEMPEL (*Zeitsch. Elektrochem.*, 1912, 18, 727—729).—The influence of a number of salts on the solubility at room temperature of calcium, ferrous and zinc carbonates, and calcium phosphate in aqueous solution has been determined in the absence of carbon dioxide and at 2 atmospheres pressure of the gas. The effect on the solubility of most cases considerable, but no general conclusions are drawn from the results. The effects of certain salts on the solubility of barium sulphate have also been determined, and it is shown that when the latter salt is prepared by mixing solutions of barium chloride and sulphuric acid, the solution remains supersaturated for some time.

G. S.

**Spontaneous Alterations of Concentration in Solutions and Gases.** I. THE SVEDBERG (*Arkiv. Kem. Min. Geol.*, 1912, 4, No. 22, 1—28).—In a previous paper the author has shown that in a solution

of polonium chloride the momentary differences of concentration in a limited volume of the solution correspond with the requirements of the molecular-kinetic theory (Abstr., 1910, ii, 1047). The experiments have now been repeated, with refined methods of measurement, partly owing to the fact that in previous work the mean deviation ( $\delta$ ) from the number of molecules which should be present in a limited volume of solution according to theory has been taken as  $2n_1^{k.e-n_1}/k!$  (for meaning of symbols, see Abstr., 1910, ii, 772), whereas it is now shown to have the theoretical value  $\sqrt{1/n_1}$ .

The results show that the experimental curve connecting  $\delta$  and  $n_1$  lies, on an average, about 9% lower than the theoretical curve for the radioactive solutions, and about 30% higher than the theoretical curve for the solid radioactive substance. In two cases the experimental and theoretical curves for the solution were in good agreement, and the tests carried out by the author indicate that the want of agreement in the other cases is due to the superposition of the action of some solid active particles present in the solution on the action of the solution itself.

The results of the experiments are taken as affording further support for the correctness of the molecular-kinetic theory. T. S. P.

**Spontaneous Alterations of Concentration in Solutions and Gases. II. THE SVEDBERG** (*Arkiv. Kem. Min. Geol.*, 1912, 4, No. 25, 1—15).—The author has extended his experiments (see preceding abstract) to the case of a radioactive gas, namely, radium emanation. The number of  $\alpha$ -particles produced in a given time in a limited volume of the dust-free gas was determined by observing the impacts on a zinc sulphide screen; the disturbing effects of the active deposit formed from the emanation were prevented, or at all events considerably diminished by exposing the emanation to the action of an electric field so arranged that the active deposit was collected on the cathode and hindered from forming on the zinc sulphide screen.

The results obtained are in approximate agreement with the theory, complete agreement being prevented by the formation of some active deposit on the screen, the amount of which could not be accurately determined. T. S. P.

**Phosphoryl Chloride as a Cryoscopic Solvent and its Applications. VIII. GIUSEPPE ODDO and ANNA MANNESSIER** (*Gazzetta*, 1912, 42, ii, 194—204. Compare Abstr., 1911, ii, 1060).—The authors controvert Walden's statements (Abstr., 1910, ii, 1036; this vol., ii, 429) concerning the freezing point and the cryoscopic constant of phosphoryl chloride.

The cryoscopic behaviour of a number of acids in phosphoryl chloride has been investigated, the results being briefly as follows: All the acids examined were found to be soluble in the chloride, and, provided the acids were anhydrous, the solutions remain unchanged at the experimental temperatures. Acids behave differently towards the solvent according to their degree of dissociation in water. Those which are feebly ionised by water, such as acetic, etc., are not only non-ionised in phosphoryl chloride, but, even in dilute solutions, exhibit

molecular weights higher than the normal ones. With monochloroacetic acid, the values obtained are normal at low concentrations and increase slowly with the concentration. Dichloroacetic acid shows an approximately constant ionisation of about 10% for concentrations varying from 0.7% to 8%, and with trichloroacetic acid the ionisation amounts to about 12% with a concentration of 3% and increases with the concentration.

Sulphuric acid shows a degree of ionisation of rather more than 50%, confirmation thus being obtained of the conclusion that this acid has the double formula  $(\text{H}_2\text{SO}_4)_2$  (compare Oddo and Anelli, *Abstr.*, 1911, ii, 717). With nitric acid the ionisation increases slightly with the concentration, and phosphorous acid is considerably ionised.

This behaviour of phosphoryl chloride is interpreted as due to its tendency to form oxonium salts,  $\text{RH}:\text{O}:\text{PCl}_3$  (R representing an acid radicle), which undergo partial ionisation in the solvent. The ability to form salts is first shown by acids, the dissociation constants of which are a little higher than that of monochloroacetic acid. Acids with a lower dissociation constant are condensed into more complex molecules by the phosphoryl chloride. With dichloroacetic acid, which shows an almost constant degree of ionisation at different concentrations, the resultant of these two opposed processes does not change.

T. H. P.

**State of Substances Dissolved in Absolute Sulphuric Acid.**  
G. POMA (*J. Chim. phys.*, 1912, 10, 177—192. Compare *Abstr.*, 1910, ii, 487).—Cryoscopic and conductivity measurements were made simultaneously in a special glass cell, the contents of which could be stirred without exposure to atmospheric moisture. The solutes examined were the hydrogen sulphates of sodium, potassium, nickel, and cobalt. The solutions were prepared by placing 25 c.c. of fuming sulphuric acid in the cell and adding from a burette a certain volume of an aqueous solution of the sulphate. The slight excess of sulphur trioxide remaining was hydrated by the careful addition of a 5% solution of water in sulphuric acid from another burette, using the freezing point and conductivity as indicators. It was assumed that when a solution attained its minimum conductivity or maximum freezing point the only substances present were the hydrogen sulphate of the metal and absolute sulphuric acid. The solutions were not analysed.

Taking the cryoscopic constant of sulphuric acid as  $70^\circ$  (Hantzsch), the values of the molecular weights obtained with nickel and cobalt hydrogen sulphates agreed with those given by Hantzsch, but the results with sodium and potassium hydrogen sulphates were considerably lower. On dissolving sodium and potassium hydrogen sulphates in absolute sulphuric acid according to Hantzsch's method, the cryoscopic values were in agreement with his, and the solutions were able to take up sulphur trioxide, giving a diminished freezing-point depression and conductivity.

Solutions prepared by the author's method evidently contain excess of sulphur trioxide. The excess may be in the form of a pyrosulphate or in loose combination with one of the ions as  $(\text{K}, n\text{SO}_3)^+$  or  $(\text{HSO}_4, n\text{SO}_3)^-$ . The former explanation is held to be improbable, since

the pyrosulphate would be in equilibrium with a large excess of sulphuric acid, and would necessarily be in very small concentration according to the equilibrium equation:  $\text{KHS}_2\text{O}_7 + \text{H}_2\text{SO}_4 = \text{KHSO}_4 + \text{H}_2\text{S}_2\text{O}_7$ . The same argument holds as regards the complex ion  $(\text{HSO}_4, n\text{SO}_3)'$ . The explanation adopted is that complex cations are produced of formula  $(\text{M}, n\text{SO}_3)'$ , and the salts,  $(\text{M}, n\text{SO}_3)\text{HSO}_4$ , are less dissociated than the corresponding hydrogen sulphates. If such cations are formed from nickel and cobalt bisulphates they must be stable in presence of small quantities of water, since the colour of the solutions in sulphuric and pyrosulphuric acids is the same. The minimum values of the equivalent conductivity of sodium, potassium, nickel, cobalt, and copper hydrogen sulphates are about 14 to 16, whereas the values obtained by Bergius with no excess of sulphur trioxide present were between 75 and 100.

Picric acid dissolved in sulphuric acid behaves in a similar way to the alkali hydrogen sulphates, taking up excess of sulphur trioxide, but in this case trinitrophenolsulphonic acid may be formed.

R. J. C.

**Reactions in Heterogeneous Systems. I. The Rate of Evaporation of Water and Aqueous Solutions.** KASIMIR JABŁCZYŃSKI and S. PRZEMYSKI (*J. Chim. phys.*, 1912, 10, 241—270).—According to the theory suggested by Noyes and Whitney and afterwards elaborated by Nernst, when a solid dissolves in a liquid there is always a stationary saturated layer in contact with the solid. The authors consider that the mechanism of the evaporation of liquids is essentially similar, and the rate of evaporation in a current of gas is governed by the rate at which the vapour diffuses across the stationary layer and the rate at which the vapour is carried away by the current.

The thickness  $\delta$  of the stationary layer adjusts itself so that at every point over the surface a condition of equilibrium is established between the amount of vapour arriving through the stationary layer and the amount carried forward by the gas stream. Using the diffusion equation put forward by Stefan (Abstr., 1891, 384), the authors are able to formulate the equilibrium thus:  $\log . p_0/(p_0 - p) = C^m x/V\delta$ , where  $p_0$  is the vapour pressure,  $p$  the partial pressure of the vapour in the gas stream over the section of surface area  $x$  wide and  $x$  long,  $C$  is the diffusion-coefficient of the vapour in air, and  $V$  the velocity of the air current. The exponent  $m$  is a correction for diffusion of vapour retrograde to the gas stream. The equilibrium equation contains two unknowns, namely,  $m$  and  $\delta$ .

In order to obtain evidence for the theory of evaporation outlined above, which is incompatible with the results obtained by Heen (1891), water was evaporated in currents of dry air and hydrogen. The water was contained in a glass bottle filled to within 14 mm. of the rubber stopper, and maintained at 25° in a thermostat. A measured quantity of gas was led in and out of the bottle by two quill tubes 46 mm. apart, and was then passed through five separately weighed drying tubes packed with calcium chloride.

The rate of evaporation increased when the level of the liquid was

raised, but with a constant level, 14 mm. below the stopper, the rate of evaporation  $K$  was related to the velocity of flow  $V$  by the equation  $\sqrt{V} \log . p_0 / (p_0 - p) = K$ . It follows that the thickness of the stationary film is inversely proportional to the square-root of the velocity of the gas stream ( $\delta = k / \sqrt{V}$ ).

According to Stefan and Winkelmann (1889), the diffusion-coefficient of water vapour in air,  $C$ , is related to the absolute temperature and pressure by the equation  $C = k_1 (T)^{1.774} / P$ . The rate of evaporation of water at various temperatures and pressures appears to indicate that  $C$  is much less dependent on  $T$  and  $P$  than this equation demands, the reason being that retrograde diffusion also varies with temperature and pressure, and in evaporation calculations  $C^m$  must be considered. On the basis of evaporation experiments at various pressures, the value of  $m$  was calculated to be 0.488, whilst experiments at various temperatures gave the value 0.49 (mean of four values ranging from 0.22 to 0.80).

Agitation of the evaporating liquid by means of a stirrer arranged near the surface increases the rate of evaporation by diminishing the thickness of the stationary film  $\delta$ .

The rate of evaporation in a current of hydrogen is about 10% higher than in a current of air, but insufficient measurements were made to enable the value of  $m$  to be calculated in this case.

The evaporation of aqueous solutions is subject to the same laws as the evaporation of pure water. The value of  $\delta$  in the equilibrium equation is less for a solution than for water, because the vapour pressure  $p_0$  is less. It is deduced that water and aqueous solutions must evaporate at rates proportional to their vapour pressures. Results obtained with solutions of sodium chloride, calcium chloride, glycerol, and albumin of various strengths showed a very satisfactory agreement with this hypothesis.

When the stream of gas passing over the liquid is efficiently agitated there is no longer any partial pressure gradient in the direction of flow, and retrograde diffusion cannot occur. The equilibrium equation becomes:  $p / (p_0 - p) = Czx / V\delta$ , but  $\delta$  still varies inversely as  $1 / \sqrt{V}$ . The evaporation constant  $K'$  equals  $\sqrt{V} p / (p_0 - p)$ . The value of  $K'$  decreases slightly as the speed of the stirrer is increased, and increases more rapidly than  $p_0$  when the temperature is increased.

R. J. C.

**Reactions in Heterogeneous Systems. II. Rate of Absorption by Potassium Hydroxide of Carbon Dioxide Mixed with a Current of Air.** KASIMIR JABŁCZYŃSKI and S. PRZEMYSKI (*J. Chim. phys.*, 1912, 10, 271—288).—The action is theoretically the converse of the evaporation of a liquid, and was investigated in the same apparatus (compare preceding abstract). The partial pressure of the carbon dioxide in the gaseous mixture was measured before and after its passage over the surface of a well stirred potassium hydroxide solution.

The equilibrium between the gaseous stream and the liquid is not expressible as a simple equation, because the distribution of carbon

dioxide between the vapour and liquid phases is an unknown function of the concentration of the potassium hydroxide. It is necessary to assume that in addition to the stationary gaseous layer  $\delta_1$  thick, there is a saturated liquid layer  $\delta_2$  thick at the dividing surface. If the concentration of the potassium hydroxide is infinitely great, these complications disappear and the equilibrium equation becomes  $\log . p_i/p_{ii} = C^n x / V \delta_1$ , where  $p_i$  and  $p_{ii}$  are the partial pressures of carbon dioxide in the air stream entering and leaving the absorption chamber respectively, and  $n$  is the retrograde diffusion exponent which has a value greater than 1, since retrograde diffusion keeps the carbon dioxide for a longer time in contact with the absorbing solution.

The ratio  $p_i/p_{ii}$  cannot be determined directly with potassium hydroxide of infinite concentration, but is obtained by extrapolation from a series of measurements with different concentrations of potassium hydroxide. Assuming that the thickness  $\delta_1$  of the stationary gas film in the absorption of carbon dioxide is the same as the thickness  $\delta$  of the film in the evaporation of water under like conditions, the value of the exponent  $n$  is calculated to be 1.30.

The ratio  $p_i/p_{ii}$  in the above equation is independent of the concentration of the carbon dioxide in the gaseous phase, that is to say, the percentage of the total carbon dioxide absorbed is not affected by alterations in the proportion of diluting air. This deduction, which is of some importance from the industrial point of view, was verified experimentally. Increased agitation of the potassium hydroxide solution increases the percentage of gas absorbed by diminishing the thickness of the stationary films  $\delta_1$  and  $\delta_2$ . The proportion of gas absorbed appears to be related to the velocity of the air stream by an equation of the form  $\log . p_i/(p_i - p_{ii}) = K \sqrt{V}$ . R. J. C.

**Hydrolysis in Absolute and Aqueous-Alcoholic Solutions.** ERIK HÄGGLUND (*J. Chim. phys.*, 1912, 10, 207—240).—Conductivity measurements were made at 18° on sodium, potassium, and ammonium hydroxides and a number of organic acids, bases, salts, ketones, and pseudo-acids dissolved in 99.8% and 80% ethyl alcohol. The conductivities at infinite dilution, ionic mobilities, affinity-coefficients, degrees of ionisation and hydrolysis, percentage enolisation of ketones, etc., were computed in the conventional manner, partly from the author's data and partly from Godlewski's results (*Abstr.*, 1904, ii, 701).

With all the ions studied, the mobility is less in alcoholic solution than in pure water, but, except in the cases of the ions  $H^+$  and  $OH^-$ , the mobility is higher in 99.8% alcohol than in 80%. Ostwald's dilution law holds for salicylic acid, cinnamic acid, acetic acid, *p*-nitrophenol, piperidine, ammonia, piperazine, and diethylamine in alcoholic solutions, and therefore, contrary to the conclusion arrived at by Wakeman (1893) and Lincoln (1899), the dissociation takes place in accordance with the law of mass action. The dissociation constants of the above substances decrease as the percentage of alcohol increases.

The conductivities of aniline salicylate,  $\alpha$ -picoline salicylate,

piperidine salicylate,  $\alpha$ -picoline acetate, ammonium acetate, and ammonium *p*-nitrophenoxide in 80% alcohol, and of aniline salicylate, piperidine salicylate, morphine salicylate, ammonium salicylate, morphine cinnamate, ammonium cinnamate, piperidine acetate, aniline acetate, diethylanmonium cinnamate in 99·8% alcohol were used to calculate the degree of hydrolysis of these salts, making an approximate allowance for the ionisation of the non-hydrolysed part. The hydrolytic dissociation of the above salts increases as the concentration of the alcohol increases. The ionic product of 80% alcohol is calculated to be  $1\cdot27 \times 10^{-15}$ , and of 99·8% alcohol,  $0\cdot5 \times 10^{-15}$ .

The percentage enolisation of acetylacetone, styryl methyl ketone, benzophenone, and benzoin by sodium hydroxide in 99·8% alcohol can be calculated from conductivity measurements. Benzoin is slowly enolised in 80% alcohol also. The neutralisation of the pseudo-acid  $\omega$ -nitrostyrene by sodium hydroxide is a bimolecular reaction, which proceeds more rapidly in 80% than in 99·8% alcohol (compare Meisenheimer and Heim, *Abstr.*, 1905, i, 269). The same is true of the reaction between trinitrotoluene and sodium hydroxide. The neutralisation of trinitrobenzene, dinitroaniline, dinitrotoluene, and nitrophenylhydrazine in alcoholic solution was also examined by the conductivity method.

R. J. C.

**Influence of Salts on the Solubility of Ethyl Acetate in Water, Considered as a Neutral Salt Action.** HARALD LUNDÉN (*Medd. K. Vetensk. Nobelinst.*, 1912, 2, No. 15, 1—10).—The influence of sodium and potassium chlorides, and of the corresponding nitrates in different concentrations on the solubility of ethyl acetate has been measured at 25°. The results are compared with the influence of the same salts on the catalysis of ethyl acetate by hydrochloric acid, on the solubility of benzoic acid (Hoffmann and Langbeck, *Abstr.*, 1905, ii, 374), and on the freezing point of solutions of ethyl acetate (Rivett, *this vol.*, ii, 130). The magnitude of the effect of the chlorides is very similar and greater than that of the nitrates, which have an almost identical effect. The results appear to indicate a specific influence which is different for different kinds of neutral salt effect.

G. S.

**Linear Velocity of Crystallisation in Capillary Tubes.** K. GRINAKOVSKY (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 788—801).—The author has investigated the influence of the diameter of a capillary tube on the velocity of crystallisation in the tube of the following compounds: formanilide, diphenylamine,  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , benzophenone, and mixtures of 100 mols. of benzophenone with 1·7, 4, and 8 mols. of salicylic acid. The diameters of the tubes used ranged from 0·06 mm. to 4 mm.

The results show that for substances which crystallise rapidly, the diameter of the capillary has a positive effect on the velocity of crystallisation in the region where the velocity-temperature curve is rising, that is, the velocity is increased by diminution of the diameter ;

for the falling part of the curve the effect is a negative one. For pure substances diminution of the diameter of the capillary displaces the maximum velocity of crystallisation in the direction of the melting point, the region of constant velocity decreasing so that the flat maximum is transformed into a pointed one. In the case of benzo-phenone, increase in the proportion of admixed substance exercises a marked influence in the falling portion of the velocity-temperature curve, where the effect of the diameter of the tube is negative; the extent of this influence increases as the radius of the tube decreases.

T. H. P.

**History of Colloid Chemistry.** P. P. VON WEIMARN (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 65—74).—A claim by the author to have been the first to give definite expression to the theory of the crystalline nature of colloids. As a supplement to the paper numerous extracts are given from Frankenheim's work, *The Doctrine of Cohesion* (Breslau, 1835).

H. M. D.

**Negative Adsorption Isotherms.** KNUD ESTRUP (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 8—12).—Previous experiments have shown the occurrence of cases of negative adsorption, and, as examples of this phenomenon, the adsorption of ammonium iodate and potassium iodate from alkaline solution and of ammonium chromate from acid and alkaline solutions has been examined in detail.

H. M. D.

**The Swelling Pressure.** E. POSNJAK (*Koll. Chem. Beihefte*, 1912, 3, 417—456).—The nature of the reversible swelling change which occurs when certain colloidal substances, such as caoutchouc and gelatin, are brought into contact with appropriate liquids has been examined by a series of measurements of the influence of pressure on the process. In the apparatus employed for these determinations, a weighed quantity of the swelling substance, in the form of a solid cake, is placed at the bottom of a cylindrical glass tube, provided at the base with a porous earthenware diaphragm, through which communication is established with the swelling liquid contained in an outer vessel. The disk of caoutchouc (or gelatin) is in contact with mercury, which completely fills the glass cylindrical tube, and partly a calibrated side-tube of small diameter, which is sealed on at right angles to the vertical wider tube. The position of the end of the mercury column in the side-tube enables the volume of the swollen substance to be determined at any time, and by means of a gas pressure cylinder and a manometer, the pressure inside the apparatus can be adjusted and measured. With this apparatus, the swelling of caoutchouc in a number of organic liquids and of gelatin in water has been examined up to pressures of about six atmospheres.

In all cases it is found that a definite condition of equilibrium between the swollen substance and the external swelling liquid is attained at a given pressure.

The connexion between the equilibrium pressure,  $p$ , and the concentration,  $c$ , of the swelling substance, expressed in grams per 1000 c.c.

of caoutchouc (or gelatin) + swelling liquid, is given by  $p = p_1 c^k$ , where  $p_1$  and  $k$  are constants. The value of  $k$  is approximately 3, varying from 2.48 in the case of cymene to 3.33 for ethylene chloride. On the other hand,  $p_1$  varies very considerably, according to the nature of the colloid and of the swelling liquid.

For a given pressure, the swelling capacity of different liquids towards caoutchouc, as measured by the percentage amount of liquid which is taken up by the caoutchouc at this pressure, diminishes in the following order: carbon tetrachloride, chloroform, tetrachloroethane, acetylene dichloride, thiophen, toluene, benzene, cymene, cumene, ethylene chloride, ethyl ether.

The method of investigation described has also permitted of approximate measurements of the velocity of the swelling process. The data agree with the equation for a unimolecular change, a result which accords with previous observations.

The general character of the results obtained seems to show that the swelling of colloids is in the nature of a capillary process rather than of a simple phenomenon of solution. H. M. D.

**Adsorption. VI. Kinetics of the Hydration and Dehydration of Colloids.** ADAM W. RAKOWSKI (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 836—849. Compare this vol., ii, 743).—The velocity of adsorption, not only of water, but also of substances dissolved in water, exhibits peculiar relations. Adsorption is very rapid at first, but it soon diminishes very considerably, and sometimes continues to proceed slowly for a very long period; thus, with starch, two-thirds of its water is taken up (or lost) during the first twenty-four hours, the remaining one-third requiring two months, the second half of which corresponds with only one-fiftieth of the total amount of water. It is hence evident that adsorption is a complex reaction, and cannot be represented by any simple equation; the equation for unimolecular reactions gives values diminishing as the time increases.

The author supposes that the adsorbing gel consists of two solutions, which are probably not independent, but one of which increases at the expense of the other. For the sake of simplicity it is, however, assumed that the two solutions take up or lose water independently of one another. At time  $t=0$ , the amount of water in the gel is taken as  $a$ , this being the sum of the amounts  $a_1$  and  $a_2$  in the two solutions. At any other time, the content of water will be given by  $x = x_1 + x_2$ . If  $k_1$  and  $k_2$  represent the coefficients of dehydration (or hydration) of the two solutions:  $-dx_1/dt = k_1 x_1$  and  $-dx_2/dt = k_2 x_2$ , so that

$$x = a_1 e^{-k_1 t} + a_2 e^{-k_2 t}.$$

Similarly, for hydration,  $x = a - a_1 e^{-k_1 t} - a_2 e^{-k_2 t}$ .

These two approximate formulæ give numbers agreeing satisfactorily with the results of experiments on the hydration and dehydration of potato starch, rice starch, blood charcoal, cotton wool, and gelatin.

The author is not of opinion that the cusp exhibited by the hydration and dehydration curves of silicic acid gels can be regarded as sufficient proof that these curves are each composed of two intersecting branches (compare Tschermak, *Abstr.*, 1905, ii, 816).

T. H. P.

**Precipitation of Colloidal Silver by Metal Plates.** MAURICE PHILIPPSON (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 49—51).—Colloidal silver, prepared by cathodic disintegration, is gradually precipitated when carefully cleaned plates of copper and zinc are introduced into the solution of the hydrosol. Sheets of gold and platinum are without action. It is shown that the precipitation occurs at the surface of the metal, and is not due to traces of dissolved substances. The precipitation is probably due to the discharge of the colloidal particles, and the difference in the behaviour of the metals to the difference in the values of the electrolytic solution pressure. H. M. D.

**Influence of Colloids on the Transport Numbers and Conductivity of Certain Electrolytes.** PAUL RICHTER (*Zeitsch. physikal. Chem.*, 1912, 80, 449—477).—Peptone, gum arabic, gelatin, and agar-agar diminish the transport number of the anion in solutions of lithium chloride, potassium chloride, and hydrochloric acid, and also diminish to some extent the electrical conductivity of the same electrolytes. The magnitude of the effects in question increases with the concentration of the colloid, and depends also on the nature of the colloid. The effect on the transport numbers are in the order of diminishing activity: agar-agar, gelatin, gum arabic, peptone; on the conductivity the order is agar-agar, peptone, gelatin, gum arabic. The colloids in question also increase the viscosity of the electrolyte solutions as measured by the rate of flow; the results of the measurements are given in detail. In solution, peptone, gum arabic, and agar-agar are negatively, gelatin positively, charged. G. S.

**Formation of Solid Solutions of Alkali Salts by Diffusion in the Solid State.** GIUSEPPE BRUNI and D. MENEGHINI (*Atti R. Inst. Veneto Sci.*, 1911, 71, 195—202).—The authors have shown previously (Abstr., 1911, ii, 703, 860) that metallic solid solutions may be obtained by a process of interdiffusion of the component metals in the solid state.

They now give the results of similar experiments on mixtures of sodium and potassium chlorides. Confirmation is obtained of Kurnakoff and Schemtschuschny's results (Abstr., 1906, ii, 443) with reference to the decomposition at low temperatures of solid solutions of sodium and potassium chlorides and to the heat of formation of these solutions. It is found also that mechanical mixtures of these salts, when suitably heated, give solid solutions as a result of diffusion in the crystalline condition. Such diffusion takes place with moderate rapidity at 600°, and more slowly at 500°.

Slow cooling of the fused mixtures or slow decomposition of the tempered mixed crystals is accompanied by the formation of eutectoid mixtures, which diffuse decidedly more rapidly than those prepared by mechanical means. This result is shown to be in accord with the theory of solid colloids. T. H. P.

**The Theory of Vulcanisation of Caoutchouc.** HEINRICH LOEWEN (*Zeitsch. angew. Chem.*, 1912, 106, 1553—1560).—A review of the subject of vulcanisation, with special reference to Ostwald's

adsorption hypothesis (Abstr., 1910, ii, 272, 697), leading to the conclusion that the process is purely chemical, and that adsorption does not play any part.

C. H. D.

**The Theory of Vulcanisation.** HEINRICH LOEWEN (*Zeitsch. angew. Chem.*, 1912, 25, 1610—1612).—A criticism of the results obtained by Spence and Scott (Abstr., 1911, i, 657). The conclusion is drawn that the assumption of adsorption is unnecessary.

C. H. D.

**Elementary Demonstration of the Law of Mass Action.** A. BERTHAUD (*Compt. rend.*, 1912, 155, 343—344).—A mathematical demonstration of this law.

W. G.

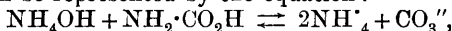
**Chemical Equilibrium of the System Ammonia Gas and Ethylenediamine Hydrochloride.** FÉLIX BIDEZ (*Compt. rend.*, 1912, 155, 279—280. Compare Abstr., 1901, i, 634; 1905, i, 686).—A study of the behaviour of ethylenediamine hydrochloride in the presence of ammonia gas and of ethylenediamine in the presence of ammonium chloride, the pressures being measured at various temperatures, and the measurements made in an apparatus already described (*loc. cit.*). In the first case, if the hydrochloride is in large excess it remains bright and there is no trace of liquid, a basic compound being probably formed between the ethylenediamine and its unchanged hydrochloride. With an excess of ammonia the salt diminishes in volume and becomes impregnated with a colourless, oily liquid, and the equilibrium pressure varies. In the second case, on mixing the ammonium chloride and ethylenediamine together, a portion of the solid disappears, and there is a rapid evolution of gas. A table of pressures observed in the two cases is given.

W. G.

**The Equilibrium between Ammonium Carbonate and Ammonium Carbamate in Aqueous Solution at 25°.** GEORGE H. BURROWS and GILBERT N. LEWIS (*J. Amer. Chem. Soc.*, 1912, 34, 993—995).—0.2- and 0.05-Molar solutions of ammonium carbamate were sealed up in glass tubes and placed in a thermostat at 25° for twelve to twenty-four hours to ensure equilibrium being attained. The tubes were then cooled in ice-water, and the carbonate formed was precipitated by the addition of an ice-cold solution of barium chloride containing a little ammonia. The precipitate was collected in a porous alundum crucible, and washed with cold water to free it from carbamate. The carbonate was then determined in the precipitate and the carbamate in the filtrate. This method of determining the equilibrium is accurate if the precipitation and washing of the precipitate does not take longer than half-an-hour, since a solution of barium carbamate, if kept cold, will remain clear for that length of time.

When equilibrium is attained the 0.05- and 0.2-molar solutions contain approximately 90 and 80 molar % of carbonate respectively; a solution made by dissolving 1 gram of carbamate in 1.5 grams of water contains 39.2 molar % of carbonate at the equilibrium point (compare Fenton, Abstr., 1886, 501).

Assuming that carbamic acid is a very weak acid, the ammonium salt would be almost completely hydrolysed. The equilibrium in solution would then be represented by the equation :



hydrolysis of the ammonium carbonate being prevented by the ammonium hydroxide formed from the ammonium carbamate. It follows that the square of the carbamate concentration should be roughly proportional to the cube of the carbonate concentration, and the figures obtained show that this is approximately the case.

T. S. P.

**Potassium Permanganate and Manganate in Aqueous Solution.** OTTO SACKUR and W. TAEGENER (*Zeitsch. Elektrochem.*, 1912, 18, 718—724).—The equilibrium relations in permanganate and manganate solutions have been determined by electrochemical methods. The normal potential of the change  $\text{MnO}_4' + \ominus = \text{MnO}_4''$  is +0.61 volt, and that of the change  $\text{MnO}_4'' + 2\text{H}_2\text{O} + 2\ominus = \text{MnO}_2 + 4\text{OH}'$  is +0.51 volt at 18°. By means of these results and the normal potential of oxygen, the equilibrium constants of the following reactions have been calculated:  $2\text{KMnO}_4 + 2\text{KOH} = 2\text{K}_2\text{MnO}_4 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$  (1);  $3\text{K}_2\text{MnO}_4 + 2\text{H}_2\text{O} = 2\text{KMnO}_4 + \text{MnO}_2 + 4\text{KOH}$  (2);  $\text{K}_2\text{MnO}_4 + \text{H}_2\text{O} = \text{MnO}_2 + 2\text{KOH} + \frac{1}{2}\text{O}_2$  (3). In agreement with experience it was found that the equilibrium points in the first and third reactions in alkaline solution, in the second reaction in neutral and acid solution, lie very near the right-hand side. The establishment of equilibrium in the first and third reactions is slow.

The solubility of potassium permanganate in water and in solutions of potassium carbonate, hydroxide, and chloride of different concentrations has been determined at intervals between 0° and 90°, as well as the solubility of potassium manganate in potassium hydroxide solutions from 0° to 80°. The results correspond with those to be expected from the influence of salts with a common ion on the solubility.

G. S.

**Equilibrium of the Reaction between Metallic Silver and Ferric Nitrate.** ARTHUR A. NOYES and B. F. BRANN (*J. Amer. Chem. Soc.*, 1912, 34, 1016—1027).—The equilibrium constant at 25° of the reaction  $\text{Ag} + \text{Fe}(\text{NO}_3)_3 \rightleftharpoons \text{AgNO}_3 + \text{Fe}(\text{NO}_3)_2$  has been determined by analysis of the equilibrium mixture, which in many cases contained nitric acid. The results show that the effect on the equilibrium constant of increasing the concentration of nitric acid is quite marked up to 0.02*N*, but that the concentration of the acid can then be further increased considerably without appreciable effect. As may be expected, the time required for equilibrium to be attained depends on the fineness of the state of division of the silver.

The values of the equilibrium constant vary considerably with the concentration of the solution, but by extrapolating to zero concentration, the value 0.128 is found for the expression  $(\text{Fe}^{++})(\text{Ag}^+)/(\text{Fe}^{+++})$ .

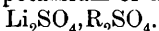
The potentials of the ferrous-ferric electrode and of the silver electrode at 25° were found to be -0.456 and -0.516 respectively,

values which are in good agreement with those previously obtained by Maitland (Abstr., 1906, ii, 328) and Lewis (Abstr., 1906, ii, 262).

From the equilibrium constant and the potential of the silver electrode, the potential of the ferrous-ferric electrode was calculated to be  $-0.463$ , in fair agreement with that derived from the direct electromotive force measurements.

T. S. P.

**Equilibrium of Lithium Sulphate and the Alkali Sulphates in Their Mixed Solutions.** (Mlle.) CÉCILE SPIELREIN (*Compt. rend.*, 1912, 155, 346—348).—Lithium sulphate, in solution at  $20$ — $25^{\circ}$ , gives definite compounds with each of the other alkali sulphates. The isothermal curves, showing the composition of the solutions in equilibrium with a solid phase, consist of three branches cutting at two points, which are constant if the temperature is constant. At one point the solution is in equilibrium with the double salt, and at the other with one of the simple salts. Sodium sulphate gives a double salt,  $\text{Li}_2\text{SO}_4 \cdot 3\text{Na}_2\text{SO}_4 \cdot 12\text{H}_2\text{O}$ , quite different in composition from that given by potassium or ammonium sulphate,



It effloresces in air and loses all its water after remaining three days over calcium oxide.

W. G.

**Mutual Solubility of Sulphates and Carbonates in the Solid State at High Temperatures.** MARIO AMADORI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 65—71).—The melting-point curve of the system  $\text{Li}_2\text{CO}_3$ — $\text{Li}_2\text{SO}_4$  consists of two branches meeting in a minimum at  $540^{\circ}$ , corresponding with 60% mol.  $\text{Li}_2\text{SO}_4$ . The solubility of the carbonate in the sulphate is from 0 to 10 mol. %, and the sulphate has probably a similar solubility in the carbonate. With the sodium salts, the solubility is complete, and the crystallisation curve shows a minimum; the transformation point of the sulphate is lowered by addition of the carbonate. The potassium salts exhibit complete solubility, and the curve of crystallisation lies entirely between the melting points of the two salts; the transformation point of the sulphate is raised by addition of the carbonate.

T. H. P.

**The System Iron-Carbon.** OTTO RUFF (*Zeitsch. Elektrochem.*, 1912, 18, 761—764. Compare Abstr., 1911, ii, 897; Smits, this vol., ii, 165).—Polemical against Smits (*loc cit.*). The author and Smits agree that in the iron-carbon system at least two other carbides besides  $\text{Fe}_3\text{C}$  exist, and differ only with regard to the composition of these compounds and the temperatures at which they exist. Smits has overlooked the fact that all the author's experiments were made in a graphite crucible at constant temperature up to complete saturation with carbon, and his thermodynamical conclusions are for this reason partly invalid. The interpretation of the curve is discussed in detail, and it is shown that there is no sufficient basis for Smits' assumption of the occurrence of a second form of graphite.

G. S.

**Critical End-points in Ternary Systems.** ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 184—192).—The former investigation of ternary systems (Abstr., 1910, ii, 1050) has now been extended to the cases in which (b) two of the binary systems contain critical end-points, but the solid phase concerned is the same in both systems; (c) the solid phase is different, so that the critical end-point curve comes in contact with a eutectic line; (d) the binary systems all possess critical end-points; (e) mixed crystals are present; (f) a binary compound appears as a solid phase.

C. H. D.

**Thermal Analysis of Binary Mixtures of the Chlorides of Univalent Elements.** IV. CARLO SANDONNINI and G. SCARPA (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 77—84. Compare this vol., ii, 162).—This paper deals with the systems CsCl—CuCl, CsCl—AgCl, and CsCl—TlCl. The first of these forms the compounds, 3CsCl, CuCl, decomposing on fusion, and CsCl, 2CuCl, melting unchanged at 274°. The second system yields the compound CsCl, AgCl, decomposing on melting, whilst caesium and thallous chlorides form mixed crystals in all or nearly all proportions.

T. H. P.

**Thermal Analysis of the System Cuprous Chloride—Cupric Chloride.** CARLO SANDONNINI (*Chem. Zentr.*, 1912, i, 1813—1814; from *Atti R. Inst. Veneto Sci.*, 1912, 71, ii, 553—559).—Mixtures containing more than 33 mol. % of cupric chloride lose chlorine on fusion until that proportion is reached. Mixtures containing less chlorine have a eutectic point at 380°, the eutectic containing 16.5 mol. % CuCl<sub>2</sub>. Cuprous chloride can retain about 6% of cupric chloride in solid solution. There is no evidence for the formation of a compound.

C. H. D.

**Anhydrous Sulphates.** III. GENNARO CALCAGNI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 71—77. Compare Abstr., 1910, ii, 1064; this vol., ii, 761).—Thermal study of the system SrSO<sub>4</sub>—Na<sub>2</sub>SO<sub>4</sub> indicates the formation of a compound, SrSO<sub>4</sub>, 3Na<sub>2</sub>SO<sub>4</sub>, which is of the type of vanthoffite, and corresponds with a maximum on the melting curve in the region of mixed crystals. With the system SrSO<sub>4</sub>—K<sub>2</sub>SO<sub>4</sub>, the melting-point curve shows a maximum corresponding with 95 mol. % of potassium sulphate, and also indicates the formation of the compound SrSO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>, which is the product of a reaction occurring in the solid state with a marked thermal effect.

T. H. P.

**Anhydrous Sulphates.** IV. GENNARO CALCAGNI and D. MAROTTA (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 93—97).—The results of thermal investigations indicate that lithium sulphate forms no compound with either barium or strontium sulphate and, indeed, no anhydrous or hydrated double or triple sulphate containing lithium sulphate as component is known. Lithium sulphate, therefore, behaves quite differently from the sulphates of other metals of the same group.

The types of anhydrous double sulphates of alkaline earth and alkali metals obtained under the experimental conditions used in this and similar investigations are  $M''SO_4, 3M'SO_4$ ;  $M''SO_4, M'SO_4$ , and  $2M''SO_4, M'SO_4$ , these being exclusively the types occurring naturally. From a geological point of view it is interesting to note that some of these double sulphates are formed by contact of their solid components at high temperatures.

T. H. P.

### Eutectic Alloys of Arsenic and Antimony Tri-iodides.

ALEXIS M. VASILIEFF (*J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1076—1078). Calculation of the composition of the eutectic alloy of arsenic and antimony tri-iodides according to Flawitzky's law (Abstr., 1906, ii, 152) gives the following results.

The lowering of the melting point of iodine by arsenic penta-iodide is:  $T_0 = 116 - 70 = 46^\circ$ , and the lowering of that of the tri-iodide,  $T_1 = 146 - 70 = 76^\circ$ . Then  $n_0$  being 2,  $M_0$  126.92, and  $M_1$  455.9,  $n_0^2 M_0 T_0 / M_1 T_1 = 0.6743$ , or approximately 2:3. Similarly, in the case of antimony, the value is 0.4141, or approximately 2:5. So that, if arsenic and antimony tri-iodides form a eutectic, the latter should answer the condition:  $n_2^2 M_0 T_0 / M_1 T_1 = 3:5$ . The eutectic prepared by cooling melts at  $135^\circ$ , and calculating from the expression just given,  $n_0 = 1.4692$ , that is, the eutectic should have the composition  $SbI_3, 1.4692AsI_3$ . Actual analysis of the eutectic corresponds with  $SbI_3, 1.4668AsI_3$ .

T. H. P.

### Experiments with Binary Systems of Silicates.

PETER LEBEDEF (Jahrb. Min., 1912, i, Ref. 386; from *Ann. Inst. Polytechn. St. Petersburg*, 1911, Abt. I, 15, 691—720).—The system olivine + diopside (selected as composed of minerals with analogous physico-chemical properties) shows a minimum melting point at  $1271^\circ$ , the eutectic consisting of 40 mol. % olivine and 60 mol. % diopside (m. p. diopside  $1363^\circ$ , olivine over  $1600^\circ$ ). The system wollastonite + anorthite (minerals with dissimilar physico-chemical properties) gives a eutectic of 30 mol. % anorthite + 70 mol. % wollastonite with m. p.  $1285^\circ$ , that is,  $225-230^\circ$  lower than that of wollastonite, and  $180-190^\circ$  lower than that of anorthite. A fusion of a mixture of aegirite and anorthite gave a felspar (between andesine and labradorite), in addition to the original components; and a mixture of olivine and anorthite produced also some diopside.

L. J. S.

**Fusion Experiments with Calcium and Magnesium [and Potassium] Silicates and Sulphates.** A. GINSBERG (*Jahrb. Min.*, 1912, i, Ref. 386; from *Ann. Inst. Polytechn. St. Petersburg*, 1906, Abt. I, 6, 489—505).—Potassium sulphate solidifies at  $1065^\circ$ . The system  $K_2SO_4 + MgSO_4$  shows a eutectic point at  $718^\circ$ , corresponding with 39.8 mol. %  $MgSO_4$ . With more magnesium sulphate, the fusion point increases to a maximum at  $922^\circ$  with 66.6 mol. %  $MgSO_4$ , corresponding with the langbeinite formula  $2MgSO_4, K_2SO_4$ .

Calcium metasilicate solidifies at  $1512^\circ$ . The system  $CaSiO_3 + MgSiO_3$  has a eutectic point between wollastonite and diopside, and the material shows in thin section a granophyric intergrowth of the

two constituents. The minimum fusion point is  $1270^{\circ}$ , with 35 mol. %  $\text{MgSiO}_3$ .  
L. J. S.

**Systems formed by Fluorobenzene with Antimony Trichloride and Tribromide.** BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1102—1107).—In view of the fact that, in many of its physical properties, fluorobenzene is more similar to benzene than to chlorobenzene, etc., the author has investigated its relations to antimony trichloride and tribromide.

Fluorobenzene has the m. p.  $-39.2^{\circ}$ , which is much nearer to that of chlorobenzene ( $-47^{\circ}$ ) than to that of benzene ( $+5.6^{\circ}$ ). With antimony trichloride it forms the hygroscopic compound,  $\text{SbCl}_3 \cdot \text{C}_6\text{H}_5\text{F}$ , which crystallises in long, white plates, m. p. about  $+10^{\circ}$  (decomp.), and in the air liquefies in a few seconds. At  $-40.5^{\circ}$ , the eutectic  $\text{SbCl}_3 \cdot 96\text{C}_6\text{H}_5\text{F}$  is formed, and this decomposes on melting and gives with the trichloride a transition point at  $5.5^{\circ}$ , corresponding with  $\text{SbCl}_3 \cdot 2.32\text{C}_6\text{H}_5\text{F}$ .

Antimony tribromide forms no compound with fluorobenzene, and the diagram of the system consists of two branches, meeting at the eutectic point,  $-39.5^{\circ}$ , which corresponds with  $\text{SbBr}_3 \cdot 286\text{C}_6\text{H}_5\text{F}$ . The long branch shows a characteristic bend, probably due to incipient interaction of the components.

It is evident that these systems have nothing in common with those containing benzene (Abstr., 1911, i, 273), but are completely analogous to those formed by chlorobenzene (*ibid.*), this analogy extending to the melting points of the compounds formed and to the eutectic temperatures and compositions.  
T. H. P.

**Benzenesulphonic Acid and Antimony Trihaloids.** BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1108—1112).—Benzenesulphonic acid and antimony trichloride form no compound, the concentration-temperature diagram consisting of two branches intersecting at the eutectic point,  $13^{\circ}$ , which corresponds with the composition  $\text{SbCl}_3 \cdot 1.32\text{Ph} \cdot \text{SO}_3\text{H}$ .

Antimony tribromide dissolves less easily than the trichloride in benzenesulphonic acid, and here, too, no compound is formed. The two branches of the curve meet at the eutectic temperature  $44^{\circ}$ , corresponding with  $\text{SbBr}_3 \cdot 3.9\text{Ph} \cdot \text{SO}_3\text{H}$ .

Thus, whilst the introduction of other acid radicles into the benzene molecule lowers its ability to combine with antimony trichloride and tribromide, the introduction of the sulphonic group destroys this ability completely.  
T. H. P.

**Systems Formed by Antimony Trichloride and Tribromide with Naphthalene and its Derivatives.** BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1079—1101).—With antimony tribromide and trichloride, naphthalene readily forms the compounds  $2\text{SbX}_3 \cdot \text{C}_{10}\text{H}_8$ , and the temperature-concentration diagrams of the corresponding systems are similar to those given by benzene (Abstr., 1911, i, 273) and by diphenyl and diphenylmethane (this vol., i, 177) with these salts. These diagrams are typical for the formation from

the components of one compound, that is, they exhibit two eutectic points, between which lies a temperature-maximum, corresponding with the melting point of the compound:  $2\text{SbCl}_3, \text{C}_{10}\text{H}_8$ , m. p.  $86^\circ$ , and  $2\text{SbBr}_3, \text{C}_{10}\text{H}_8$ , m. p.  $66^\circ$ . The eutectic points and the corresponding compositions ( $n$  = mols. of hydrocarbon per mol.  $\text{SbX}_3$ ) are as follows:

	M. p. hydro- carbon.	1st eutectic point.		2nd eutectic point.		M. p. $\text{SbX}_3$ .
		Tem- perature.	$n$ .	Tem- perature.	$n$ .	
$2\text{SbCl}_3 - \text{C}_{10}\text{H}_8$ .....	$79.4^\circ$	$59^\circ$	2.35	$65^\circ$	0.113	$73^\circ$
$2\text{SbBr}_3 - \text{C}_{10}\text{H}_8$ .....	$79.4$	57	1.78	65	0.43	94

The compound  $2\text{SbCl}_3, \text{C}_{10}\text{H}_8$  forms rhombic plates, and  $2\text{SbBr}_3, \text{C}_{10}\text{H}_8$ , rhombohedra or rhombic or hexagonal plates; both are virtually non-deliquescent. The former compound was described by Watson Smith and Davis (Trans., 1882, 41, 411), but these authors ascribed to it the erroneous composition  $3\text{SbCl}_3, 2\text{C}_{10}\text{H}_8$ .

The system  $\text{SbCl}_3 - \alpha\text{-C}_{10}\text{H}_7\text{Cl}$  forms the compound  $2\text{SbCl}_3, \text{C}_{10}\text{H}_7\text{Cl}$ , in rhombic plates, m. p.  $46^\circ$ . The first eutectic point lies at about  $-21^\circ$ , the composition being  $\text{SbCl}_3, 15.7\text{C}_{10}\text{H}_7\text{Cl}$ , whilst the second is almost coincident with the m. p. of the compound, namely,  $46^\circ$ , the corresponding composition being  $\text{SbCl}_3, 0.47\text{C}_{10}\text{H}_7\text{Cl}$ .  $\alpha$ -Chloronaphthalene has m. p.  $-17^\circ$ .

The system  $\text{SbBr}_3 - \alpha\text{-C}_{10}\text{H}_7\text{Cl}$  forms no compound, and the diagram exhibits only a eutectic point at about  $-24.5^\circ$  corresponding with the composition  $\text{SbBr}_3, 7.6\text{C}_{10}\text{H}_7\text{Cl}$ .

With  $\text{SbCl}_3 - \beta\text{-C}_{10}\text{H}_7\text{Cl}$ , a compound is not always formed, and it is possible, by seeding the carefully cooled solution, to obtain a curve with only two branches meeting at a eutectic point corresponding with the composition  $\text{SbCl}_3, 0.96\text{C}_{10}\text{H}_7\text{Cl}$ . Rapid cooling of solutions containing 52—64%  $\text{SbCl}_3$  in ice-water leads to the formation of the compound  $\text{SbCl}_3, \text{C}_{10}\text{H}_7\text{Cl}$ , m. p.  $29.5^\circ$ , in rhombic plates or rhombohedra. The eutectic points then lie at (1)  $25^\circ$ ,  $\text{SbCl}_3, 1.27\text{C}_{10}\text{H}_7\text{Cl}$ , and (2)  $28^\circ$ ,  $\text{SbCl}_3, 0.78\text{C}_{10}\text{H}_7\text{Cl}$ .

The system  $\text{SbBr}_3 - \beta\text{-C}_{10}\text{H}_7\text{Cl}$  gives no compound, and the diagram consists of two curves intersecting at the eutectic point  $37.5^\circ$ , the corresponding composition being  $\text{SbBr}_3, 1.88\text{C}_{10}\text{H}_7\text{Cl}$ .

The system  $\text{SbCl}_3 - \alpha\text{-C}_{10}\text{H}_7\text{Br}$  yields the compound  $\text{SbCl}_3, \text{C}_{10}\text{H}_7\text{Br}$ , m. p.  $35^\circ$ , crystallising in long thin plates. The eutectic points are (1)  $-1^\circ$ ,  $\text{SbCl}_3, 12.1\text{C}_{10}\text{H}_7\text{Br}$ , and (2)  $31.5^\circ$ ,  $\text{SbCl}_3, 0.6\text{C}_{10}\text{H}_7\text{Br}$ . This system resembles  $\text{SbCl}_3, \text{C}_6\text{H}_5\text{Br}$  (Abstr., 1911, i, 273); in both, the compound formed undergoes marked dissociation at its melting point, as is shown by the flat maxima of the diagrams.

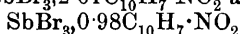
Antimony tribromide gives no compound with  $\alpha$ -bromonaphthalene, the diagram of the system showing a single eutectic point at  $-3.5^\circ$ , corresponding with  $\text{SbBr}_3, 3.8\text{C}_{10}\text{H}_7\text{Br}$ .

$\alpha$ -Bromonaphthalene is found to melt at  $3^\circ$ , which is somewhat lower than the m. p. usually given; the same is the case with the m. p. obtained for  $\alpha$ -nitronaphthalene, namely,  $57^\circ$ .

The system  $\text{SbCl}_3 - \alpha\text{-C}_{10}\text{H}_7\text{NO}_2$  gives the compound  $\text{SbCl}_3, \text{C}_{10}\text{H}_7\text{NO}_2$ , in rhombohedra or rhombic plates, m. p.  $39^\circ$ ; this is obtained, and

even then not always, only on prolonged cooling of solutions containing 36—72%  $\text{SbCl}_3$  at  $-20^\circ$ . The two eutectics separate at (1)  $30^\circ$ ,  $\text{SbCl}_3, 2.35\text{C}_{10}\text{H}_7\cdot\text{NO}_2$ , and (2)  $34.5^\circ$ ,  $\text{SbCl}_3, 0.49\text{C}_{10}\text{H}_7\text{NO}_2$ .

Antimony tribromide and  $\alpha$ -nitronaphthalene form a similar compound,  $\text{SbBr}_3, \text{C}_{10}\text{H}_7\cdot\text{NO}_2$ , m. p.  $38.2^\circ$ , but also only after intense cooling. The eutectics are: (1)  $\text{SbBr}_3, 2.01\text{C}_{10}\text{H}_7\cdot\text{NO}_2$  at  $33.5^\circ$ , and (2)



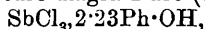
at  $38^\circ$ . The two outer branches of the temperature-concentration diagram may be prolonged to meet at a third eutectic point,  $23^\circ$ , corresponding with  $\text{SbBr}_3, 0.77\text{C}_{10}\text{H}_7\cdot\text{NO}_2$ . T. H. P.

**Systems Formed by *cyclo*Hexane and *cyclo*Hexene with Antimony Trichloride and Tribromide.** BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1137—1145).—Antimony trichloride does not form a compound with *cyclo*hexane. Addition of the salt to the hydrocarbon at first causes a very slight depression of the melting point, but the curve almost immediately rises to a maximum considerably higher than the melting point of either component, and then falls continuously to the melting point of the pure salt. Exactly similar relations are found with antimony tribromide and *cyclo*hexane.

Neither antimony trichloride nor tribromide gives a compound with *cyclo*hexene. The temperature-concentration diagrams are continuous curves exhibiting no maxima.

Thus, these two hydrocarbons differ from those of the aromatic series, all of these which have been examined giving molecular compounds with one or both of these salts. T. H. P.

**Antimony Trichloride and Tribromide in Their Relations to Phenol and Some of its Ethers.** BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1113—1127).—Antimony trichloride forms with phenol only one compound,  $2\text{SbCl}_3, \text{C}_6\text{H}_5\cdot\text{OH}$ , in deliquescent, colourless plates, m. p.  $37^\circ$ . The eutectic points of the concentration-temperature diagram are (1) at  $5^\circ$ ,



and (2) at  $36.5^\circ$ ,  $\text{SbCl}_3, 0.47\text{Ph}\cdot\text{OH}$ .

Antimony tribromide also gives but one compound,  $2\text{SbBr}_3, \text{Ph}\cdot\text{OH}$ , in rhombohedra-like crystals, m. p.  $66.5^\circ$ . The single eutectic is  $\text{SbBr}_3, 4.75\text{Ph}\cdot\text{OH}$ , m. p.  $28.5^\circ$ ; the third branch of the curve begins at the melting point of the compound, so that there is no second eutectic point.

Comparison of these two diagrams with those given by benzene (Abstr., 1911, i, 273) shows that replacement of one of the hydrogen atoms of benzene by hydroxyl has no influence on the type of compound formed, and but little on the form of the diagram.

von Schneider (Abstr., 1896, ii, 290) gave  $-37.8^\circ$  for the melting point of anisole, and Wroczynski and Guye (Abstr., 1910, ii, 699)  $-37.3^\circ$ . The author finds  $-34^\circ$ , his preparation probably being purer than those examined by these investigators.

Antimony trichloride forms two compounds with anisole: (1)  $\text{SbCl}_3, \text{Ph}\cdot\text{OMe}$ , rectangular, deliquescent plates, m. p.  $25.2^\circ$  (decomp.),

and (2)  $2\text{SbCl}_3 \cdot \text{Ph} \cdot \text{OMe}$ , long plates, m. p.  $41.5^\circ$ . The eutectic points lie at  $25^\circ$ ,  $\text{SbCl}_3 \cdot 1.2\text{Ph} \cdot \text{OMe}$ , and at  $40^\circ$ ,  $\text{SbCl}_3 \cdot 0.39\text{Ph} \cdot \text{OMe}$ . The tribromide gives only one compound, m. p.  $30.5^\circ$ , the eutectic points being  $35^\circ$ ,  $\text{SbBr}_3 \cdot 129\text{PhOMe}$ , and  $30^\circ$ ,  $\text{SbBr}_3 \cdot 0.96\text{Ph} \cdot \text{OMe}$  (compare Abstr., 1911, i, 532).

Phenetole melts at  $-28.5^\circ$ , and not at  $-33.5^\circ$ , as stated by von Schneider (Abstr., 1897, ii, 304). With antimony trichloride it forms one compound,  $\text{SbCl}_3 \cdot \text{Ph} \cdot \text{OEt}$ , in deliquescent, rhombic, or hexagonal plates, m. p.  $42.2^\circ$ . The eutectic points are (1)  $-29^\circ$ ,  $\text{SbCl}_3 \cdot 130\text{Ph} \cdot \text{OEt}$ , and  $30^\circ$ ,  $\text{SbCl}_3 \cdot 0.46\text{Ph} \cdot \text{OEt}$ . Antimony tribromide and phenetole give a similar diagram, the compound,  $\text{SbBr}_3 \cdot \text{Ph} \cdot \text{OEt}$ , forming rhombic plates, m. p.  $48.8^\circ$ ; the eutectic points lie at  $-29^\circ$ ,  $\text{SbBr}_3 \cdot 182\text{Ph} \cdot \text{OEt}$ , and  $47^\circ$ ,  $\text{SbBr}_3 \cdot 0.84\text{Ph} \cdot \text{OEt}$ .

Thus the systems formed by antimony trihaloids with phenol and its ethers exhibit marked similarity to those given by these salts with benzene and its alkyl derivatives.

T. H. P.

**The System Aniline-Antimony Trichloride.** BORIS N. MENSCHUTKIN (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1128—1136).—Antimony trichloride forms five compounds with aniline: (1)  $\text{SbCl}_3 \cdot 6\text{NH}_2\text{Ph}$ , m. p.  $7-8^\circ$  (decomp.); (2)  $\text{SbCl}_3 \cdot 4\text{NH}_2\text{Ph}$ , m. p.  $80^\circ$  (decomp.); (3)  $\text{SbCl}_3 \cdot 3\text{NH}_2\text{Ph}$ , m. p.  $88^\circ$ ; (4)  $\text{SbCl}_3 \cdot 2\text{NH}_2\text{Ph}$ , m. p.  $95^\circ$ , and (5)  $\text{SbCl}_3 \cdot \text{NH}_2\text{Ph}$ , m. p.  $100.5^\circ$ . These compounds increase in stability as the proportion of aniline present decreases, and it seems probable that they differ in structure from other molecular compounds formed by antimony trichloride. The temperature-concentration diagram shows the following points: eutectic points at (1)  $-7.2^\circ$ , about  $\text{SbCl}_3 \cdot 219\text{NH}_2\text{Ph}$ ; (2)  $87^\circ$ ,  $\text{SbCl}_3 \cdot 2.37\text{NH}_2\text{Ph}$ ; (3)  $89.5^\circ$ ,  $\text{SbCl}_3 \cdot 1.51\text{NH}_2\text{Ph}$ , and (4) about  $31^\circ$ ,  $\text{SbCl}_3 \cdot 0.33\text{NH}_2\text{Ph}$ , and a distectic point at  $77^\circ$ , about  $\text{SbCl}_3 \cdot 5.6\text{NH}_2\text{Ph}$ .

Other salts have been found to form a series of compounds with aniline (compare Abstr., 1907, ii, 751; also Kablukoff and Sachanoff, Abstr., 1910, i, 163).

T. H. P.

**Variation with Temperature of the Rate of a Chemical Change.** A. VERNON HARCOURT and WILLIAM ESSON (*Phil. Trans.*, 1912, A, 212, 187—204).—The velocity of the reaction between ferric chloride and stannous chloride in aqueous solution has been measured at temperatures between  $9^\circ$  and  $30^\circ$ . Potassium thiocyanate was added in large excess to the reaction mixture, and the speed of the change determined by measuring the time required for a definite colour change. In order to prevent the precipitation of stannic hydroxide from the solution, it was also found necessary to add excess of hydrochloric acid to the reaction mixture.

Denoting by  $t$  and  $t'$  the times required for the change in colour at the absolute temperatures  $\theta$  and  $\theta'$ , then it is found that the observed data are very satisfactorily represented by means of the relation  $t/t' = (\theta'/\theta)^m$ , in which  $m$  is a constant characteristic of the reaction.

The influence of the nature of the acid present on the velocity has also been examined, and it appears that the speed, although

accelerated by hydrochloric acid, is diminished by the addition of sulphuric acid, whilst nitric acid is without effect.

In an appendix it is shown that the results obtained by other observers for the influence of temperature on velocity of change can in many cases be more satisfactorily represented by means of the above formula than by the formulæ adopted by the authors. For some reactions, however, the data seem to show that  $m$  is not constant over the range of temperature covered by the experimental measurements.

H. M. D.

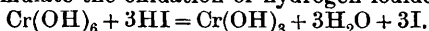
**Iron in Blood. II. Iron Poisons.** HRRMANN W. FISCHER and E. BRIEGER (*Zeitsch. physikal. Chem.*, 1912, 80, 412—448).—The effect of different substances on the rate of decomposition of hydrogen peroxide by ferrous salts has been further investigated as a function of the acidity and alkalinity of the solutions (compare this vol., ii, 269). A very large number of substances, including inorganic acids, phenols, hydrazine, cyanides, hydrogen sulphide, etc., have been used. The effects in general are comparatively small, and depend greatly on the degree of alkalinity or acidity of the solution. Arsenious oxide, hydrogen sulphide, hydrazine, and especially phenol are fairly strong poisons, as is carbon monoxide. The possible connexion of these results with the behaviour of blood poisons is discussed.

G. S.

**The Order of the Reaction between Hydriodic and Chromic Acids.** H. GOLBLUM and (Mme.) L. LEW (*J. Chim. phys.*, 1912, 10, 310—331. Compare De Lury, *Abstr.*, 1903, ii, 471).—The interaction was studied at 30° with concentrations of chromic and hydriodic acid ranging between 0.005 and 0.1 normal. Samples were taken at intervals and poured into twenty volumes of cold water to arrest the action during titration with thiosulphate. Calculated by van't Hoff's method, the order of the reaction is from 3.84 to 4.17. By Noyes' method, considering the first 1/8th of the action, the order is 4.2 to 4.4. By direct calculation of the velocity coefficients, those of the first, second, and third orders show an increasing tendency towards constancy. The conclusion is drawn that the reaction is quadrimolecular.

Applying Ostwald's "method of isolation," when a large excess of chromic acid is used, the reaction becomes termolecular, the velocity constant being proportional to the concentration of chromic acid at the commencement of the action. The velocity equation is therefore  $dx/dt = k(C_{CrO_3} - x)(C_{HI} - x)^3$ .

A solution of chromium trioxide contains several hydroxides in equilibrium, among which orthochromic acid may be supposed to figure. The authors formulate the oxidation of hydrogen iodide thus:



It is supposed that this action is made possible by the partial dissociation of orthochromic acid as a sexavalent base, and the above equation is abbreviated thus:  $Cr^{+++++} + 3I^- = Cr^{+++} + 3I$ .

The oxidation of hydrogen iodide is notably accelerated by hydrogen chloride. It proceeds 200 times as fast in *N*/10-hydrogen chloride solution. Since the ion  $H^+$  does not appear in the reaction equation,

the influence of hydrogen chloride must be of a catalytic nature. The presence of a large excess of hydrogen chloride converts the action from a quadrimolecular to a termolecular one. The products of the action and also certain salts, such as the nitrates of the rare earth metals and auric chloride, are without perceptible influence on the rate of oxidation.

R. J. C.

**Reactions of Double Decomposition in Organic Chemistry.** GIUSEPPE BRUNI [with ANGELO CONTARDI and COSTANTE DA PONTE] (*Atti R. Ist. Veneto Sci.*, 1911, 70, 921—936. Compare Abstr., 1906, i, 621).—With mixtures of ethyl acetoacetate and menthol in the molecular proportion 2 : 1, equilibrium is reached when 63·5% of the menthol is esterified, whilst with the proportions 3 : 1 and 4 : 1, 72·5% and 78·2% respectively of the menthol are esterified. The equilibrium is displayed by addition of one of the reagents, but not by change of temperature. The addition of sodium ethoxide effects a decided acceleration of the reaction.

The results have been calculated by means of the following equation, referring to non-equivalent quantities of the two reagents :

$K = [\log(A - x) - \log(B - x) - \log A - \log B] / 0.4343(A - B)\delta$ , and those obtained in the reverse reaction by the equation :  $K = x/A(A - x)\delta$ . All the values of  $K$  vary within certain limits, and in all cases decrease as the time increases, this result being doubtless connected with the browning taking place during the heating. Increase in the proportion of ethyl acetoacetate causes an increase in the values of  $K$  for the direct action, and a decrease in those for the inverse reaction. In the experiments where sodium ethoxide was present, the values of  $K$  were sensibly higher than, but varied similarly to, those obtained in the other experiments.

Two series of measurements with the molecular proportion 2 : 1 gave divergent results as regards the time of attainment of the equilibrium. This is probably due either to the presence of small and different proportions of free alcohol in the samples of ethyl acetoacetate used, or to varying catalytic effects of the different kinds of glass employed.

The results obtained on boiling a mixture of ethyl acetoacetate (1 mol.) and *isoamyl* nitrite (1 mol.) in a reflux apparatus show that the alkyl radicles undergo interchange to a considerable extent. Pfannl (Abstr., 1910, i, 480) made no reference to the work of Purdie (Trans., 1887, 51, 627) and a number of others on this subject. T. H. P.

**Velocity Coefficients of the Reaction between Ethyl Iodide and Silver Nitrate in Ethyl and Methyl Alcohols and Mixtures of these Solvents.** J. N. PEARCE and OTIS M. WEIGLE (*Amer. Chem. J.*, 1912, 43, 243—259. Compare Donnan and others, Trans., 1904, 85, 555; 1910, 97, 1882; Abstr., 1909, ii, 987).—The velocity coefficients of thirty-three of the possible combinations of concentrations, using 0.05, 0.025, and 0.0125 *N*-solutions of silver nitrate and ethyl iodide in ethyl alcohol, methyl alcohol, and three of their binary mixtures (25, 50, and 75% of methyl alcohol), have been determined. The bimolecular coefficients are only approximately constant, showing a decrease as the reaction proceeds; this decrease is more marked in

methyl alcohol as solvent and in the mixed solvents than in ethyl alcohol as solvent.

Comparison of the time-constant curves for any one pair of concentrations in the solvents used shows that ethyl alcohol has a greater influence on the reaction than has methyl alcohol, the curve showing a displacement towards the ethyl alcohol as solvent.

The coefficients are always greater in methyl alcohol than in ethyl alcohol as solvent.

For any given initial concentration of ethyl iodide, the bimolecular coefficients increase as the initial concentration of the silver nitrate increases. For a given initial concentration of silver nitrate, they decrease as the initial concentration of the ethyl iodide increases, but the change in the coefficients is very much less in the latter case.

The difference in the effects of the two reacting constituents, which is apparently due to the presence of an excess or large amount of silver nitrate, increases as the proportion of methyl alcohol in the solvent increases.

T. S. P.

**Rate of Formation of Sodium Acetothiosulphate.** SERGEI KRAPIWIN (*J. Chim. phys.*, 1912, 10, 289–305).—Carefully purified sodium chloroacetate and sodium thiosulphate in aqueous solution were allowed to interact at 25° thus:  $\text{CH}_2\text{Cl}\cdot\text{CO}_2\text{Na} + \text{Na}_2\text{S}_2\text{O}_3 = \text{NaCl} + \text{NaS}_2\text{O}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$ . With concentrations between 0.4*N* and 0.1*N* the course of the reaction is easily followed by titrating the excess of thiosulphate with iodine solution.

The reaction is bimolecular, and as the velocity diminishes with dilution, the conclusion is drawn that the undissociated molecules are concerned. An excess of thiosulphate produces an acceleration about twice as great as the acceleration produced by an equivalent excess of chloroacetate, because the thiosulphate is more dissociated and its sodium ions diminish the dissociation of the chloroacetate. When sodium chloride, bromide, or iodide is added, the reaction is accelerated for a similar reason. Sodium iodide, however, produces an unduly large acceleration, which is attributed to the formation of sodium iodoacetate.

Sodium sulphate produces a very marked acceleration equal to that produced by an equivalent quantity of extra sodium thiosulphate. This is explained as due to the two salts being about equally dissociated.

R. J. C.

**Velocity of Formation of Oxonium Dibromides in Different Organic Solvents. Rôle of the Medium in Chemical Kinetics.** WLADIMIR W. TSCHELINZEFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 865–895. Compare Abstr., 1911, i, 256; ii, 706).—The author has investigated the mechanism of the formation of oxonium dibromides and the influence of the nature of the solvent on the velocity constant of the reaction, the solvents used being chloroform, ethyl bromide, ethylene dibromide, and bromobenzene.

The formation of oxonium compounds, like that of ammonium and sulphonium compounds, follows the law for bimolecular reactions.

The velocity constants with 2·5- and 1·5-*N* concentrations of the reacting products are :

Solvent.	2·5 <i>N</i> .		1·5 <i>N</i> .	
	Actual constant.	Relative constant.	Actual constant.	Relative constant.
Ethylene dibromide.....	0·00076	1·0	—	—
Ethyl bromide .....	0·00120	1·5	—	—
Bromobenzene .....	0·00254	3·3	0·00081	3·3
Chloroform .....	0·00301	4·0	0·00137	5·6

These results, and also those obtained by other investigators in experiments on the influence of the nature of the solvent on the velocity of reaction, are discussed in their relation to various physical properties of the solvents.

T. H. P.

**Hydrolysis of Metallic Alkyl Sulphates.** GEORGE A. LINHART (*Amer. J. Sci.*, 1912, [iv], 34, 289—292).—The velocity of hydrolysis of barium-methyl, -ethyl and -propyl sulphates under the catalytic influence of hydrochloric acid has been measured at 60° in order to ascertain the influence of the alkyl group. On the assumption that the barium alkyl sulphates and the corresponding alkylsulphuric acids are hydrolysed at the same rate, concordant values are obtained for the velocity coefficient. The rate of decomposition of the salts decreases as the weight of the alkyl group increases, the values of the velocity coefficient for 1*N*-hydrochloric acid being 0·0085, 0·0083, and 0·00685 respectively.

H. M. D.

**Hydrolysis of Esters of Substituted Aliphatic Acids.** WILLIAM A. DRUSHEL and E. W. DEAN (*Amer. J. Sci.*, 1912, [iv], 34, 293—296. Compare this vol., ii, 147).—The influence of the hydroxy- and alkyloxy-groups on the rate of ester hydrolysis has been investigated by a series of experiments with the ethyl esters of glycollic, methoxy-, ethoxy- and propoxy-acetic acids at 25·2°, 35°, and 45° in presence of 0·1*N*-hydrochloric acid. At 25·2° the following values were obtained for  $K \cdot 10^5$ : acetate 64·7, glycollate 70·4, methoxyacetate 38·1, ethoxyacetate 36·2, propoxyacetate 35·8. These numbers show that the rate of hydrolysis is increased by the hydroxy- but retarded by the alkyloxy-group, the retardation effect increasing with the size of the alkyl radicle.

H. M. D.

**Selective Catalytic Reactions.** EMIL ABEL (*Zeitsch. Elektrochem.*, 1911, 18, 705—708).—In a previous paper (Abstr., 1908, ii, 26), it has been shown that the sole product of the action of hydrogen peroxide on sodium thiosulphate in acetic acid solution, either alone or in the presence of an iodide as catalyst, is tetrathionate. It is now shown that when molybdic acid is used as catalyst, the thiosulphate is oxidised directly to sulphate, according to the equation  $4\text{H}_2\text{O}_2 + \text{S}_2\text{O}_3^{2-} = 2\text{SO}_4^{2-} + 2\text{H}^+ + 3\text{H}_2\text{O}$ , without the intermediate production of tetrathionate.

G. S.

**Optical Activation of Racemic Bromocamphorcarboxylic Acid by means of Catalysts. Specificity of Catalysts.** HENRY J. M. CREIGHTON (*Trans. Nova Scotia Inst. Sci.*, 1912, 13, 1—34. Compare Fajans, Abstr., 1910, ii, 599).—The rate of elimina-

tion of carbon dioxide from bromocamphorcarboxylic acid in acetophenone solution, alone and in the presence of certain alkaloids, has been investigated. The decomposition of the free acid is a unimolecular reaction, and the temperature-coefficient for  $10^\circ$  between  $60^\circ$  and  $80^\circ$  is about 2.4.

The reaction is greatly accelerated by the addition of quinine or quinidine, the rate rising to a maximum and then falling practically to zero. Further, the optical isomerides decompose at different rates in the presence of the same optically active base, the difference in some cases amounting to 30%. On this basis it was found possible to bring about the activation of part of the inactive acid by heating with quinine until partial decomposition had occurred, and then interrupting the reaction. The undecomposed acid, as anticipated, was levorotatory, the bromocamphor dextrorotatory. Corresponding results were obtained with quinidine.

The specificity of catalysts is discussed (compare Fajans, *loc. cit.*).

G. S.

**Chemical Stability.** FRANK W. CLARKE (*J. Washington Acad. Sci.*, 1912, 2, 339—344).—Chemical stability is favoured by various conditions, but equality or approximate equality between the combining masses is one of them. The molecules of the diatomic elements  $H_2$ ,  $O_2$ ,  $Cl_2$ ,  $N_2$ , etc., in which two equal masses are combined, may be regarded as typical stable compounds. Similarly, also carbon monoxide and sulphur dioxide are more stable than carbon dioxide and sulphur trioxide respectively, whilst amongst the halogen acids, hydrofluoric is the most, hydriodic acid the least, stable. Further, in certain series, such as chlorides, iodides, and sulphates of the alkali metals, the solubility of the salts in water attains a minimum when the masses of the combining radicles are most nearly equal. The latter rule does not appear to be universal.

H. W.

**Apparent Change in Weight during Chemical Reaction.** J. J. MANLEY (*Proc. Roy. Soc.*, 1912, A, 87, 202—204 \*).—Minor errors involved in Landolt's work on the relationship between the total masses of the reacting substances and the products of reaction are indicated, and further experiments have been undertaken in which these are eliminated or neutralised. For this purpose, the action of barium chloride on sodium sulphate in aqueous solution was made use of. Whereas Landolt's estimated limit of accuracy in weighing was  $\pm 0.03$  mg., that attained in the author's experiments in the case of charged Jena glass vessels is equal to  $\pm 0.006$  mg. With the additional precautions taken in the measurements now described, it has been found that the apparent change in mass for this particular reaction is not greater than 1 in 100 millions, whereas Landolt's results only showed that the change was not greater than 1 in 10 millions.

H. M. D.

**Atomic Weights.** THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1912, 34, 959—971).—A lecture delivered to the Chicago Section of the American Chemical Society.

T. S. P.

\* and *Phil. Trans.*, 1912, A, 212, 227—260.

**International Table of Atomic Weights.** ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1912, 47, 861—877).—The author criticises the alterations made annually in the table of atomic weights authorised by the International Committee. These alterations are often trivial; for instance, the value, 87·6, given in the first table for the atomic weight of strontium, was changed subsequently to 87·62, and still later to 87·63; for iron, too, the number 55·85 (1910 and 1911) has been altered to 55·84 (1912). Further, the alterations are often made without any proof being furnished of the inaccuracy of the determinations on which the earlier numbers were based, the result being that, in some cases, a return is made later to these earlier numbers.

After discussing several of the more important publications dealing with the determination and calculation of the atomic weights, the author recommends: (1) that for practical laboratory purposes a table be used giving the atomic weights as integers or to the first decimal place; (2) that such table be modified only in exceptional cases and after repeated confirmatory experiments, and that such modification be made, not annually, but once in five, or even ten, years; (3) that a table of theoretical atomic weights be published and be altered every year in accordance with the results obtained by recognised authorities in this field of work—this table to contain also the numbers of the preceding one, in order that the extent of the changes made may be seen immediately.

T. H. P.

**Certain Physical Properties of the Alkali Nitrates and Chlorides.** F. L. HAIGH (*J. Amer. Chem. Soc.*, 1912, 34, 1137—1159).—The relation of some physical constants of the nitrates and chlorides of the alkali metals to the atomic weights is discussed, the properties examined being specific gravity of the solids, melting points, heat of solution, solubility, and the specific gravity, expansion and index of refraction of their solutions. Where the existing data were found insufficient or incomparable, as in the case of rubidium and caesium, new determinations have been made and complete series of values are given.

The properties are, roughly, functions of the atomic weights, but the exceptions are so many that no generalisations can be made. The elements tend, however, to form two series, lithium, sodium and potassium, and potassium, rubidium and caesium, and, as a rule, the latter group shows more regularity than the former. Nevertheless, rubidium takes an irregular position in the case of the nitrates, the melting point and molecular volume of rubidium nitrate having minimum values and the solubility a maximum, although, on the other hand, the chlorides are not exceptional.

Sodium gives values which approach more nearly those of potassium, although the equivalent volumes and heats of solutions of the salts approximate to the mean between lithium and potassium. Ammonium seems to be quite irregular, although in the molecular volume of its salts and the index of refraction of the solutions it occupies its proper position immediately after rubidium (compare Tutton, *Trans.*, 1903, 83, 1049).

The curves for the specific gravity and molecular volumes of the salts bear a resemblance to those of the free elements, but the melting points are quite irregular. The solubility curves are very similar, as are also those of the heats of solution, and the fact that potassium, rubidium, and caesium salts have nearly equal heats of solution would suggest that the degree of hydration of the dissolved salts is nearly the same. The specific gravities of equivalent solutions at 20° increase regularly with atomic weights, and the values for half-normal solutions are almost a mean between those for normal solutions and that of water. The coefficients of expansion for normal solutions of the salts of potassium, rubidium, and caesium appear to be identical, whereas the expansion of sodium salt solutions is slightly more rapid and that of lithium and ammonium considerably less. Lithium nitrate is irregular in comparison with the chloride. The index of refraction curves for equivalent solutions are nearly parallel, and the indices for  $N/2$ -solutions approximate to the mean between the values for  $N$ -solutions and that of water.

J. C. W.

**The Electron Conception of Valency. II. The Organic Acids.** K. GEORGE FALK (*J. Amer. Chem. Soc.*, 1912, 34, 1041).—A reply to Fry's criticism (this vol., ii, 547) of the author's first paper (Abstr., 1911, ii, 711).

T. S. P.

**Suggested Explanation of Allotropism Based on the Theory of Directive Valency.** FREDERICK B. GUTHRIE (*J. Roy. Soc., New South Wales*, 1912, 45, 318—336).—On the basis of the electron theory of valency, in accordance with which the valency bonds may be regarded as having definite direction, an attempt is made to explain certain cases of allotropy exhibited by non-metallic-elements. It is suggested that the relative directions of the valency bonds in the molecule may be determined by the conditions under which the molecule is formed. Variation in the direction gives rise to molecular configurations which differ from one another in respect of the mode of distribution of the electric charge amongst the atoms, and those molecules in which the charge is neutralised or symmetrically distributed may be regarded as being more or less stable molecules and as representing the various allotropic forms of the elements. The hypothesis is applied to the case of sulphur, selenium, phosphorus, tellurium, and arsenic. The fact that the monatomic and the univalent non-metallic elements do not give rise to allotropic forms is considered as evidence in support of the hypothesis.

H. M. D.

**Source of Error in the Characterisation of Chemical Individuals.** RUDOLF WEGSCHEIDER (*Zeitsch. physikal. Chem.*, 1912, 80, 509—512).—In the course of the investigation of certain compounds derived from nitrohemipinic acid, which exist in different allotropic modifications (compare Abstr., 1908, i, 793, 794), the following generalisation has been established. When two isomerides at all temperatures follow accurately the rule of Carnelley and Thomson as regards constant solubility ratio, and when the ratio of the solubilities is the same as the composition of the eutectic mixture, the mixture of the two isomerides on recrystallisation yields among

other products a mixture which cannot be separated into its components otherwise than by mechanical means or by means of supersaturation phenomena. G. S.

**Origin of the Names of the Chemical Elements.** ALEXIS M. VASILIEFF (Pamphlet, Kasan, 1912).—A discussion of the etymology of the names used, principally in Russia, but also in other European countries, for the chemical elements (compare Diergart, *Abstr.*, 1900, ii, 593). T. H. P.

**Knowledge of the Ancients Regarding Vitriols and Stypteria.** KARL B. HOFMANN (*J. pr. Chem.*, 1912, [ii], 86, 305—318).—Historical. F. B.

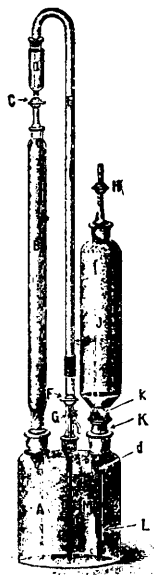
**Some Apparatus and Methods for the Photochemical Laboratory.** A. COBENZL (*Chem. Zeit.*, 1912, 36, 913—914).—The appliances described are a kneading mill and a washing apparatus for gelatin emulsions, a filtering cylinder, having the filtering material stretched across the lower opening, whilst pressure is applied above by means of a rubber ball, and a tube viscosimeter for collodion and emulsions.

The quality of insoluble substances, such as barium sulphate, is best determined by shaking with water after passing through a sieve, and noting the time required to settle through a given distance in a cylinder.

C. H. D.

**New Gas-Generating Apparatus.** K. BORMANN (*Zeitsch. anal. Chem.*, 1912, 51, 641—643).—The apparatus (see Fig.) consists essentially of the three-necked acid container, *A*, the acid-tube, *B*, with ground jointed centre-piece, *D*, and stopcock, *C*, and the safety-tube, *E*, which continues below in the tube *M*. This is ground into the middle neck of *A*, and carries the stopcocks *F* and *G*. Into the neck at the right of *A* passes the ground tube, *K*, with its joint and its prolongation, *L*. On *K* is placed the generating vessel, *J*, into the upper neck of which is placed the ground tube with the gas-regulating stopcock *H*. The latter carries a bent delivery tube (not shown in the Fig.). Below, in *J*, is found a rubber disk perforated like a sieve. When required for use, the tubes *B* and *D* are removed, the container, *A*, is filled with dilute acid, and *B* is then replaced. The generating vessel, *J*, is now taken from *K*, filled with the gas-generating material and then replaced. The openings *b* and *c* should face the hole *m*, also directed inwards. The ground tube is then placed on the neck of *J*, and *H* is closed. Acid is now poured through tube *B*, stopcock *F* being opened and stopcock *G* being closed, until the tube *B* is nearly filled; *D*, with stopcock *C* opened, is then inserted, and the apparatus is ready for use.

On carefully turning *H*, the evolution of gas starts at once. The



fresh acid enters at *b*, and forces its way through the tubes *b* and *k* to the gas-generating material, whilst the heavier spent acid is carried off through the tube *L*, and runs through *c* to the bottom of the container *A*. The fresh, supernatant acid does not mix to any extent with the spent acid at the bottom, so the material is constantly brought into contact with fresh acid. The introduction of fresh generating material does not involve the removal of the acid. The stopcocks *C* and *F* are closed, *H* is removed from *J*, and fresh material introduced into *J*. If fresh acid is required, *H* is closed, *C*, *F* and *G* are opened, and by means of a rubber tube attached to *G* the acid is siphoned off and fresh acid is then introduced.

The stopcocks *C* and *F* should be always open whether the apparatus is in use or not. The tube *D* prevents solid particles from getting into *A*, which would give off gas and so disturb the acid. Tube *E* acts as a safety tube in case of a too sudden evolution of gas if *H* is closed too suddenly.

L. DE K.

**A Modification of Ostwald's Hydrogen Sulphide Apparatus.** A. M. SKLEPINSKI (*Chem. Zeit.*, 1912, 36, 884).—The middle bulb is provided with two inner tubes, one connected with the upper bulb and terminating at the bottom of the bulb, the other communicating with a tap leading to the lowest bulb, in which the ferrous sulphide is placed. The delivery tube is on the lowest vessel, and closing the delivery tap stops the supply of acid. The air-tube at the top passes through a washing flask containing a solution of an iron salt.

C. H. D.

**New Thermometers for Melting-point Determinations.** ALVIN S. WHEELER (*J. Amer. Chem. Soc.*, 1912, 34, 1189\*).—A set of thermometers, each having a scale of 35 mm., extending over 50°, has been patented; the stem is lengthened to permit of suspension in a Thiele apparatus.

J. C. W.

**Thermometer Holder for Distilling Flasks, the Entire Scale being Visible.** MICHAEL FREUND (*Chem. Zeit.*, 1912, 36, 969).—A glass tube, of slightly less diameter than the neck of the flask, is fitted into the latter by a rubber ring, whilst its lower end is drawn out and sealed, and just encloses the bulb of the thermometer. A cork is thus dispensed with. A few drops of mercury may be introduced into the sealed portion.

C. H. D.

**An Electrically Heated Distillation Apparatus for Difficult Distillations.** I. C. ALLEN and WALTER A. JACOBS (*Chem. Zentr.*, 1912, i, 1801; from *J. Ind. Eng. Chem.*, 1912, 4, 118—123).—The flask is heated by means of nickel chromium steel wire, the coating being a paste of magnesia, asbestos, sodium silicate, and magnesium chloride. The correct winding of the wire is of importance.

C. H. D.

**A New Sublimation Apparatus and Results Obtained with it.** E. PHILIPPE (*Chem. Zentr.*, 1912, ii, 82; from *Mitt. Lebensmittelunters. Hyg.*, 1912, 3, 41—53).—The apparatus consists of a glass dish with ground edge, closed by a slightly larger clock glass, concave side

\* and *Chem. News*, 1912, 106, 155.

downward. To the upper surface of the clock glass is clamped by means of a rubber ring and springs a metal capsule with inflow and outflow tubes to serve as condenser. The loss in sublimation is usually less than 5%. The apparatus is particularly suitable for the estimation of salicylic and benzoic acids in milk and other foods.

C. H. D.

**A Phosphorus Pipette of Coloured Glass.** FRITZ FRIEDRICH (Zeitsch. angew. Chem., 1912, 25, 1905).—In order to avoid the formation of red phosphorus under the influence of light, a Hempel phosphorus pipette is conveniently constructed of reddish-brown glass.

C. H. D.

**A Mercury Pump (Laboratory Type).** ALBERT F. O. GERMANN and ETTORE CARDOSO (J. Chim. phys., 1912, 10, 306—309).—A modification of the improved Töpler pump recently described by Antropoff (Abstr., 1910, ii, 947). The pump is made of soda glass and is mounted on an ordinary retort stand. To reduce the lift of the mercury reservoir in manipulation, the main cylinder is placed almost horizontal. A non-return valve is rendered unnecessary by a long vertical inlet tube, which also serves as a manometer. The tube leading from the mercury reservoir is provided with an air bubble trap when high vacua are required.

R. J. C.

**A Simple Valve for Filter-Pumps.** HENRY B. HUTCHINSON (Chem. News, 1912, 106, 99).—The valve consists of a wide vertical tube, closed by corks, through which glass tubes pass, the top of the lower one being flush with the cork, whilst the lower end of the upper tube is cut obliquely. A rubber stopper, moving loosely in the outer tube, serves as a valve, and prevents the return of water.

C. H. D.

**A New Mercury Volumenometer.** PAUL VERBEEK (Chem. Zeit., 1912, 36, 1029—1030).—The volume vessel is provided with a T-tube below, and a ground-on glass cap above, the latter terminating in a capillary neck and funnel. The graduated burette communicates with the lower end of this vessel. The upper end of the burette forms a bulb, fitted with a T-piece, of which one branch is closed by a tap, whilst the other communicates through a rubber tube and pinchcock with a pair of large mercury bulbs, connected by flexible tubing. The weighed substance is introduced by removing the glass cap, and the volume is read in the burette.

C. H. D.

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### Inorganic Chemistry.

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**Atomic Weight of Chlorine.** GEORGES BAUME and F. LOUIS PERROT (*Compt. rend.*, 1912, 155, 461—464).—The method used depends on the combination of gaseous hydrogen chloride with a known quantity of liquid ammonia. The apparatus used is a development of that

described already (Abstr., 1911, ii, 581) and is figured in the original and its working explained.

The value found is 35·465, taking the atomic weight of nitrogen as 14·009.  
T. A. H.

**Synthesis of Nitrosyl Chloride Gas and the Atomic Weight of Chlorine.** EUGÈNE WOURTZEL (*Compt. rend.*, 1912, 155, 345—346).—The nitrosyl chloride was prepared by adding pure nitric oxide in very slight excess to a known weight of pure chlorine in a small flask of special form, the excess of nitric oxide being removed at low temperature. The weight of nitric oxide entering into combination was then determined, and from the ratio NO:Cl, taking N=14·008, the author obtained, as a mean of five experiments, the value 35·460 for the atomic weight of chlorine, the maximum error being 0·003.  
W. G.

**The Non-Existence of Perbromic Acid.** PHILIP W. ROBERTSON (*Chem. News*, 1912, 106, 50).—Attempts to prepare perbromic acid by the action of bromine on potassium perchlorate in presence of potassium bromide, by heating potassium bromate with lead peroxide, and by the action of bromine on sodium periodate, have led to entirely negative results.  
C. H. D.

**Behaviour of Iodine towards Tannin and Peptone.** CARLO CASANOVA and LUIGI CARCANO (*Boll. Chim. Farm.*, 1912, 51, 289—299).—The authors bring forward evidence in support of the view that, in the interaction of a halogen with water, the halogen combines with the ions of the water, giving  $\text{HCl} + \text{HClO}$ , these products then reacting further, yielding partly  $\text{Cl}_2 + \text{H}_2\text{O}$ , and partly  $2\text{HCl} + \text{O}$ . The system  $\text{HI} + \text{HIO}$ , formed from iodine and water, is not demonstrable directly, as it is destroyed with regeneration of water and halogen, but it is possible to fix it by means of an alkali.

When iodine acts on tannin in presence of water, the tannin molecule is partly oxidised into simpler derivatives, but no organic iodine compounds are formed, as the whole of the iodine is found to be transformed completely into hydriodic acid. When treated with iodic acid, however, tannin is partly oxidised to simpler products, but is mostly oxidised and iodinated to a compound not less complex than tannin itself.

In the interaction of peptone, water, and iodine, the last is converted entirely into hydriodic acid, but in the action of aqueous iodic acid on peptone (and, probably, on all proteins), the latter is mostly oxidised and simplified to aliphatic compounds; with some of the peptone, which escapes such profound oxidation, the halogen is fixed in the aromatic nucleus, giving iodo-compounds, these giving the biuret reaction, and hence being more complex than the amino-acids, but less so than the peptones.  
T. H. P.

**The Volatility of Sulphur and its Action on Water.** FRANCIS JONES (*Mem. Manchester Phil. Soc.*, 1912, 56, No. XIV, 1—5).—It is well known that sulphur is volatilised when boiled with water. The author now shows that sulphur volatilises at 100° in the absence of

water, and is subsequently deposited in aggregations of octahedral crystals elongated so as to appear needle-shaped, together with smaller quantities of  $\beta$ -sulphur which, however, remain transparent indefinitely. Even the purest forms of sulphur appear to possess sensible volatility at the ordinary temperature, since silver foil suspended over them becomes blackened, especially in the presence of moisture.

The author points out that the use of glass vessels to investigate the action of water on sulphur is untrustworthy, owing to the invariable presence of alkali. When, however, sulphur is boiled with water in vessels of platinum or fused silica, hydrogen sulphide and thiosulphuric acid are formed, whilst, in the presence of oxygen, hydrogen sulphide and sulphuric acid are obtained. H. W.

**A Spectrographic Study of Tellurium.** WILLIAM L. DUDLEY and E. V. JONES (*J. Amer. Chem. Soc.*, 1912, 34, 995—1014).—By fractional precipitation with hydrazine hydrochloride, the authors have obtained tellurium free from all impurities, as indicated by the spark spectrum. The twenty fractions obtained showed no variations in their spectra except the appearance of the copper lines in the last fractions, indicating that no breaking down or separation of the tellurium into parts differing in properties had been effected.

Tellurium, which was apparently chemically pure, but had not been fractionally precipitated by hydrazine hydrochloride, was found to contain traces of copper, iron, and silver when examined spectroscopically.

A group of six new lines in the tellurium spectrum is recorded, namely, 2002·6, 2001·8, 2000·4, 1997·6, 1994·8, and 1993·8. A number of strong lines given in Hartley and Adeney's measurements belong to silver, copper, and gold. T. S. P.

**Chemically Active Modification of Nitrogen Produced by the Electric Discharge.** IV. (Hon.) ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1912, A, 87, 179—188. Compare Abstr., 1911, ii, 482; this vol., ii, 153, 447).—The nature of the chemically active modification of nitrogen and of the change by which it is converted into ordinary nitrogen has been further examined. From a rough comparison of the heat liberated in the reversion of active nitrogen to the ordinary form with that generated in the chemical reaction between the active nitrogen and nitric oxide, it has been found that active nitrogen is highly endothermic, but that its energy content is of the same order of magnitude as that of an equivalent of other substances.

In the ionisation which accompanies the decay of active nitrogen, the number of ions produced is very small in comparison with the total number of nitrogen atoms. The ionisation is accordingly a subordinate effect, and may possibly be due to the action of light rays of very short wave-length, which are emitted in the process of decay.

Further evidence has also been obtained in favour of the view that the decay of active nitrogen is more rapid at low temperatures. If it is assumed that active nitrogen consists of monatomic molecules, it follows that the internal energy of the molecules will not be altered by a change of temperature, and the fact that the velocity of conversion

into ordinary nitrogen increases with fall of temperature indicates that high translational velocity of the molecules is in itself unfavourable to the change. It must, therefore, be inferred that the reaction is mainly conditioned by something internal to the molecule.

H. M. D.

**Preparation of Ammonia by the Catalytic Combination of Nitrogen and Hydrogen.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 246377. Compare this vol., ii, 946).—The direct combination of nitrogen and hydrogen to form ammonia can be carried out in the presence of many salts of molybdenum, or of other catalytic agents at a red heat.

F. M. G. M.

**Electrolytic Oxidation of Ammonia.** FRITZ FICHTER (*Zeitsch. Elektrochem.*, 1912, 18, 647—652. Compare Abstr., 1910, ii, 98).—It is known that formamide can be oxidised in ammoniacal solution to carbamide, and it is now shown that the oxidation can also be carried out electrolytically. The conclusion is drawn that in the oxidation of organic compounds in ammoniacal solution, those yield carbamide which give formamide as intermediate product.

This view has a bearing on the anodic formation of carbamide from ammonium carbamate in strongly ammoniacal solution, which may be represented by the equations:  $2\text{NH}_2\cdot\text{CO}_2\text{H} + 2\text{NH}_2\cdot\text{OH} = 2\text{NH}_2\cdot\text{COH} + 2\text{H}_2\text{O} + \text{H}_2\text{N}_2\text{O}_2$ , the formamide being further oxidised to carbamide in presence of excess of ammonia. Up to the present, neither hydroxylamine nor hyponitrous acid has been detected in the electrolytic oxidation of ammonia, but the former, if produced, would be immediately reduced, as shown in the equation. The evidence in favour of the formation of hyponitrous acid is indirect. Müller and Spitzer (Abstr., 1906, ii, 158) found that the gaseous and dissolved products of oxidation were less by 20 to 30% than that calculated from the current used, which would be accounted for by the escape of nitrous oxide; explosion experiments seem also to indicate the presence of the latter gas among the gaseous products of oxidation of an ammoniacal carbamate solution. Experiments carried out to determine whether ammonium carbamate can be reduced by hydroxylamine to formamide did not lead to definite results. It is shown that carbamide is formed in the electrolytic oxidation of ammonium formate in aqueous and in liquefied ammonia, and also in the electrolytic oxidation of ammonium acetate.

When a saturated solution of ammonium carbonate containing ethyl alcohol is electrolysed, the solution yields on evaporation acetamidine nitrate,  $\text{CH}_3\cdot\text{C}(\text{:NH})\cdot\text{NH}_2\cdot\text{HNO}_3$ , which is obtained in colourless crystals.

G. S.

**Determinations of the Vapour Pressure of Nitrogen Tetroxide.** F. E. C. SCHEFFER and J. P. TREUB (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 166—178. Compare this vol., ii, 132).—The critical temperature of nitrogen tetroxide, observed by reflected light in a paraffin bath, is found to be  $158.2^\circ$ . The vapour pressure has been determined in a manometer similar to that previously used,

but more elongated and smaller. In one form of apparatus the manometer is enclosed in a combustion tube attached to a Cailletet apparatus and provided with an outer jacket containing liquid, which may be heated electrically. The highest pressure thus obtainable is 67 atmospheres, which is below the critical pressure. In a second form of apparatus, the combustion tube is replaced by a copper tube, provided with transverse tubes opposite the needle of the manometer, closed with glass plates cemented into steel mounts by an enamel of sodium and potassium carbonates, lead oxide, and silica. The copper tube is surrounded by two spiral lead tubes, through which heated oil is circulated in opposite directions. A pressure of 150 atmospheres may be reached. The critical pressure is  $100 \pm 2$  atmospheres. Calculation shows that at the critical point the substance must consist almost entirely of  $\text{NO}_2$  molecules. The calculated latent heat of evaporation at the boiling point is 9200 cal. C. H. D.

**Absorption of Phosphoric Acid by Zeolites (Permutite).** S. GRAF ROSTWOROWSKI and GEORG WIEGNER (*J. Landw.*, 1912, 60, 223—235).—Potassium permutite (Gans, *Chem. Ind.*, 1909, 32, No. 8) failed to absorb phosphate ions in amounts which could be detected. Fixation of phosphoric acid by aluminium hydroxide-silicic acid gels can therefore only take place by secondary reactions with previously liberated cations which form insoluble phosphates.

N. H. J. M.

**The Supposed Penta-iodides of Arsenic and Antimony.** EMANUELE QUERCIGH (*Chem. Zentr.*, 1912, i, 1812; from *Atti R. Accad. Inst. Veneto Sci.*, 1912, 70, ii, 667—673. Compare Jaeger and Doornbosch, this vol., ii, 640).—The penta-iodides do not exist, the eutectics having approximately the corresponding composition. The arsenic-arsenic iodide eutectic point is at  $71.5^\circ$ , and that for antimony at  $80^\circ$ .

C. H. D.

**Volatility of Boric Acid in Steam: Boiling of its Saturated Solutions with the Solid Phase.** RAFFAELE NASINI and FERNANDO AGENO (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 125—132).—The authors dispute the conclusions drawn by Skirrow (*Abstr.*, 1901, ii, 448) and give the results of experiments on the distillation of aqueous boric acid solutions under various conditions. Increase of the concentration of the initial solution is accompanied by increase in the proportion of the acid in the distillate; this proportion is about 0.01—0.02%, higher values being obtained only with extremely concentrated solutions and lower values only with extremely dilute ones.

If great care is taken to avoid superheating, saturated solutions of boric acid in presence of the solid phase may be made to begin to boil at  $103.12^\circ/760$  mm., the distillate then containing 0.039% of boric acid or 0.0113 mols.  $\text{H}_3\text{BO}_3$  per 100 mols. of water. But if such care is omitted and the solution in contact with the solid phase attains a temperature higher than that corresponding with the boiling point of the saturated solution ( $103.12^\circ$ ), the boiling point rises and the

proportion of acid in the distillate increases rapidly. This result is hardly explainable on the ground of supersaturation or superheating, as the solution is in contact with the solid phase, and it may be related to some change in the solid, the most probable being the conversion of orthoboric into metaboric acid.

Müller and Abegg (Abstr., 1907, ii, 157) showed that dilution of solutions of borax is accompanied by decomposition of the borax into metaborate and free boric acid, but the authors find that distillation of saturated borax solutions, even when these contain 5% of added boric acid, gives no appreciable proportion of the acid in the distillate; this is explained as due to the consumption of the boric acid in the formation of polyborates.

T. H. P.

**Borohydrates.** I. MORRIS W. TRAVERS and RAMES C. RAY (*Proc. Roy. Soc.*, 1912, A, 87, 163—179).—When the product, obtained by heating a mixture of magnesium powder and anhydrous boric acid to a bright red heat in an atmosphere of hydrogen, is treated with water, a yellow-coloured solution is obtained, which has powerful reducing properties, and experiments have been made to ascertain the nature of the substances which are formed in these circumstances.

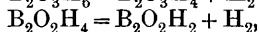
The solution is slightly alkaline towards litmus, and gives off hydrogen on boiling. On addition of dilute acids, a considerable volume of gas is evolved, which consists of hydrogen together with a trace of some boron compound. Both the original and acidified solutions are strong reducing agents; they take up iodine, and precipitate the heavy metals from solutions of their salts. Quantitative measurements of the hydrogen evolved from the solutions on the addition of dilute acid and of the iodine absorbed by the solutions show that the ratio of hydrogen and iodine equivalents lies between 1:1 and 2:1, and usually approaches closely to the one value or to the other. It has also been found that the solutions contain one atom of boron for every atom of hydrogen given off on the addition of acid.

When the solutions are evaporated in a vacuum at low temperature with the aid of a condenser cooled by liquid air, little or no gas is evolved until the water has disappeared. The viscous residue then begins to give off hydrogen rapidly, the evolution of gas continuing until the viscous material has set to a semi-crystalline or glassy solid. The volume of hydrogen evolved at this stage is equal to one-half the volume given off on addition of acid to the original solution.

If the bulb containing the solid residue is allowed to remain in connexion with the pump, hydrogen continues to be evolved slowly, and when the gas given off during this stage is measured, its volume is found to be equal to that of the gas evolved during the process of rapid emission of gas. If, at this point, the residue in the bulb is gently heated, a further quantity of gas is evolved, which is sensibly equal to the quantity evolved on evaporation or during the subsequent stage of slow evolution.

From estimations of the amount of boron in the residue obtained after evaporation of the solution, it is found that one-half of the boron distils over during the process of vaporisation. This portion is collected

in the liquid distillate, and since the distillate absorbs but very little iodine, it would appear that the boron compound carried over is fully oxidised. Special experiments have shown that the compound is not boric acid, and the authors conclude, therefore, that a substance exists, which is non-acid, volatile, and has the formula  $(B_2O_3)_n$ . On this assumption, the whole of the reactions investigated can be accounted for, if the substances first formed in the original solution are hydrated derivatives of the oxides  $B_4O_2$  and  $B_4O_3$ . These compounds are spontaneously transformed in accordance with the equations:  $B_4O_2 + 3H_2O = (B_2O_3)_2 + B_2O_2H_6$ ,  $B_4O_3 + 3H_2O = (B_2O_3)_2 + B_2O_3H_6$ . The changes taking place on addition of acid are:  $B_2O_2H_6 = B_2O_2H_2 + 2H_2$ ,  $B_2O_3H_6 = B_2O_3H_2 + 2H_2$ ; on evaporation of the original solution:  $B_2O_2H_6 = B_2O_2H_4 + H_2$ ,  $B_2O_3H_6 = B_2O_3H_4 + H_2$ ; on standing:



$B_2O_3H_4 = B_2O_3H_2 + H_2$ ; on heating the residue:  $B_2O_2H_2 = B_2O_2 + H_2$ ,  $B_2O_3H_2 = B_2O_3 + H_2$ .

These equations are also in agreement with the fact that when the ratio of hydrogen to iodine in the original solution was 1 : 1, the heated residue absorbed a quantity of iodine approximately equivalent to the hydrogen evolved during each of the three stages described above; further, with the observation that when the ratio was 2 : 1, no iodine was absorbed by the residue.

In reference to the reaction between magnesium boride and water, measurements of the relation between the boron passing into solution and the hydrogen evolved during the reaction, when this is allowed to take place in a vacuum, indicate that in addition to  $Mg_3B_2$ , another boride exists, for which the formula  $Mg_2B_4$  is suggested. H. M. D.

**Use of High Pressures in Chemical and Technical Chemical Changes.** FRIEDRICH BERGIUS (*Zeitsch. Elektrochem.*, 1912, 18, 660—662).—An apparatus has been constructed in which a pressure of 150 atmospheres can be kept constant for twenty days at 300°. In this apparatus it has been found that carbon, heated with liquid water near its critical point, burns to carbon dioxide and hydrogen. The formation of material similar to coal has been effected by heating wood, etc., with liquid water under pressure, the water in this case serving to absorb the heat given out in the coaling process. The gases given off are mainly carbon dioxide and methane. The composition of the product depends greatly on the duration of the heating and the temperature; that obtained in eight hours at 340° corresponds closely with good natural coal. From the rate of change at 310° and 340° it is calculated that the formation of the coal measures took 7—8 million years, in good agreement with geological estimates.

G. S.

**Reduction of Quartz by Hydrogen.** H. VON WARTENBERG (*Zeitsch. Elektrochem.*, 1912, 18, 658—660).—When heated at 200° in the presence of finely divided nickel, silicon hydride,  $SiH_4$ , is decomposed to the extent of 90% into silicon and hydrogen. From the displacement of the equilibrium with temperature, the heat of formation of silicon hydride is found to be about 9000 calories, in

good agreement with the value deduced from the heats of combustion of the hydride and free silicon. The vapour pressure of silicon has been determined at 1200—1300° by the dynamical method, hydrogen and argon being used to carry off the vapour. On the basis of these results it is shown that when silicon dioxide is reduced by hydrogen at 1300°, the first product is almost entirely silicon and not the hydride. The latter is almost completely decomposed at 1300°.

When a current of hydrogen is passed through a quartz tube heated to 1300°, silicon collects in a cooled capillary attached to the wider tube. There is evidence that silicon in the state of vapour is poly-atomic, but the degree of complexity has not been determined. Quartz sublimes fairly readily in hydrogen at 1300°, but not in nitrogen under the same conditions. G. S.

**Tendency of Halides and Phosphates of the Same Metal to Combine. I. Alkali Chlorides and Phosphates.** MARIO AMADORI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 182—188).—Owing to the different behaviour exhibited by the alkali chlorides and fluorides towards the sulphates (compare Jänecke, *Abstr.*, 1908, ii, 841; Karandéeff, *Abstr.*, 1910, ii, 33), the author is making investigations to ascertain if a similar difference is shown in the behaviour of potassium chloride and fluoride towards potassium phosphates. The present paper deals with potassium chloride and the three potassium phosphates.

The melting and transformation temperatures of the salts used are as follows: KCl, m. p. 774°;  $KPO_3$ , m. p. 798° (Parravano and Calcagni, *Zeitsch. anorg. Chem.*, 1910, 65, i, gave 823° and van Klooster, *Abstr.*, 1911, ii, 110, 810°), trans. p., 450°;  $K_4P_2O_7$ , m. p. 1090° (Parravano and Calcagni, *loc. cit.*, gave 1092°), trans. p., 278°;  $K_3PO_4$ , m. p. 1340°.

With the system KCl- $KPO_3$ , no compound is formed, but a tendency to the formation of solid solutions is observed; probably this solubility is zero at 450°, since the transformation point of the metaphosphate is the same in the mixtures as for the pure salt. Also, with the systems KCl- $K_4P_2O_7$  and KCl- $K_3PO_4$ , no indication is obtained of the formation of compounds between the constituents.

T. H. P.

**Sodium Carbonate and Sodium Hydrogen Carbonate.** A. GAWALOWSKI (*Chem. Zentr.*, 1912, i, 1751—1752; from *Zeitsch. allg. österr. Apoth.-Ver.*, 1912, 50, 63—64).—Pure sodium carbonate is obtained from the commercial salt by boiling with freshly precipitated lead carbonate, adding sodium hydrogen carbonate to the decanted liquid, and evaporating in a vacuum, when potassium and sodium hydrogen carbonates crystallise out. The mother liquor is evaporated and the first fractions rejected, the main fraction being redissolved, crystallised from water with refined wood-charcoal, and filtered through platinum wool. C. H. D.

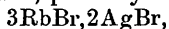
**Solubility of Silver Chloride in Water.** C. VAN ROSSEM (*Chem. Weekblad*, 1912, 9, 657—665. Compare this vol., ii, 643).—An

investigation of the influence of the nitrates of ammonium and potassium on the solubility of silver chloride, and a review of the work of Stas on the solubility of this substance. A. J. W.

**Silver Subfluoride.** ANTOINE GUNTZ (*Bull. Soc. chim.*, 1912, [iv], 11, 845—847).—A reply to Vanino and Sachs (Abstr., 1911, ii, 884) suggesting that their failure to obtain silver subfluoride and the dihydrate of silver fluoride is due to their not securing the proper experimental conditions. T. A. H.

**Tendency of Alkali Halides to Combine with Silver Halides.** I. CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 196—202).—The marked solubility of silver halides in concentrated solutions of alkali halides is regarded as due to the formation of complexes of the two classes of compounds. The tendency to form complex compounds increases from the chloride to the iodide of one and the same element, and the object of the author's investigations was to ascertain if such regularity is rendered manifest by the results of thermal analysis.

The system KBr-AgBr yields neither compound nor mixed crystals. RbBr-AgBr gives a compound, probably  $2\text{RbBr}\cdot\text{AgBr}$  or



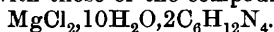
decomposing on melting. KI-AgI gives a compound which decomposes when fused, and the same is the case with RbI-AgI.

The results show that the tendency of silver halides to form complexes increases from the chloride to the iodide, and increases also with the electropositive character of the alkali metal, which functions as a simple ion of the complex. T. H. P.

**Argentio Persulphate.** GIUSEPPE A. BARBIERI (*Gazzetta*, 1912, 42, ii, 7—14).—The addition of a solution containing silver nitrate and pyridine to cold potassium persulphate solution results in the formation, in golden-yellow microscopic needles, of a compound which contains bivalent silver and has a composition in agreement with the formula  $\text{AgS}_2\text{O}_8\cdot 4\text{Py}$ . It remains unchanged in diffused light, is instantly reduced by dilute ammonia solution, and yields argentic oxide, AgO, when treated with dilute acids or sodium hydroxide solution (compare Abstr., 1906, ii, 612; 1907, ii, 767; Barbieri and Calzolari, Abstr., 1911, ii, 889). T. H. P.

**Unstable Nitrites Fixed by means of Organic Bases.** I. GINO SCAGLIARINI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 88—92).—Although Vogel's work (Abstr., 1903, ii, 591) has established the formulæ of the hydrates of magnesium nitrite, uncertainty still exists with regard to manganese nitrite. The aim of the author's experiments was to fix these compounds in more stable forms.

With hexamethylenetetramine, magnesium nitrite gives the compound,  $\text{Mg}(\text{NO}_2)_2\cdot 10\text{H}_2\text{O}\cdot 2\text{C}_6\text{H}_{12}\text{N}_4$ , which forms triclinic crystals [BILLOWS:  $a:b:c = 0.8461:1:0.8460$ ;  $\alpha = 126^\circ 5'$ ,  $\beta = 49^\circ 10'$ ,  $\gamma = 121^\circ 15'$ ] isomorphous with those of the compound



This is the first case observed among inorganic compounds of isomorphism between  $\text{Cl}'$  and  $\text{NO}_2'$ .

Manganese nitrite gives the compound,  $\text{Mn}(\text{NO}_2)_2 \cdot 10\text{H}_2\text{O} \cdot 2\text{C}_6\text{H}_{12}\text{N}_4$ , which forms white crystals with a red reflexion and isomorphous with those of the manganese compound.

Attempts to separate cobalt and nickel nitrites in a similar manner were unsuccessful, owing to the very ready solubility of these nitrites. The latter can, however, be isolated in the form of mixed crystals with magnesium or manganese nitrite.

T. H. P.

**Unstable Nitrites Fixed by means of Organic Bases. II.** GINO SCAGLIARINI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 151—154).—By making use of pyridine in place of hexamethylenetetramine (see preceding abstract), the author has prepared the following crystalline compounds: (1)  $\text{Cu}(\text{NO}_2)_2 \cdot 2\text{C}_5\text{H}_5\text{N}$ ; (2)  $\text{Ni}(\text{NO}_2)_2 \cdot 2\text{C}_5\text{H}_5\text{N} \cdot 2\text{H}_2\text{O}$ , and (3)  $4\text{Co}(\text{NO}_2)_2 \cdot \text{CoO} \cdot 10\text{C}_5\text{H}_5\text{N}$ .

T. H. P.

**The History of Zinc.** W. HOMMEL (*Chem. Zeit.*, 1912, 36, 905—906, 918—920).—The name zinc is erroneously attributed to Basil Valentine, and the discovery of the metal to Paracelsus. The identification of zinc as the metal from blende was only accomplished by Homberg in 1695. The history of the subject is discussed in detail.

C. H. D.

**Cuprous Sulphantimonites.** NICOLA PARRAVANO and PIETRO DE CESARIS (*Gazzetta*, 1912, 42, ii, 189—193).—The authors have investigated the melting-point diagram of the system  $\text{Sb}_2\text{S}_3$ — $\text{Cu}_2\text{S}$ , the fusion being carried out in an atmosphere of nitrogen. The results indicate the formation of cuprous metasulphantimonite,  $\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ , corresponding with the mineral wolfsbergite, and of cuprous orthosulphantimonite,  $3\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$ , corresponding with the principal constituent of stylotypite. A mixture of the composition  $3\text{Cu}_2\text{S} \cdot \text{Sb}_2\text{S}_3$  exhibits two arrests, at  $607^\circ$  and  $570^\circ$  respectively (compare Pélabon, *Abstr.*, 1905, ii, 435). The more the mixtures differ in composition from the eutectics, the lower are the temperatures at which the eutectic arrests occur, this being evidently due to the low thermal conductivity of the fused masses. The results of the thermal analysis are confirmed by those of a micrographic study.

T. H. P.

**Purification of Mercury.** W. R. FORBES (*Chem. News*, 1912, 106, 74).—Large quantities of mercury are best purified by oxidation with air, followed by shaking with charcoal powder saturated with oxygen.

C. H. D.

**The Compounds of Cerium with Nitrogen and Hydrogen.** FRANZ W. DAFERT and R. MIKLAUZ (*Monatsh.*, 1912, 33, 911—918).—The absorption of hydrogen by cerium takes place readily at  $310^\circ$ , and is complete at  $450^\circ$ , with the formation of the hydride,  $\text{CeH}_3$  (compare Muthmann and Kraft, *Abstr.*, 1903, ii, 212). It is dark blue to black in colour, and takes fire spontaneously in the air. When the pure compound is treated with a slow stream of moist air, no ammonia is

formed (compare Lipski, *Abstr.*, 1909, ii, 478), but when allowed to take fire spontaneously the cerium formed by the dissociation of the hydride partly combines with nitrogen from the air, and then gives ammonia with moisture. Cerium often contains traces of nitrogen, with the result that the hydride then smells of ammonia on exposure to the air.

The pure nitride is obtained by heating the hydride at 800–900° in a current of nitrogen; it cannot be produced by heating the metal in nitrogen (compare Muthmann and Kraft, *loc. cit.*). No ammonia is produced during the reaction, neither is ammonia produced by heating the nitride in a current of hydrogen (compare Whitehouse, *Abstr.*, 1907, ii, 680; Lipski, *loc. cit.*)

By the action of a mixture of nitrogen and hydrogen on cerium at relatively low temperature, the chief product is the hydride, together with some nitride; at higher temperatures the nitride only is formed. There is no appreciable formation of ammonia.

No evidence has been obtained of the formation of an imide or other compound of cerium containing both nitrogen and hydrogen.

T. S. P.

**Hydrates of Lanthanum Oxalate.** CHARLES JAMES and C. F. WHITEMORE (*J. Amer. Chem. Soc.*, 1912, **34**, 1168–1171).—In order to ascertain whether the oxalonitrate of lanthanum exists at 25°, the system lanthanum oxalate, lanthanum nitrate, and water has been studied. It is found that no such compound exists at this temperature, but that hydrates of lanthanum oxalate, with 3, 5, and 8 molecules of water, do exist, and that the hydrate with 11H<sub>2</sub>O is unstable in contact with lanthanum nitrate.

J. C. W.

**Action of Seltzer Water on Aluminium.** A. BARILLÉ (*J. Pharm. Chim.*, 1912, [vii], **6**, 110–113).—The author has shown previously (*Abstr.*, 1911, ii, 889) that the metals and alloys commonly used for siphon heads are attacked by seltzer water. He now finds that aluminium is slowly attacked by seltzer water, a flocculent precipitate of aluminium hydroxide being formed in the water. A similar observation has been made by Leo Taylor, of London, for aluminium bronze, and by Heyn and Bauer for ordinary water and seltzer water, in contact with aluminium, rolled cold. The latter authors, however, find that aluminium, after being heated to 450°, is only slightly acted on by ordinary water. As insoluble aluminium compounds are not toxic, and since aluminium has certain practical advantages, the author recommends that siphon heads should be constructed of this metal and lined with porcelain.

T. A. H.

**Preparation of Pure Aluminium Oxide from Bauxite and other Aluminium-containing Material.** OTTOKAR SERPEK (D.R.-P. 246419).—When bauxite or other aluminium-containing material is heated with coal in the presence of nitrogen or air, a nitride is formed, which, when heated with water under pressure, is decomposed according to the equation:  $2\text{AlN} + 3\text{H}_2\text{O} = 2\text{NH}_3 + \text{Al}_2\text{O}_3$ .

A sample of bauxite (5 parts) containing Al<sub>2</sub>O<sub>3</sub> = 83·7% and SiO<sub>2</sub> 16·1%

when heated with two parts of carbon during two hours at  $1400^{\circ}$  furnished a product containing  $N=3\%$  and  $SiO_2 4\%$ ; at  $1600^{\circ}$   $12\%$  of nitrogen was absorbed, whilst after one hour at  $1800^{\circ}$  the product contained  $AlN=97.5\%$ ,  $Al_2O_3=1.9\%$ , and  $SiO_2=0.7\%$ . F. M. G. M.

**Aluminium Peroxide.** A. TERNI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 104—108).—The addition of excess of 30% hydrogen peroxide solution to a solution of aluminium hydroxide in the minimal quantity of 50% potassium hydroxide solution results in the precipitation of the compound,  $Al_2O_3 \cdot Al_2O_3 \cdot 10H_2O$ , which, in the dry state, forms an amorphous, white powder. This compound shows all the properties of a true peroxide.

Further experiments indicate that the initial product of the oxidation of aluminium hydroxide by means of hydrogen peroxide is the dioxide,  $Al_2O_3$ , which, however, undergoes gradual decomposition in presence of water into the oxide described above. T. H. P.

**Crystalline Form of Manganous Chloride Tetrahydrate.** VASILE C. BUTUREANU (*Ann. Sci. Univ. Jassy*, 1912, 7, 179—182).—Monoclinic crystals of  $MnCl_2 \cdot 4H_2O$ , with a habit tabular to the orthopinacoid, show the new crystal-forms  $r(101)$  and  $r'(\bar{1}01)$ . L. J. S.

**The Preparation of Ferrous Chloride by the Electrolysis of an Ethereal Solution of Ferric Chloride.** H. EARNEST WILLIAMS (*J. Amer. Chem. Soc.*, 1912, 34, 1014—1016).—The electrolysis of concentrated ethereal solutions of ferric chloride, using a high current density, gives metallic iron and hydrogen at the cathode, and a few bubbles of gas, probably oxygen, at the anode. Dilute solutions give ferrous chloride at the cathode when a low current density is employed; no chlorine or other gas is evolved, but hydrochloric acid accumulates in the solution as the electrolysis continues. Monochloroethyl ether could not be detected as a product of reaction, but the author assumes its formation as an intermediate product in order to explain the results obtained. T. S. P.

**Normal Chromium Nitrate.** O. M. HALSE (*Chem. Zeit.*, 1912, 36, 962).—A solution of chromic hydroxide in dilute nitric acid deposits, on very slow evaporation, violet crystals, m. p.  $100^{\circ}$ , having the composition  $Cr_2(NO_3)_6 \cdot 15H_2O$ . Decomposition takes place during dehydration (compare Jovitschitsch, this vol., ii, 261). C. H. D.

**A Study of the Change from Violet to Green in Solutions of Chromium Sulphate.** MINNIE A. GRAHAM (*Amer. Chem. J.*, 1912, 48, 145—190).—The yield of violet chromic sulphate, when prepared from chromic acid by Richards and Bonnet's method (Abstr., 1904, ii, 343), is increased by carrying out the reduction at low temperatures, by allowing considerable time for the deposition of the salt, and by keeping all solutions as cold as possible during the process of purification.

Solutions of the violet salt are not stable at room temperature, and

the results of any measurements are made more trustworthy by keeping the solutions at a low temperature until needed for experiments.

Measurements of the density, viscosity, and electrical conductivity of solutions of different concentrations, both with rising and falling temperatures, indicate that there is a condition of equilibrium between the violet and green modifications for each temperature and each concentration.

The hydrolysis, as determined by the conductivity method, is increased in both the violet and green solutions by dilution. At 0° the violet solution is hydrolysed to a small extent only; the green solution shows a tendency to dehydrolyse at low temperatures.

The percentage hydrolysis of solutions of different concentrations and ages was determined by measurements of the velocity of catalysis of sucrose solutions; such measurements also showed that the change from violet to green is much more rapid than the reverse process.

The absorption spectra of the various solutions indicate that the change in colour which occurs is not due to simple hydrolysis, but is the result of a process involving both hydrolysis and a change in structure.

As a result of the numerous measurements made, the author draws the conclusion that the reaction to which the change in colour is due does not take place in successive steps involving the formation of a number of intermediate compounds, but that it is a single process tending to an equilibrium defined by the variables: time, temperature, and concentration.

T. S. P.

**The Reaction between Sodium Thiosulphate and a Mixture of Potassium Dichromate and Sulphuric Acid. A Contribution to the Chemistry of Chrome Tannage.** EDMUND STIASNY and B. M. DAS. (*J. Soc. Chem. Ind.*, 1912, 31, 753—759).—In the two-bath chrome tannage process, the hides or skins are first treated with a solution of potassium dichromate containing various amounts of mineral acid, and then reduced in a second bath, the reducing agent being generally sodium thiosulphate. From an investigation of the reactions which take place, the authors draw the conclusion that the reduction is a complex process, consisting of the three single reactions: (A)  $\text{K}_2\text{Cr}_2\text{O}_7 + 6\text{H}_2\text{SO}_4 + 6\text{Na}_2\text{S}_2\text{O}_3 = \text{K}_2\text{SO}_4 + 2\text{Cr}(\text{OH})\text{SO}_4 + 3\text{Na}_2\text{S}_4\text{O}_6 + 3\text{Na}_2\text{SO}_4 + 5\text{H}_2\text{O}$ ; (B)  $4\text{K}_2\text{Cr}_2\text{O}_7 + 9\text{H}_2\text{SO}_4 + 3\text{Na}_2\text{S}_2\text{O}_3 = 4\text{K}_2\text{SO}_4 + 8\text{Cr}(\text{OH})\text{SO}_4 + 3\text{Na}_2\text{SO}_4 + 5\text{H}_2\text{O}$ ; (C)  $\text{K}_2\text{Cr}_2\text{O}_7 + 3\text{H}_2\text{SO}_4 + 3\text{Na}_2\text{S}_2\text{O}_3 = \text{K}_2\text{SO}_4 + 2\text{Cr}(\text{OH})\text{SO}_4 + 3\text{Na}_2\text{SO}_4 + 3\text{S} + 2\text{H}_2\text{O}$ . The extent to which each of these reactions takes place depends on the dilution and on the amounts of acid and thiosulphate present. Dilution increases slightly the share of reaction A, diminishes considerably the share of B, and increases considerably the share of C. Excess of acid increases the share of reactions A and B, and greatly diminishes the share of C, whilst excess of thiosulphate increases the share of A, and especially that of C, and diminishes the share of B.

Very little sulphur is present in the reduced liquor, the sulphur formed according to equation C reacting to a great extent with the tetrathionate, forming pentathionate; some of it is present in the colloidal form.

Seventy to eighty % of the process takes place too quickly for measurement ; speed measurements can be made only on the last stages of the reaction.

Full details are given of the methods of analysis of the various reaction mixtures, in which the following substances may be simultaneously present : potassium dichromate, chromic acid, sulphuric acid, basic chromic sulphate, thiosulphate, tetra- and penta-thionate, sodium and potassium sulphate, and sulphur in colloidal solution. T. S. P.

**Formation of Combined Striations and Combined Faces, and Destruction of Crystals of Chrome Alum on Solution.** K. GRINAKOWSKY (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 802—818).—The results of observations on crystals of chrome alum immersed in either moving or still solutions of the alum show that the equivalent elements of the crystal do not all possess identical solubilities, and that the degree of supersaturation or the opposite of the solution has different values for the different faces of the polyhedron, and is dependent on the temperature. At low temperatures the edges and angles are the less soluble, and at high temperatures, the faces ; the edges of obtuse angles are more stable than the summits of four-faced angles at low temperatures, whilst at high temperatures the reverse holds. Pawloff's statement, that the surface layer of a crystalline substance is vectorial in character and influences the direction and general course of the deformation, applies to some extent, especially in the case of twinning deformation. The latter indicates the existence of a temperature-limit for a possible equilibrium of the system crystal-mother liquor, the surface energy being, for a given crystallographic form, a maximum.

The direction and course of the deformation of crystals of chrome alum show that the octahedron is the most stable form, and is followed in order by the rhombic dodecahedron, cube, and trapezohedron.

The electrical conductivities and absorption spectra of solutions of chrome alum are in agreement in indicating 78° to be the transition point of the violet to the green modification. T. H. P.

**Preparation of Molybdenum Compounds Containing Nitrogen.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 246554).—When molybdenum oxide, hydroxide, or mixtures of the above with the element are heated at 500—600° with equal parts of nitrogen and hydrogen under a pressure of about 60 atmospheres, a *molybdenum nitride* is formed, which finds technical employment, and when subsequently heated in a vacuum furnishes a continuous method for the preparation of pure metallic molybdenum and ammonia.

F. M. G. M.

**The Preparation of Ductile Tungsten. Melting Point and Other Properties of Pure Tungsten.** OTTO RUFF (*Zeitsch. angew. Chem.*, 1912, 25, 1889—1897).—A review of the best methods of preparation. Tungsten trioxide is purified by reduction at 1000° in a current of hydrogen and steam to the dioxide, which is then heated in

chlorine, the oxychloride being sublimed and transferred to hydrochloric acid, when pure tungsten trioxide is precipitated. The precipitate is washed, dried, and ignited at  $1200^{\circ}$ , when considerable shrinkage takes place. The finely powdered product is then reduced in hydrogen at  $1250^{\circ}$ , nickel boats being used in a porcelain tube. The crystalline metal is compressed into the form of rods under about 5000 atmospheres pressure, and the brittle rods are rendered stronger by heating in hydrogen at  $1300^{\circ}$ . The presence of 0.05% of carbon is favourable. The final sintering takes place by electrical heating at a temperature of  $2620$ — $2650^{\circ}$ . An electric furnace for this purpose is described. The tungsten contracts by about 14%. The sintered rods are still quite brittle, and have to be rendered malleable and ductile by hammering at  $1250^{\circ}$  in an atmosphere of hydrogen. A special apparatus for the hammering is described. The hammered rods are then drawn at  $400$ — $600^{\circ}$  to the required size through diamond dies. The thin wires finally obtained are perfectly flexible, and may be drawn cold. The worked metal is silver-white, and does not oxidise appreciably below a red heat. It is not attacked by concentrated acids, including hydrofluoric acid. C. H. D.

**Specific Resistance and Absorptive Power of Tungsten at High Temperatures.** MARCELLO VON PIRANI (*Physikal. Zeitsch.*, 1912, 13, 753—754).—Measurements have been made of the variation of the electrical resistance of tungsten with temperature between  $1100^{\circ}$  and  $2000^{\circ}$ . By means of a special arrangement of the electrically heated ribbon of metal, it was possible to ascertain the true temperature by optical observations. The data thus obtained differ to only a small extent from those recorded in the previous series of measurements (*Ber. Deut. physikal. Ges.*, 1910, 12, 301). H. M. D.

**Photochemical Properties of Tungstic Acid.** (Mlle.) A. F. VASILIEVA (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 819—835).—The author has investigated the photochemical properties of the compound obtained by Graham by acidifying a solution of sodium tungstate, and described by him as colloidal tungstic acid, but by Sabanéeff (*Abstr.*, 1897, ii, 456) as an amorphous modification of sodium metatungstate,  $\text{Na}_2\text{O}, 4\text{WO}_3$ .

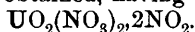
In presence of an organic reducing agent, such as dextrose, sucrose, dextrin, cellulose, formaldehyde, etc., a solution of this compound becomes blue when exposed to sunlight. The solution gradually loses this property, such transformation of the sensitive into the non-sensitive compound obeying the law of reactions of the first order. The reverse change is found to be brought about by heating the solution, this result being in agreement with observations on the absorption spectra.

It may be that colloidal tungstic acid exists in two modifications, the one sensitive to the action of light being converted into the other by absorption of water, or the compound showing photochemical properties may be tungsten trioxide, which adsorbs a molecule of sodium tungstate, giving the insensitive colloid. T. H. P.

**Compounds of Silicotungstic Acid with Antipyrine and Pyramidone.** MAURICE JAVILLIER (*Chem. Zentr.*, 1912, ii, 36; from *Bull. Sci. Pharm.*, 1912, 19, 70—72).—Antipyrine, even in 1:10,000 solution acidified with hydrochloric acid, gives a white precipitate,  $\text{SiO}_2, 12\text{WO}_3, 2\text{H}_2\text{O}, 4\text{C}_{11}\text{H}_{12}\text{ON}_2, 7\text{H}_2\text{O}$ . Pyramidone gives a yellow precipitate containing  $\text{SiO}_2, 12\text{WO}_3, 2\text{H}_2\text{O}, 3\text{C}_{13}\text{H}_{17}\text{ON}_3, 8\text{H}_2\text{O}$ . The method may be used quantitatively. C. H. D.

**Density of Uranous Oxide and its Solubility in Nitric Acid and Aqua Regia.** ALBERT RAYNAUD (*Bull. Soc. chim.*, 1912, [iv], 11, 802—804. Compare this vol., ii, 166).—Uranous oxide, prepared by igniting recrystallised uranyl oxalate in a current of hydrogen at 300—320°, has D 8.2, and is slightly more soluble in nitric acid than in aqua regia. In each of these solvents the solubility increases slowly and regularly between 0° and 20°, more rapidly between 20° and 50°, and shows very little change from 50° to 100°. T. A. H.

**A Compound of Uranyl Nitrate with Nitrogen Dioxide.** ERNST SPÄTH (*Monatsh.*, 1912, 33, 853—857).—When partly dehydrated uranyl nitrate (22.5 grams), having approximately the composition  $\text{UO}_2(\text{NO}_3)_2, 2\text{H}_2\text{O}$ , is dissolved in fuming nitric acid (D=1.52, 30 c.c.), the solution cooled, and then treated with a mixture of nitrogen pentoxide (20 grams) and excess of liquid nitrogen dioxide (12 c.c.), a light yellow precipitate is obtained, having the composition



It is decomposed by water into uranyl nitrate and nitrogen dioxide; at 163—165° anhydrous uranyl nitrate is formed (compare Marketos, this vol., ii, 848). It is not identical with uranous nitrate. T. S. P.

**The Preparation of Pure Thoria from Monazite Sand by means of Hypophosphoric Acid.** FRITZ WIRTH (*Zeitsch. angew. Chem.*, 1912, 25, 1678—1679. Compare Rosenheim, this vol., ii, 869).—Thorium is best precipitated quantitatively by means of sodium hypophosphate. The precipitate may be boiled with potassium hydroxide and purified by precipitation as oxalate, or oxidised by nitric acid to phosphate and so rendered soluble in acids.

If other earths are present, the solution should contain 15—20% of free sulphuric acid, and the precipitation should be performed in a boiling solution. C. H. D.

### Mineralogical Chemistry.

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Pseudomorphs after Stibnite from Mexico. WILLIAM E. FORD and WALTER M. BRADLEY (*Amer. J. Sci.*, 1912, [iv], 34, 184—186).—Prismatic crystals, from veins in limestone near Charcas in San Luis Potosi, have the form of stibnite, but they consist of a fine-grained, yellow material, which appears to be amorphous and of somewhat variable composition (anal. I and II).

	Sb <sub>2</sub> O <sub>3</sub> .	CaO.	H <sub>2</sub> O.	Total.	Sp. gr.
I.	85.53	9.71	4.80	100.04	4.906
II.	90.43	7.36	3.83	101.62	

L. J. S.

**Arsenoferrite, a New Member of the Iron-pyrites Group.** HEINRICH BAUMHAUER (*Zeitsch. Kryst. Min.*, 1912, 51, 143—145).—Dark brown pseudomorphous crystals with a form (*o* 111, *a* 100, *d* 110, *f* 310) similar to that of iron-pyrites are occasionally found with crystals of felspar and quartz on the gneiss of the Binnenthal, Switzerland. Analysis of a small fragment showed the presence of iron and arsenic in the ratio 1:2, suggesting that the original mineral was iron diarsenide,  $\text{FeAs}_2$ . For this hypothetical mineral the name arsenoferrite is suggested. L. J. S.

**Manganese and Iron Minerals from the Valley of Borca, Roumania.** VASILE C. BUȚUREANU (*Ann. Sci. Univ. Jassy*, 1912, 7, 183—186).—The minerals analysed are from a new locality in the area of crystalline schists in the neighbourhood of Broșteni, Roumania. A compact, greyish-pink material, resembling rhodocrosite in appearance and containing intermixed rhodonite, gave anal. I (after deducting insoluble 15·44,  $\text{Al}_2\text{O}_3$  1·90%). This agrees with the same formula,  $5\text{MnCO}_3\cdot\text{FeCO}_3$ , as similar carbonates from the same district (Abstr., 1908, ii, 955; 1909, ii, 745), and the name *ponite* is proposed.

	FeO.	MnO.	MnO <sub>2</sub> .	CaO.	MgO.	CO <sub>2</sub> .	H <sub>2</sub> O.	Sp. gr.
I.	5·17	51·10	—	4·25	1·53	38·00	—	3·46
II.	27·28	6·32	49·47	4·79	1·15	—	10·98	2·85

A compact, brownish-black mineral (anal. II, after deducting insoluble 17·32,  $\text{Al}_2\text{O}_3$  1·57%) is referred to brostenite (P. Poni, Abstr., 1901, ii, 26). This is a manganite,  $\text{R}'\text{H}_2\text{MnO}_4$ , and has resulted from the alteration of the associated carbonate. L. J. S.

**Russian Phosphorites.** JAKOV SAMOILOFF (*Jahrb. Min.*, 1912, i, Ref. 414—415; from *Arb. d. Komm. d. Moskauer Landwirtsch. Inst. zur Untersuchung d. Phosphorite*, 1910, Heft. 2, 131—150).—Anal. I of phosphorite of Portlandian age from Pustoch Gorki, Kisteg, govt. Kostroma. II (by V. Winogradoff) of Lower Neocomian age from the same locality. These results are recalculated under Ia and IIa, there being an excess of fluorine 0·69 and 0·73% respectively. There is also some intermixed clay, iron hydroxide, and quartz, and the alkalis must be present as glauconite. III and IV of phosphorites of Portlandian age from Reptyevka and Gorodishche, govt. Simbinsk, and V (by A. Sabanin) of Oxfordian age from Gorodishche.

	P <sub>2</sub> O <sub>5</sub> .	CaO.	MgO.	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	K <sub>2</sub> O.	Na <sub>2</sub> O.	CO <sub>2</sub> .	SO <sub>3</sub> .
I.	28·98	44·60	0·64	2·60	1·34	0·34	0·74	5·54	0·99
II.	25·10	47·07	0·69	1·64	1·26	0·33	0·59	11·72	0·87
III.	25·49	41·32	0·54	1·85	3·67	0·55	—	6·98	5·35
IV.	25·35	40·48	0·61	3·01	5·33	0·62	—	6·16	3·16
V.	28·03	41·41	0·76	5·69	1·78	0·46	—	6·61	2·27

	SiO <sub>2</sub> .	F.	Cl.	FeS <sub>2</sub> .	Insol.	Organic matter.	H <sub>2</sub> O ignition.	H <sub>2</sub> O at 105°.	Total (less O for F).
I.	0·40	3·28	trace	0·60	2·96	7·96	—	0·90	100·10
II.	0·14	2·97	trace	0·72	0·76	7·72	—	0·73	100·63
III.	9·31	n.d.	—	—	—	2·92	1·09	1·36	100·43
IV.	9·90	n.d.	—	—	—	1·21	3·34	1·20	100·37
V.	7·83	n.d.	—	—	—	0·54	3·70	0·74	99·82

	$\text{Ca}_5\text{F}(\text{PO}_4)_3$	$\text{CaCO}_3$	$\text{MgCO}_3$	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	$\text{FeS}_2$
Ia.	68.57	11.00	1.34	2.13	0.60
IIa.	59.37	24.93	1.44	1.87	0.72

The minerals present in the phosphorite deposits include: iron-pyrites (containing up to 1% arsenic), glauconite, calcite, lublinit, hydrated iron sulphates, gypsum, and barytes.

L. J. S.

**Fusion Experiments with Tremolite and Diopside.** FRANZ LOEWINSON-LESSING (*Jahrb. Min.*, 1912, i, Ref. 386; *Ann. Inst. Polytechn. St. Petersburg*, 1907, Abt. I, 7, 159–163).—Experiments by A. Ginsberg show that fused tremolite, or a mixture having the same composition, consolidates as diopside. Green diopside when fused in an atmosphere of water vapour recrystallises as a complex intergrowth of individuals, suggesting that these have resulted from the breaking down of a solid solution.

L. J. S.

**Didymolite, a New Mineral.** A. MEISTER (*Jahrb. Min.*, 1912, i, Ref. 403–404; from *Verh. Min. Ges. St. Petersburg*, 1908, 46, 151–161).—The mineral occurs in crystalline limestone near a contact with nepheline-syenite on the Tatarka, a tributary of the Angara in Yeniseisk, Siberia. It forms small, greyish-white, bladed crystals resembling kyanite in appearance. The crystals are monoclinic ( $a:b:c = 0.6006:1:0.2867$ ;  $\beta = 106^\circ$ ) and are invariably twinned (hence the name, from  $\delta\delta\upsilon\mu\sigma$ , twin). Analysis I gives the formula  $2\text{CaO}, 3\text{Al}_2\text{O}_3, 9\text{SiO}_2$ . The mineral is unattacked by acids with the exception of hydrofluoric, and it is difficultly fusible to a white blebby glass; the optical characters are stated.

	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	C.	Total.	Sp. gr.
I.	53.33	30.13	4.07	10.83	1.22	0.40	99.98	2.71
II.*	42.17	31.65	1.09	0.17	8.61	—	98.92	—
III.	37.96	44.68	9.52	0.46	6.89	—	99.51	—

\* Also  $\text{TiO}_2$ , 0.50;  $\text{FeO}$ , 3.46;  $\text{Na}_2\text{O}$ , 0.90;  $\text{K}_2\text{O}$ , 0.86; loss on ignition, 8.14.

Associated with the didymolite are black crystals, which are optically uniaxial and probably hexagonal, and which perhaps represent new minerals (anal. II and III).

L. J. S.

**Analyses of Silicates from the Neighbourhood of Pyatigorsk, Caucasus.** N. ORLOFF (*Jahrb. Min.*, 1912, i, Ref. 421–422; from *Annuaire Géol. Min. Russie*, 1911, 13, 21–32).—A black to greyish mineral with granular structure and white streak was found on the screens of Mt. Maschluk, which consists of marls and limestones. It is incompletely decomposed by acids, and fuses readily before the blowpipe with intumescence to a greenish enamel. Several analyses show only slight variations, suggesting that the material is not wanting in homogeneity. The mean result (I) gives the formula  $\text{Na}_2\text{SiO}_3 + 3(\text{Al}, \text{Fe})_2(\text{SiO}_3)_3 + 11\text{CaB}_2\text{O}_4 + 24\text{CaSiO}_3 + 13\text{H}_2\text{O}$ .

	$\text{SiO}_2$	$\text{B}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{Fe}_2\text{O}_3$	$\text{CaO}$	$\text{MgO}$	$\text{Na}_2\text{O}$	$\text{K}_2\text{O}$	$\text{H}_2\text{O}$	Total.	Sp. gr.
I.	41.43	12.48	2.49	5.05	32.21	0.40	1.83	0.24	3.85	99.98*	3.01

\* Also  $\text{TiO}_2$ , 0.15; F, 0.07.

The soda-rich quartz-porphyry (beshtauite) of the Pyatigorsk laccolite contains porphyritic crystals of anorthoclase, aegirite, and arfvedsonite. Analyses of anorthoclase gave: II from Mt. Beshtau; III from Mt. Shelesnaya; IV (*a* the heavier fraction and *b* the lighter) from Mt. Beshtau (Orlinaya Rocks); V (*a* and *b*) from Mt. Shelesnaya; VI from Mt. Medovka. These anorthoclases contain barium, but no strontium.

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	BaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.	F.	Total.	Sp. gr.
II.	67.64	19.21	—	—	0.49	0.71	—	5.05	7.62	—	—	100.72	—
III.	—	19.98	—	—	1.38	0.87	0.28	7.43	5.47	—	—	—	—
IVa.	65.93	22.24	—	—	0.85	0.53	0.07	4.22	7.11	—	—	101.05	2.667
IVb.	67.25	19.52	—	—	—	0.89	—	6.07	6.20	—	—	99.93	—
Va.	65.95	20.89	—	—	1.10	0.75	0.32	5.25	6.79	—	—	101.05	2.662
Vb.	67.51	20.91	—	—	0.57	1.05	0.18	6.52	4.21	—	—	100.05	2.566
VI.	67.09	20.65	—	—	0.67	0.93	—	7.54	3.32	—	—	100.20	—
VII.	41.72	16.83	14.60	4.30	1.31	—	14.07	1.59	1.87	1.23	0.96	98.48	—
VIII.	40.05	15.24	20.29	—	1.05	—	10.92	6.65	1.89	4.26	0.86	101.22	—
IX.	44.81	8.00	11.76	13.54	1.33	0.21	10.21	6.54	1.44	1.25	0.64	99.73	—
X.	44.13	14.15	9.05	5.92	2.10	—	14.25	6.15	1.14	1.51	0.55	98.91	—

Analyses of biotite: VII reddish-brown from the rock at Rasvalka; VIII olive-green from Tupaya; IX greyish olive-green from Shelesnaya; X yellowish-green from Solotoy-Kurgan.

L. J. S.

### Physiological Chemistry.

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**Respiration Experiments in Man in the Fasting Condition, and After the Administration of Various Proteins.** WILHELM LOEFFLER (*Pflüger's Archiv*, 1912, 147, 197—214).—The spirometer results described agree completely with those obtained with Jaquet's and the Tigerstedt-Soudén apparatus. In the same person, the results remain constant for more than four years. On the administration of 50 grams of caseinogen or of edestin, the gaseous metabolism increases by about 5 grams of both oxygen and carbon dioxide.

W. D. H.

**Gaseous Exchange and Activity of the Heart Under the Influence of Poisons and Nerve Stimulation.** ERWIN ROHDE and SAGORO OGAWA (*Arch. exp. Path. Pharm.*, 1912, 69, 200—238).—The experiments were made on the isolated cat's heart. Adrenaline and strophanthine increase the heart's activity, and the increase in oxygen consumption runs parallel to this. No such parallelism exists, however, in the case of many paralyzants (chloral hydrate, atropine, potassium cyanide, veratrine, muscarine), and also in natural death; the activity of the heart fails more rapidly than its oxygen consumption, that is, a smaller quantity of the available energy is converted into work. Differences, however, occur in the action of the agents employed. The paralysis can be either partly or wholly restored by adrenaline, and the thesis is advanced that the sympathetic

nerve is the agent for regulating the transformation of energy in the heart.  
W. D. H.

**Work and Gaseous Exchange in the Frog's Heart. II. Action of Cyanide.** VIKTOR WEIZSÄCKER (*Pflüger's Archiv*, 1912, 147, 135—152).—The gaseous exchange in the frog's heart was estimated as in Warburg's work with the Barcroft apparatus. In potassium cyanide poisoning the oxygen consumption and carbon dioxide production fall in a parallel manner.  
W. D. H.

**Investigations of the Oxygen Content of the Blood by Haldane's Method in Stabbing.** PUPPE (*Chem. Zentr.*, 1912, i, 2079; *Vrtjschr. ger. Med. öffentl. Sanitätswesen*, 1912, 43, Suppl. ii, 49—58).—The oxygen is liberated from the blood by means of potassium ferrocyanide after addition of ammonia, and measured. It is not possible to conclude the occurrence of stabbing from the absence of oxygen from the blood, oxygen being always present in the heart even in such cases.  
C. H. D.

**The Influence of Intravenous Blood-transfusion on Gaseous Metabolism.** PAUL HÁRI (*Biochem. Zeitsch.*, 1912, 44, 1—5).—Gaseous metabolism of two dogs was investigated, into which blood from another dog had been transfused. From one animal more blood had been withdrawn than had been infused. From the results of the determination of gaseous metabolism, the conclusion was drawn that the increased energy consumption resulting from the transfusion is due to increased work of the heart, and not to any special stimulus to metabolism caused by a foreign blood.  
S. B. S.

**Has the Temperature of the Food any Influence on the Gaseous Metabolism of Man?** PAUL HÁRI and STEFAN VON PESTHY (*Biochem. Zeitsch.*, 1912, 44, 6—39).—A cooling of  $0.25^{\circ}$  to  $0.8^{\circ}$  in the body temperature results from ingestion of 1 litre of milk at  $4^{\circ}$ . One litre at about  $50^{\circ}$  causes, however, a rise of temperature of  $0.12^{\circ}$  to  $0.40^{\circ}$ , lasting for some time. Both the hot and the cold milk cause an increased oxygen consumption of about 13—15%, lasting for three hours. After the hot milk, the increased oxygen consumption ceases after three hours, whereas after cold milk it continues for some hours longer. This fact is apparently due to the longer time taken to empty the stomach after cold milk ingestion. From the result of experiment on one individual, it was found that almost twice as much nitrogen is excreted in the urine after cold than after hot milk.  
S. B. S.

**The Influence of Intraperitoneal Infusion of Blood on the Gaseous Metabolism.** CAMILLA RUDÓ and STEPHAN CSERNA (*Biochem. Zeitsch.*, 1912, 44, 40—65).—The blood directly introduced from the carotid artery of one dog into the peritoneum of another dog (either fasting or fed) is resorbed to the extent of 50% within a very few hours. In the case of a fasting animal, this causes an increase of decomposition of protein lasting for some days, without any increase

of consumption of oxygen. In the case of a fed animal in nitrogenous equilibrium, it causes a diminution of decomposition of protein and a retention of the food-nitrogen in the body. The energy consumption is only slightly altered. The diminution of the metabolism of matter affects only the proteins, the protein spared being replaced by consumption of isodynamic quantities of fat and carbohydrate. The increase of the quotient Calories:nitrogen also confirms the supposition that the non-nitrogenous products undergo combustion in the organism to a larger extent after the blood transfusion.

S. B. S.

**Theory and Practice of Transfusion.** JAMES J. HOGAN and MARTIN H. FISCHER (*Koll. Chem. Beihefte*, 1912, 3, 385—416).—The paper is mainly concerned with the conditions under which a circulating liquid, such as blood, is maintained in the veins. When other blood is injected into the veins it remains, but a salt solution is not retained in the veins. The explanation given is that blood (and similar fluids) remains in the veins because it contains no "free" water, all the water being associated with colloids, consequently the water in a salt solution, being largely "free," cannot be retained. Evidence in favour of this view has been obtained by injecting various solutions into the veins of animals and finding to what extent it is found in the urine. A gelatin solution containing a certain proportion of salts is retained, as would be anticipated from the theory. The importance of these principles in the medicinal treatment of cases of abnormally low blood pressure is discussed.

G. S.

**The Influence of Carbohydrates on Energy Metabolism.** PAUL HÁRI (*Biochem. Zeitsch.*, 1912, 44, 66—83).—The experiments were carried out on dogs, both the heat production and the gaseous metabolism being measured, the Rubner respiration calorimeter and the Zuntz-Geppert apparatus being employed. From the increase of oxygen consumed and from the heat production, the conclusion was drawn that after oral ingestion of sugar, a large proportion is immediately metabolised and not stored as glycogen in the liver. The ingestion of dextrose sufficient to cover 50—80% of the energy needs of the organism of a fasting animal is accompanied by increase in the heat production.

S. B. S.

**The Action of Intraperitoneal Infusion of Blood on the Consumption of Energy.** PAUL HÁRI (*Biochem. Zeitsch.*, 1912, 44, 84—94).—By intraperitoneal transfusion of blood into a fasting dog, at any rate in cases where there is no accidental increased output of nitrogen, a diminution of energy consumption is caused, which may be due, partly to the prolonged period of fasting, and partly, and probably to a greater extent, to the action of the transfused blood itself.

S. B. S.

**The Capacity of the Blood Pigment to Combine with Gases.** WILHELM MANCHOT (*Biochem. Zeitsch.*, 1912, 43, 438—444).—In reply to certain criticisms of Heubner and Rosenberg (this vol., ii,

313), the author explains the greater capacity of the blood pigment to combine with gases, when the corpuscles are diluted with isotonic or hypertonic salt solutions, in the following way. He assumes that the corpuscles contain carbon dioxide. This competes with other gases in the combination with the pigment. When the corpuscles are diluted, carbon dioxide can pass the cell walls, and its concentration is therefore less; it is then less effective in competing with other gas for combination with the pigment. The author quotes analogous cases in the competition of various gases for combining with metallic salts, notably cuprous chloride. This will combine with more carbon monoxide when in dilute than when in more concentrated hydrochloric acid. Criticisms are also offered on the spectroscopic work of Heubner and Rosenberg.

S. B. S.

**The Lipoid Content of the Blood of Normal and Pregnant Women and of New-born Children.** EDMUND HERRMANN and JULIUS NEUMANN (*Biochem. Zeitsch.*, 1912, 43, 47—55).—The lipoid content of blood varies greatly with regard to the quantities of cholesterol esters and neutral fats. The blood of pregnant women, as compared with that of normal individuals, shows a large increase in the amounts both of cholesterol esters and neutral fats. The blood of new-born children contains less of both these constituents than that of normal female adults. The quantity of the phosphatides present does not, on the other hand, show great variations. These remarks refer to the total blood. The serum seems to contain the chief quantities of the cholesterol esters, and the corpuscles, the free cholesterol.

S. B. S.

**Blood Coagulation in Man.** J. VON ANGYÁN and R. VON DEN VELDEN (*Biochem. Zeitsch.*, 1912, 43, 207—223).—Coagulation time was altered by injection of saline, and by ligaturing the limbs, the methods being those already employed by the authors, and comparison was made by the use of Wohlgemuth's methods of the times of clotting of the units of fibrin ferment and fibrinogen contained in the blood. It was found that the ferment and fibrinogen content ran parallel with one another, and with the changes in the concentration of the circulating blood. By parenteral administration of peptone, it is possible to increase the fibrinogen content of blood. The increase has, however, no effect on the time factor in the clotting by blood from the capillaries.

S. B. S.

**The Electrical Charge of the Red Blood Corpuscles.** PIERRE GIRARD (*Compt. rend.*, 1912, 155, 308—310).—Höber (compare Abstr., 1904, 55, 352) found that the electrical charge on the red corpuscles of blood in serum, in isotonic solutions of sucrose, or in solutions of different neutral salts is negative. The author has made fresh measurements, using a small cell with parallel faces, and obtained good results in serum and isotonic solutions of sucrose. In solutions of neutral salts the slight convection currents set up by the electrolysis prevented accurate determinations. Working with isotonic solutions of salts of the rarer tervalent metals, such as

lanthanum, a marked modification occurs in the electrical charge on the blood corpuscles, the sign changing to positive. Commencing with a maximum negative charge in isotonic solutions of sucrose or other sugars, it is possible to diminish its density progressively almost to neutrality, when the globules agglutinate, and finally to change its sign. W. G.

**Comparative Investigations on Old and Young Blood Corpuscles. Resistance and Regeneration.** J. SNAPPER (*Biochem. Zeitsch.*, 1912, 43, 256—266).—The destructive effect of hypotonic salt solutions on corpuscles was investigated by a colorimetric method. It is claimed that by this procedure, the regeneration of corpuscles can be studied better than by any other, in that the young erythrocytes are more resistant to destruction by hypotonic solutions. The blood corpuscles of a rabbit show greater and greater resistance to hypotonic solutions after each succeeding venesection. This resistance is greater than can be accounted for by the mere removal of the older corpuscles in the act of blood-letting. The author draws from his results the conclusion that young corpuscles are regenerated from the old, and that the Weigert pathological law holds true, namely, the reparation is greater than the loss. S. B. S.

**The Influence of Washing on the Resistance of Red Blood Corpuscles.** J. SNAPPER (*Biochem. Zeitsch.*, 1912, 43, 266—274).—Blood corpuscles, after washing with 4% dextrose solution, have the same degree of resistance to hypotonic sodium chloride solutions as those which have not been washed. On the other hand, after washing with 0.9% saline solutions, the resistance is diminished. This diminished resistance is not due to the removal of any substance which inhibits hæmolysis, but to a disturbance of the osmotic equilibrium of the erythrocytes. There is no diminished resistance if to the 0.9% sodium chloride solution, 0.1% calcium chloride is added. For determining the resistance, the blood should not be collected therefore in a solution of 0.9% sodium chloride + 0.4% sodium citrate. The injury caused by collection in such a fluid can, however, be repaired if the corpuscles are washed afterwards in a solution of 0.9% sodium chloride + 0.1% calcium chloride. The increased resistance of young blood corpuscles in anæmic animals is not due to the relatively large amount of serum, but is an actual property of the corpuscles themselves, which does not disappear after washing with 0.9% sodium chloride solution. S. B. S.

**Mineral Metabolism in a Rabbit Fed on Oats with Sodium Oxalate.** FRIEDRICH LUTHLEN (*Arch. expt. Path. Pharm.*, 1912, 69, 375—379).—Poisoning with sodium oxalate leads in the rabbit to a loss of bases, a demineralisation. The increase of excretion falls especially on potassium, and then on calcium; magnesium is hardly affected. Sodium is retained in the body. This alteration is regarded as important, as an upset in the proportion of bases interferes with the normal functions of the body. W. D. H.

**Metabolism Experiments with Parenteral Nutrition.** L. ORNSTEIN (*Biochem. Zeitsch.*, 1912, 44, 140—156).—Dogs burn up completely a mixture of foreign blood-serum and dextrose introduced under the skin over a period of eight to twelve days. The utilisation of chemical energy is good, but it is less than that of the corresponding foodstuff introduced orally. If the food is introduced under the skin for longer periods, protein decomposition of the organism sets in, the animals become lean, and finally die, showing the symptoms of anaphylaxis. A mixture of blood-serum, dextrose, and olive oil is not suitable for subcutaneous feeding; it causes protein decomposition of the organism immediately after introduction, and the animal dies after a very short period. S. B. S.

**Behaviour of Inorganic Constituents of Nutriment in the Alimentary Canal.** 1. **The Behaviour of the Iron and Calcium of Flesh in Digestion.** EMIL ABDERHALDEN and RUDOLF HANSLIAN (*Zeitsch. physiol. Chem.*, 1912, 80, 121—135).—All recent research on organic foods has shown that these are broken down into simple products before they are absorbed. The question arises whether the same is true for inorganic food, and special attention is directed to calcium and iron. In former days iron was supposed to be nutritive only if absorbed in organic union. The present experiments carried out *in vitro* show that during digestion both iron and calcium are resolved into soluble inorganic compounds. W. D. H.

**Formic Acid as an Intermediate Product in Sugar Cleavage in Animals.** O. STEPPUHN and H. SCHELLBACH (*Zeitsch. physiol. Chem.*, 1912, 80, 274—286).—That formic acid is an intermediate product in the fermentation of sugar by micro-organisms has been established by several workers. It is now shown that the same is true during metabolism in the higher animals (dogs). The amount of formic acid in the urine and tissues is increased by feeding on dextrose. The ready oxidisability of formic acid renders the detection of larger quantities difficult. W. D. H.

**The Decomposition of Pyruvic Acid by Animal Organs.** M. TSCHERNORUTZKY (*Biochem. Zeitsch.*, 1912, 43, 486—490).—In view of the fact that pyruvic acid is destroyed by yeast, it is conceivable that it is an intermediary product of carbohydrate metabolism. It was, therefore, of interest to ascertain whether it is destroyed by animal organs. This was found to be the case, the liver and muscles of the dog exerting a particularly powerful action in this respect. The products of change have not been isolated. The pyruvic acid was estimated by precipitation with *p*-nitrophenylhydrazine. S. B. S.

**The Substitution of Protein, or an Equivalent Mixture of Amino-acids, by Gelatin and Ammonium Salts.** EMIL ABDERHALDEN and ARNO ED. LAMPÉ (*Zeitsch. physiol. Chem.*, 1912, 80, 160—174).—A preliminary account of a series of experiments on dogs, who received abundant fat and carbohydrate in their food, but only gelatin and ammonium salts as nitrogenous constituents. The salt used

was the acetate, and all ammonium salts are not of equal nutritive value. The nitrogen balance was negative throughout; ammonium acetate, moreover, easily sets up vomiting and diarrhœa. W. D. H.

**Synthetic Capacity of Cells in Mammalia. Protein Need in Dogs Fed on Ammonium Salts and Single Amino-acids.** EMIL ABDERHALDEN and PAUL HIRSCH (*Zeitsch. physiol. Chem.*, 1912, 80, 136—159).—A detailed account of experiments on dogs, some lasting about a hundred days, which confirm the findings of previous workers that single amino-acids and ammonium salts can supply the necessary nitrogen. Ammonium citrate was the salt employed, and some discussion on the merits of different preparations is given. W. D. H.

**Observations on Growth During Feeding with Isolated Articles of Food.** THOMAS B. OSBORNE, LAFAYETTE B. MENDEL, and EDNA L. FERRY (*Zeitsch. physiol. Chem.*, 1912, 80, 307—370).—This paper deals at length and with full experimental details on a subject previously treated by the authors in various preliminary articles. The nutritive value of individual proteins in relation to their chemical composition is considered *inter alia*, and the important distinction between foods capable of maintaining equilibrium and those essentials for growth is insisted on. W. D. H.

**The Influence of Optical Stimula on the Gaseous Metabolism of the Brain.** FRANZ G. ALEXANDER and GEZA RÉVÉSZ (*Biochem. Zeitsch.*, 1912, 44, 95—126).—Experiments were made on curarised animals with carefully regulated artificial respiration, which was produced by a Meyer pump. The eyes were submitted to illumination, and the gaseous metabolism was measured during a period of rest and during a period of stimulation. There was an increase of carbon dioxide output and oxygen consumption during the stimulation period, which also continued after the spinal chord was cut. From the results, the conclusion was drawn that by a sensory stimulus (in these experiments an optical one) there is an increased consumption both of matter and energy in the brain. The stimulus causes a greater increase in oxygen consumption than in carbon dioxide output. S. B. S.

**The Gaseous Metabolism of the Brain.** FRANZ G. ALEXANDER (*Biochem. Zeitsch.*, 1912, 44, 127—139).—The results of direct measurement of the gaseous metabolism confirm the results of Alexander and Révész (see previous abstract) that optical stimulation increases the metabolism of the brain. The gas in the arterial and venous blood was measured by the Barcroft method. Side by side with increased gaseous metabolism there was found, as is the case in increased activity in other organs, a greater blood-flow during activity, as demonstrated by the rate of flow through a pipette (Barcroft's method), and by plethysmographic measurements. S. B. S.

**Non-existence of Free or Combined Lecithins in the Yolk of Eggs and in Biological Structures.** N. ALBERTO BARBIERI (*Compt. rend.*, 1912, 155, 312—314. Compare Abstr., 1910, i, 704).—The so-called lecithin, m. p. 150°, obtained from egg-yolk by extraction

with alcohol (compare Abstr., 1907, ii, 708), is really a mixture of tripalmitin, oleopalmitin, ovochromin (this vol., ii, 783), and alkali metaphosphates. When submitted to the action of alcoholic sulphuric acid for five hours on a water-bath, it shows no trace of glycerol or glycerophosphoric acid. By ethereal dialysis, ovochromin and alkali metaphosphates can be separated from the tripalmitin and oleopalmitin. Examination by physiological methods also proves it to be a mixture of the above-mentioned substances. Ovovitellin when saponified by potassium hydroxide gives no trace of glycerol or fatty acids, thus proving the absence of combined lecithin. W. G.

**The Occurrence of Nucleic Acid in Ripe Herring Eggs.** HELENE TSCHERNORUTZKY (*Zeitsch. physiol. Chem.*, 1912, 80, 194—197).—From the amount of purine bases, it is calculated that ripe herring's eggs contain only 1.2% of nucleic acid, whereas reckoned from the yield of phosphorus, it is nearly ten times greater. The nature of this phosphorus combination is not known. W. D. H.

**Changes in the Chemistry of the Skin by Different Diets and Poisons.** FRIEDRICH LUTHLEN (*Arch. expt. Path. Pharm.*, 1912, 69, 365—374).—The skin shows an alteration of chemical composition (change in the amount of cations) on various diets, in chronic acid poisoning, and on the administration of sodium oxalate. This leads to alterations in the capacity of the skin to resist injury and in the liability to skin diseases. W. D. H.

**The Origin and Destiny of Cholesterol in the Animal Organism. IX. The Cholesterol Content of the Tissues, other than Liver, of Rabbits under Various Diets and During Inanition.** GEORGE W. ELLIS and JOHN A. GARDNER (*Proc. Roy. Soc.*, 1912, B, 85, 385—393. Compare this vol., ii, 275).—The cholesterol content of the blood after food depends on the sterol content of the food taken. In the case of animals in a state of inanition which are living on their own tissues, the blood, just as in the case of the liver, contains an increased amount of both free and combined cholesterol.

In muscle the quantity of cholesterol appears to bear no relation to the sterol in the diet. The free cholesterol in the brain varied in different animals from 2.02 to 2.88%, whilst in no case was there any evidence of the presence of cholesterol ester.

In the kidney the cholesterol content also appears to be independent of the diet. In the case of starved animals the total cholesterol is much higher than in normal animals, the increase in the cholesterol esters being specially marked. A similar increase in the ester over the free cholesterol was noticed in the kidneys of animals which had received injections of oil into the peritoneal cavity.

The lungs were found to contain a higher proportion of cholesterol than any other organ excepting brain; in this case, also, the quantity was independent of the diet. W. J. Y.

**Nitrogenous Extractives of the Liver.** J. SMORODINZEFF (*Zeitsch. physiol. Chem.*, 1912, 80, 218—231).—Carnosine and

carnitine, which are characteristic muscle-extractives, are absent from the liver. Methylated purines are also not present. Adenine, guanine, methylguanidine, and choline were found. W. D. H.

**The Influence of Acids and Alkalis on Autolysis with the Use of Different Antiseptics.** M. KASCHIWABARA (*Zeitsch. physiol. Chem.*, 1912, 80, 45—63).—Details are given of the course of autolysis in the liver under the influence of certain antiseptics (oil of mustard, chloroform water, formaldehyde). An alkaline reaction favours the growth of putrefactive organisms. The hydrolytic decomposition of protein goes further when formaldehyde is employed than when chloroform water is used. Details of the amounts of protein cleavage products under various conditions are given in tabular form. W. D. H.

**Physiology of the Pancreatic Secretion.** A. J. SMIRNOFF (*Pflüger's Archiv*, 1912, 147, 234—248).—A flow of pancreatic juice occurs about twenty to twenty-five minutes after fat is introduced into the duodenum, and while the duodenal contents are usually neutral or alkaline. When fat-splitting begins, the amount of secretion increases considerably. The juice secreted as a result of placing neutral fat in the duodenum is rich in nitrogen, solids, and enzymes. If atropine is injected subcutaneously at the height of fat-splitting, the quantity of juice is not lessened, but the amount of nitrogen and solids rises in about fifteen minutes. W. D. H.

[Human Pancreatic Juice.] JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1912, 43, 224—225).—Polemical. A reply to Glaessner (this vol., ii, 778). S. B. S.

[The Relationship between the Pancreas and Suprarenals.] JULIUS WOHLGEMUTH (*Biochem. Zeitsch.*, 1912, 43, 226—227).—A reply to Glaessner and Pick, consisting chiefly of a criticism on the interpretation of results (this vol., ii, 782). S. B. S.

**Physiology of the Kidney Secretion.** OTTO COHNHEIM (*Zeitsch. physiol. Chem.*, 1912, 80, 95—112).—The heteropod snails lend themselves to the study of biological questions by means of pigments on account of their transparency. The uptake of nutriment is governed by a touch reflex, and not by optical or chemical stimuli. In the choice of nourishment, a chemical organ does, however, play a part. The substances which lead to urine formation are stored in the kidney cells before secretion, and are contained as salts within their protoplasm. W. D. H.

**Physiology of Glands. XVIII. The Function of the Spleen as an Organ Controlling the Metabolism of Iron.** LEON ASHER and HANS VOGEL (*Biochem. Zeitsch.*, 1912, 43, 386—409. Compare this vol., ii, 660).—According to Asher's theory, the spleen plays an important rôle in the control of iron metabolism. This is confirmed by experiments carried out on a splenectomised animal on diets free from,

or rich in, iron. Two animals from the same litter were employed, one was used as a control, and the spleen was removed from the other. It was found that if young animals are kept (without splenectomy) for some weeks on a diet free from iron, the number of blood corpuscles and the hæmoglobin content at first rise, and then return to the normal. The removal of the spleen from an animal on a diet free from iron causes marked diminution of the number of corpuscles and of the hæmoglobin content, lasting for some weeks. A control animal under similar conditions shows nothing abnormal. On giving the splenectomised animal meat or a diet rich in iron, the condition of the blood becomes normal again. These results explain the contradictory experiments of former investigators of the physiology of the spleen, who used different diets.

Withdrawal of a small amount of blood from a splenectomised animal causes a transient increase in the erythrocytes and hæmoglobin; in a normal animal it causes a slight decrease. S. B. S.

**The Lipoid Content of Placenta.** BIANCA BIENENFELD (*Biochem. Zeitsch.*, 1912, 43, 245—255).—During the course of pregnancy, the content of the placenta in substances soluble in light petroleum, in cholesterol and its esters markedly diminishes. In mature placenta the petroleum extract contains phosphorus only in traces, and in much smaller quantities than are found in the case of immature placenta, and in placenta from cases of eclampsia and syphilis. The lipoids (cholesterol and its ester with lecithin) are much higher in immature placenta than in the mature, and also appreciably higher in syphilitic than in normal cases. Neutral fats diminish during the course of pregnancy. Placenta in cases of eclampsia contain a little more, and in cases of syphilis a little less, than the normal amount of neutral fats. S. B. S.

**Relationship of Electrical, Mechanical, and Chemical Changes in Muscle.** WOLFGANG PAULI (*Koll. Chem. Beihefte*, 1912, 3, 361—384).—The explanation of the source of the *E.M.F.* in muscular action is based on the view that the acid formed at the boundary between the plasma and fibrillæ penetrates into the latter and enters into combination with protein. The  $H^+$  ion combines with several molecules of protein, forming a highly complex cation and rapidly diffusing anions. The latter, in virtue of their greater speed, impart a negative charge to the surrounding medium, whilst the protein ions remain positively charged. Another factor which comes into consideration is that neutral salts completely discharge a complex protein ion, so that a cell made up as follows: acid protein | acid | acid protein + neutral salt will give a definite *E.M.F.* According to the author's theory, the acid protein corresponds with the muscle fibrillæ, the acid layer to the sarcoplasm, and the tissue fluid to the combination of acid protein and neutral salt. The explanation suggested for the mechanical changes in the contraction of muscle is that on the entry of lactic acid into the fibrillæ a swelling of the doubly refracting substance in the latter takes place, accompanied by contraction.

G. S.

**The Chemistry of Muscular Tissue. II. The Content of Striated and Plain Muscular Tissue of Mammals in Organic and Inorganic Phosphorus.** A. COSTANTINO (*Biochem. Zeitsch.*, 1912, 43, 165—180. Compare this vol., ii, 67).—In striated muscles, the sum of the quantities of chlorine and phosphorus is greater than that of the equivalents of sodium and potassium. This statement also holds when the inorganic phosphorus is not included in the total. The equivalents of chlorine and phosphorus are also in excess of those of sodium and potassium in plain muscle. This statement does not hold, however, when the inorganically combined phosphorus is not included in the total. The analyses in this case indicate the existence of organic substances containing alkali metals. S. B. S.

**The Fat of the Smegma of the Horse.** FRANZ ZARIBNICKY (*Zeitsch. physiol. Chem.*, 1912, 80, 232—236).—The physical constants for the fatty material in the horse's prepuce are given. There is nearly 5% of cholesterol, most of which is in the form of esters; other higher alcohols are more abundant, but their nature is undetermined. The fatty acids present are mostly free. W. D. H.

**Lecithin and Other Lipoids Extracted from Tissues Fixed with Formaldehyde.** JOHN CRUICKSHANK (*J. Path. Bact.*, 1912, 17, 118—119).—The lecithin fraction extracted from tissues fixed by formaldehyde is less in amount than from normal tissues, but gives the same tests, chemical and biological. This is especially the case if 80—85% alcohol is used as the extracting agent, but "lecithins" obtained in the ether extract have a low iodine value, and do not act as syphilitic antigens or as hæmolysins with cobra venom. W. D. H.

**Some Analyses of Urine Composites.** JOHN H. LONG and FRANK GEPHART (*J. Amer. Chem. Soc.*, 1912, 34, 1229—1242).—This paper presents a series of complete analyses of the urine of six men living under the same conditions, and on a controlled diet for a period of over thirty days. It is found, in harmony with previous experience, that the order of distribution of nitrogen is very generally the same, the percentage falling in the order: urea (about 80% of the whole), creatinine, ammonia, uric acid, purine. The creatinine varied between 21.5 and 27.8 mg. daily per kilo. of body-weight, the highest value being found in the case of a rather lean man, and the lowest in the case of a fat man. That the creatinine excretion is independent of the total nitrogen is shown in the case of three other men who were kept for ten days on a low protein diet, and then for ten days on a higher protein diet, since, although the total nitrogen increased, the creatinine excretion was almost the same, and the relation of the percentage amounts for the three men was constant. The undetermined nitrogen is shown to be no matter of diet, for a decrease in meat nitrogen with a corresponding increase in that derived from milk did not result, as has been suggested, in a decrease in this item. Individual peculiarity is said to be an important factor, which is also the case with the indican excretion, for this was found to be quite unrelated to diet or to the ethereal sulphates in the urine.

On the other hand, a close relation is established between creatinine and neutral sulphur, which were found to vary in percentage amount in the same manner with change of diet. They may both be of endogenous origin. The connexion between the acid and the basic ions is shown, and attention is drawn to the fact that, even in these normal cases, the ammonia excretion must play an important part in fixing the acids, for it exceeds the combining power of calcium and magnesium together. It is also pointed out that in attempting to balance the basic and acidic ions, account must be taken of the degree of acidity of the phosphoric acid and also such organic acids as hippuric acid as well as carbonic acid.

J. C. W.

**Composition of Bladder Stones in the Natives of Asia Minor.** EMIL ABDERHALDEN and RUDOLF HANSLIAN (*Zeitsch. physiol. Chem.*, 1912, 80, 113—120).—Stone in the bladder appears to be very common in Asia Minor, and qualitative analyses are given of many of these; nearly all were specially rich in inorganic and particularly in calcium salts. The hard water of these parts, and the high inorganic content of the principal grain (Burghul) eaten are considered to be important in the etiology of the complaint. The wheat of Asia Minor is not richer in calcium and magnesium than that grown in other parts.

W. D. H.

**Studies of Oxidation. The Rôle of Oxidising Enzymes. Oxydases containing Iron. Application of the New Ideas to Diseases of Nutrition.** J. SARTHOU (*Chem. Zentr.*, 1912, i, 1629—1630; from *Bull. Sci. Pharm.*, 1912, 18, 671—676).—An account of the action of oxidising enzymes and co-enzymes. Diseases of nutrition may be explained by the absence of one or other of the specific oxydases of the system.

C. H. D.

**Etiology of Beri-Beri. I. The Phosphorus Content of Animals Ill from Nutrition Defects.** HERMANN WIELAND (*Arch. exp. Path. Pharm.*, 1912, 69, 293—306).—Schaumann's hypothesis that the amount of organically combined phosphorus in the food leads to a similar poverty of phosphorus in the body, and thus to beri-beri, is not confirmed in a series of analyses in mice. A method for estimating phosphorus (inorganic and organic) in animal material is described.

W. D. H.

**Effect of Röntgen and Radium Emanations on the Vitality of the Cells of Mouse Carcinoma.** B. H. WEDD and SIDNEY RUSS (*J. Path. Bact.*, 1912, 17, 1—11).—Freshly excised mouse tumours sufficiently irradiated with X-rays do not "take" when inoculated into other mice. This is more marked when the rays used are not of a very penetrating type. The same is true for tumours irradiated by  $\beta$ -rays for one hour, but not after an exposure of eighteen hours to  $\gamma$ -rays from the same quantity (5.6 mg.) of radium bromide.

W. D. H.

**The Action of Antiglycosuric Medicaments and Liver Glycosuria.** ERNST NEUBAUER (*Biochem. Zeitsch.*, 1912, 43, 335—385).—As effect of the piqûre can be observed a rise of blood-pressure

and increase of the liver volume as a result of hyperglycæmia. This increase of blood-pressure, accompanied as it is with a changed respiration and the presence of lactic acid in the urine, indicates that the *piqûre-diabetes* belongs to the class of glycosuria which results from asphyxia. Like adrenaline, barium chloride, but in a lesser degree, exerts a vaso-constrictor action. Chloral hydrate and alcohol, which in larger doses paralyses the vessels, antagonise the *piqûre* action both on the vaso-motor system and on the glycosuria. The antiglycosuric action of these medicaments can only be partly attributed to the retention by the kidneys, and not at all to the withdrawal of the carbohydrates from the system to form glycuronates with them. Plethymographic observations on the liver indicate hyperglycæmia in this organ as the result of adrenaline action and of *piqûre*. The change of liver volume in these cases runs more or less parallel with the changes in the general blood-pressure. Chloral hydrate administered in these cases causes a diminution in both the blood-pressure and in the liver volume. The temporary hyperglycæmia produced by a ligature of the hepatic vein, and the subsequent release of the stasis, also causes glycosuria.

S. B. S.

The Influence of Nutrition, Body-weight, and Water Diuresis on Phloridzin Diabetes. MAX ROTH (*Biochem. Zeitsch.*, 1912, 43, 10—30).—The sugar excretion after phloridzin administration can vary very considerably in the same animal. Different animals also show great variations in the amount excreted, which variations have no relation to the weight of the animal. It is therefore useless, in making comparisons, to calculate the sugar excretion in terms of grams per kilo. weight of animal. In examining the influence of various factors on the secretion, the same animal must be used. One mg. phloridzin suffices to cause glycosuria in healthy animals. The sugar secretion is smallest in fasting animals. It increases after increasing amounts of meat ingestion, up to 250 grams. After starchy diets, the excretion is somewhat greater than after a diet of the same weight of meat. It is largest after dextrose administration (where, of course, there is no alimentary glycosuria). After casein ingestion the excretion was greater than that of a fasting animal, but less than that after the ingestion of the same weight of meat. The length of the existence of glycosuria is shortest in a fasting animal and after fat ingestion, and longest after dextrose administration. The greatest amount of excretion takes place within three hours of food ingestion. The magnitude of water diuresis is without effect on the sugar secretion. When the urine is strongly alkaline (and only then), the sugar excretion appears to be increased. The fact that sugar secretion is lowest at the time at which the liver becomes most enriched in glycogen (twelve to fifteen hours after a meal) negatives Biedl and Koli's theory of the primary extra-renal production of sugar in the liver, and subsequence hyperglycæmia. The authors do not support the Pavy-Brodie-Siau hypothesis, but rather the elimination theory of Erlandsen.

S. B. S.

**Excitability of Organisms by Ultra-violet Light. Latent Period. Law of Thermic Independence, Fatigue, and Recovery Phenomena.** VICTOR HENRI and (Mme.) V. HENRI (*Compt. rend.*, 1912, 155, 414—417).—The authors have shown previously that ultra-violet rays produce involuntary movements in small animals, that a fixed minimum exposure (initial period) is required to produce this effect, and that a definite time (latent period) elapses between the termination of the initial period and the movement. The present paper describes experiments carried out to determine what processes occur during the initial period.

The results show that during the initial period photochemical reactions take place in the peripheral organs, and that the products of these reactions are distributed by diffusion and osmosis. The initial and latent periods are not affected by change of temperature. Prolonged exposure to ultra-violet rays renders *Cyclops* immobile, but it responds to ultra-violet rays, and the "initial period" is then longer, but gradually returns to its primitive value. This is also the case with an animal in which the nerve terminals have been anæsthetised by cocaine, but not in one in which the nerve centres have been anæsthetised by ether. The phenomena of fatigue and recovery of excitability by ultra-violet light, therefore, have their seat in the peripheral organs. T. A. H.

**The Purgative Action of Sulphur.** HERMANN TAEGEN (*Arch. expt. Path. Pharm.*, 1912, 69, 263—267).—Boedeker's reaction for sulphurous acid is not applicable to the animal organism, as it is also positive for cysteine. After the administration of sulphur, hydrogen sulphide is formed both in the large and small intestine of the dog. Its purgative action is not due, as Frankl considers, to the formation of sulphurous acid, but of hydrogen sulphide. W. D. H.

**Chemistry of Silver Therapy.** ANGELO ANGELI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 12—15).—Owing to the publication of Paul's results (this vol., ii, 788), the author draws attention to his own work with Marchetti (Abstr., 1908, ii, 841), Castellana and Ferrero (Abstr., 1909, i, 739), and Alessandri (Abstr., 1910, i, 605). T. H. P.

**Mesothorium, Thorium-X, and Thorium Emanation Therapy.** ADOLF BICKEL (*Chem. Zentr.*, 1912, i, 1792—1793; from *Berl. klin. Woch.*, 1912, 49, 777—779).—It is not yet possible to determine whether long- or short-lived radioactive substances are more suitable for therapeutic purposes. Thorium-X and thorium emanation appear to be of therapeutic value, and have the advantage over radium of being available for internal administration. C. H. D.

**The Biological Action of Mesothorium. The Biological Action of Thorium Emanation on Men after Administration by the Alimentary Canal.** KENJI KOJO (*Chem. Zentr.*, 1912, i, 1793; from *Berl. klin. Woch.*, 1912, 49, 779—780. Compare preceding abstract).—After the ingestion of thorium-X solution, the

emanation is readily detected in the breath and in the urine for at least five or six hours when 1 c.c. of solution (1900 Mache units) is used. After one hour's inhalation, the emanation is not to be detected in either the breath or urine. C. H. D.

**The Biological Action of Mesothorium. The Action of Thorium Emanation on Digestive Ferments and Autolysis.** MINAMI (*Chem. Zentr.*, 1912, i, 1793; from *Berl. klin. Woch.*, 1912, 49, 781—783. Compare preceding abstracts).—The action of thorium- $X$  and thorium emanation on pepsin, trypsin, and diastase may be an accelerating or a retarding one, depending partly on the duration of exposure.  $\alpha$ -Rays are more active than  $\beta$  or  $\gamma$ , and the latter are without influence on autolytic enzymes. C. H. D.

**The Action of Certain Medicaments on the Healthy Alimentary Canal.** L. KLOCMAN (*Zeitsch. physiol. Chem.*, 1912, 80, 17—34).—Various drugs (quinine, arsenic, sodium salicylate, digitalis, etc.) were given to dogs with fistulæ in stomach and small intestine, and their effects, mainly on the rate of progress through the alimentary canal and amount of secretions formed, are recorded. W. D. H.

**Action of Crystallised Aconitine on Respiration.** CURT HARTUNG (*Arch. expt. Path. Pharm.*, 1912, 69, 176—199).—Aconitine slows respiration, but vagotomy lessens the length of the expiratory pauses. Death is due to respiratory failure, or in other cases to paralysis of the heart. It is antagonised by atropine. By repeated doses, the animal (rabbit) develops a high resistance to aconitine. Some of the alkaloid is excreted in the urine unchanged. W. D. H.

**Action of Adrenaline in Producing Cardiac Hypertrophy.** HUGH A. STEWART (*J. Path. Bact.*, 1912, 17, 64—81).—In rabbits, injections of adrenaline produce an increase in the muscular tissue of the heart; the muscle fibres are, however, degenerated, and the hypertrophy is regarded, not as a result of increased work, but as due to the action of a toxic agent. The chemical nature of the metabolic disturbance is not yet known. W. D. H.

**Behaviour of *p*-Iodoanisole in the Animal Organism.** RICCARDO LUZZATO and G. SATTÀ (*Arch. Farm. speriment.*, 1912, 13, Reprint, 14 pp.).—*p*-Iodoanisole is neither a toxic substance nor a local irritant, and is therefore tolerated by the animal organism better than *o*-iodoanisole (compare Abstr., 1911, ii, 1015). Its administration is accompanied by an increase in the proportions of organic sulphate and conjugated glycuronic acid in the urine. T. H. P.

**The Behaviour of Atophan in the Organism.** MAX DOHRN (*Biochem. Zeitsch.*, 1912, 43, 240—244).—From the urine of animals to which atophan had been administered, a hydroxy-derivative, m. p. 245° (corr.), could be isolated, which appears to be 8-hydroxy-2-phenyl-

quinoline-4-carboxylic acid. In addition, another hydroxyl derivative was found, which appears to be a hydroxypyridineuric acid. A third substance, of m. p. 310°, which was only slightly soluble in acetic acid (and could in this way be separated from the other two), was also obtained, which contained C 70.57, H 6.88, N 3.96%.

In further confirmation that the hydroxyatophan isolated from urine contains the hydroxyl group in position 8, the author shows that after ingestion of 8-methoxy-2-phenylquinoline-4-carboxylic acid, the same hydroxyatophan is excreted. Here again several other products were isolated.

S. B. S.

**Action and Relationships of Atropine in the Organism. II. The Relation of the Thyroid to the Atropine-destroying Power of the Blood.** RENÉ METZNER and E. HEDINGER (*Arch. exp. Path. Pharm.*, 1912, 69, 272—292).—The microscopical differences seen in the rabbit's thyroid have no relation to the varying powers of the animal's blood to destroy atropine.

W. D. H.

**The Rôle of Caffeine in the Cardiac Action of Coffee.** H. BUSQUET and MARC TIFFENEAU (*Compt. rend.*, 1912, 155, 362—365).—From experiments on the isolated heart of the rabbit, the authors find that caffeine commences to be active with a dose of 1 in 100,000, and is very toxic at 1 in 5000. With ordinary coffee, the toxic effect is probably due to other agents, such as potassium salts, besides caffeine, their effect being shown with coffee deprived of caffeine. From these results no conclusion can be drawn as to the cardiac action of coffee under the conditions where it is consumed by man.

From experiments on the dog *in vivo*, it was found that caffeine and ordinary coffee infusion both produce a marked acceleration of the heart-beat, which effect lasts about one hour. Coffee deprived of its caffeine has no such effect even in strong doses. Caffeine is therefore the principal agent in the cardiac action of coffee.

W. G.

**The Comparative Cardiac Action of the Physiological Extract of Digitalis and Other Digitalis Preparations.** H. BUSQUET (*Compt. rend.*, 1912, 155, 509—512).—The cardiac effect of a physiological extract of *digitalis* in some respects resembles, and in others differs from, the effect of other preparations from this plant. Experiments were performed on rabbits, cats, and dogs, and on the isolated heart of the rabbit. Like other digitalis preparations, the physiological extract exerts a tonic action on the heart with rise in arterial pressure (compare Etienne, *Archiv. int. Pharm. Thér.*, 1909, 19, 146). It produces an acceleration in the heart-beat, followed by an irregular beat. It also suppresses the cardio-inhibitory power of the vagus, generally during the acceleration period of the heart-beat (compare Franck, *Cliniques de la Charité*, 1894, 549—750). The irregularity of heart-beat provoked by toxic doses ceases a few minutes before death. In other respects the physiological extract differs from ordinary pharmaceutical preparations of digitalis. In the case of the dog no injection of physiological extract, however modified the dose, produces

any slowing of the heart-beat. With ordinary extracts, Franck (*loc. cit.*) has shown that, prior to death, the heart-beat becomes regular, and then there is produced a state of tetanus followed by fibrillary tremors. With the physiological extract death takes place suddenly during the period of regular heart-beat. W. G.

**The Occurrence of Trigonelline and Nicotinuric Acid in the Urine after the Administration of Nicotinic Acid.** D. ACKERMANN (*Zeitsch. Biol.*, 1912, 59, 17—22).—His was the first to show that after giving dogs pyridine as the acetate, they secrete pyridyl-methylammonium hydroxide in their urine. Later, Cohn found that 2-picoline was oxidised to 2-pyridinecarboxylic acid, and secreted in combination with glycine as  $\alpha$ -pyridinuric acid. In the present research, the 3-carboxylic acid, nicotinic acid, was employed; this also was methylated in the body and excreted as the alkaloid trigonelline, hitherto only known in plant-life; part was combined with glycine and excreted as nicotinuric acid. W. D. H.

**Estimation of Physiological Values in the Small Intestine. Action of Pilocarpine.** P. NEUKIRCH (*Pflüger's Archiv*, 1912, 147, 153—170).—Isolated portions of a rabbit's small intestine were employed, and suspended in Tyrode's solution (a modification of Ringer's solution containing dextrose like Locke's solution), in which they maintained well their tonus and rhythm. Pilocarpine added to this in the proportion of 0.005 mg. per 100 c.c. acts as a stimulant, and the effect of the alkaloid is reversible when the Tyrode's solution is restored. W. D. H.

**[Pharmacological] Action of  $\beta\beta$ -Dichloroisopropyl Carbamate. (Aleudrin.)** TH. A. MAASS (*Biochem. Zeitsch.*, 1912, 43, 65—88).—This substance has the formula  $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{O}\cdot\text{CO}\cdot\text{NH}_2)\cdot\text{CH}_2\text{Cl}$ , m. p.  $82^\circ$ , and is sparingly soluble in water (100 parts dissolve 0.75 part at room temperature). It dissolves in most organic solvents, but not in light petroleum. It has been manufactured on account of its hypnotic properties. The author has investigated its pharmacological action. In the case of fish, the toxic dose is twenty-six times as great as that necessary to produce distinct narcosis. In frogs, the hypnotic dose is 0.06 to 0.08 gram, and the anæsthetic dose 0.22 to 0.24 gram per gram of body-weight. The toxic dose is larger than 1 mg. per gram of body-weight. In dogs, the smallest active dose is 0.1 to 0.15 gram, and the toxic dose 0.7 gram per kilo. of body-weight. In cats the corresponding toxic dose is 0.5 gram. Rabbits are more resistant than dogs or cats. Experiments on dogs show that in narcotising doses the antipyretic action is only slight. The effect on respiration is also small, as determined by experiments on rabbits. In concentrations of 1:5000 to 1:1000, aleudrin causes a diminution of activity of the isolated frog heart. In experiments on cats, it was shown that the circulation is not very markedly affected, the chief action being a slight dilatation of the vessels in the splanchnic area. In man, doses of 1 gram produce hypnosis; a dose of even three times as large has been tolerated. The general effect is pleasant. S. B. S.

**Physiological Behaviour of Certain Organic Arsenic Derivatives (Salvarsan and Sodium Cacodylate) in the Organism.** ADRIANO VALENTI (*Arch. Farm. speriment.*, 1912, 13, Reprint 21 pp.).—After hypodermic, gastric or intramuscular administration of "salvarsan," the elimination of arsenic in the urine lasts about twenty-five days. "Salvarsan" differs markedly from sodium cacodylate and other organic arsenic preparations in that the arsenic is largely transformed into the ionic condition, and it is suggested that this property is related to its antisyphilitic action.

T. H. P.

**Toxicity of Mineral Salts in the Cerebro-spinal Fluid.** JEAN CAMUS (*Compt. rend.*, 1912, 155, 310—312).—A study of the toxic effect of a number of mineral salts when injected into the cerebro-spinal fluid. The salts studied are grouped into sulphates and chlorides and arranged in ascending order of toxicity in tables which are given showing the fatal doses in weight of salt or in c.c. of *N*/100-solutions of the salts. The toxicity does not seem to be regularly proportional to any figure, but the author suggests from his results that, the rarer the salts the more toxic they are.

W. G.

**Poisonous Properties of Methyl Alcohol.** JACOB BÖESEKEN and H. I. WATERMAN (*Chem. Weekblad*, 1912, 9, 694—696).—The poisonous nature of methyl alcohol is attributed to its conversion into formaldehyde by oxidation, the aldehyde then exerting a powerful chemical influence on the substances present in the organism.

A. J. W.

**The Relative Toxicity of Methyl and Ethyl Alcohols as Determined by the Rate of Reproduction in *Hydatina senta*.** DAVID D. WHITNEY (*Amer. J. Physiol.*, 1912, 30, 463—465).—Methyl alcohol is less toxic than ethyl alcohol, as determined by the rate of reproduction in the rotifer, *Hydatina senta*. Families subjected to 1% methyl alcohol during many (ten to fifteen) generations recover from its influence in the second generation after the alcohol is removed.

W. D. H.

**Hæmatinæmia in Toxic Destruction of Blood Corpuscles.** OTTO SCHUMM (*Zeitsch. physiol. Chem.*, 1912, 80, 1—5).—In a case of chronic acid poisoning, the urine contained oxyhæmoglobin and methæmoglobin. The blood-serum contained these substances, but free hæmatin was also detected spectroscopically; as the case proceeded, the amount of hæmatin increased.

W. D. H.

**The Formation of Succinic Acid in the Animal Body in Chronic Oxalate Poisoning.** A. BEHRE (*Chem. Zeit.*, 1912, 36, 933—934).—In a case of death from chronic poisoning by potassium hydrogen oxalate, succinic acid was found in almost all internal parts of the body, but especially the stomach, intestines, and kidneys, only traces of oxalic acid being present. Administration of potassium hydrogen oxalate to dogs also leads to the accumulation of succinic acid, especially in the kidneys.

C. H. D.

**The Inhibition of the Toxic Action of Iodide, Nitrate, Thiocyanate, and Other Salts of Sodium.** JACQUES LOEB (*Biochem. Zeitsch.*, 1912, 43, 181—202).—The toxic action of nitrate, iodide, thiocyanate, acetate, and butyrate of sodium on *Fundulus* is inhibited by the chlorides of sodium and calcium, the deintoxicating action of the latter being greater than that of the former salt. The salts of calcium, other than the chloride, have little action in this respect. Although the essential action is due to the chlorine ions, only the chlorides of sodium and calcium, and, to a very minor extent, magnesium, are effective. The toxic effect of sodium sulphate is not inhibited by sodium chloride, although it is by small doses of calcium chloride. Other calcium salts tried were without effect, and the action appears to be due to the whole molecule and not to the ions. A mixture of the chlorides of sodium, potassium, and calcium in the proportions in which they are contained in sea-water has a more powerful inhibiting action on the toxic effects of sodium salts than any other solution. The deintoxicating action of the mixture is discussed, and it is suggested that the particular mixture of salts which is found in sea-water keeps the surface layers of the cells intact, and thus inhibits the diffusion of toxic substances.

S. B. S.

**Toxicity of  $\beta$ -Iminazolyethylamine [4- $\beta$ -Aminoethylglyoxaline].** ALBERT BERTHELOT and D. M. BERTRAND (*Compt. rend.*, 1912, 155, 360—362).—Dale and Laidlaw (*Abstr.*, 1911, ii, 137, 1017) by a physiological study of 4- $\beta$ -aminoethylglyoxaline have established its great toxicity for the guinea-pig and rabbit, the cat being less sensitive. The authors have studied the effects on monkeys, as being much more nearly allied to human beings. The fatal dose is proportionally much greater for a monkey than for a guinea-pig or rabbit, being about 50 mg. per kilo. weight, and the animal succumbs in about twenty minutes. The narcotic effects are more marked than in the case of the two other animals, and the intoxication is less rapid.

W. G.

**Diminution of the Toxic Action of Poisons by Proteins.** H. BORUTTAU (*Biochem. Zeitsch.*, 1912, 43, 418—423).—Comparison was made between the toxic action of "arsan," a product made by the action of arsenic chloride on oat protein, and a mechanical mixture of the same protein containing the same amount of arsenic. The latter was found to yield much less arsenic to water than the chemical compound; it was also appreciably less toxic. The mechanical mixture became much more toxic after digestion with proteoclastic ferments. When "arsan" is submitted to dialysis under various conditions, a large amount of the arsenic remains in the dialyser, although in solution. This solution is slightly less toxic than the corresponding amount of inorganic arsenic. This fact indicates that in "arsan" the arsenic is in organic combination. Nevertheless, the arsenic is more toxic than in the mechanical mixture of protein and arsenious oxide, and this fact indicates the importance of the adsorptive properties of the proteins in rendering poisons less toxic.

S. B. S.

**The Synergic Action of Poisons. II. Mixed Hæmolysis.** HERMANN FÜHNER and W. GREB (*Arch. expt. Path. Pharm.*, 1912, **69**, 348—364. Compare this vol., ii, 792).—The combination of various hæmolytic agents produced on ox-blood corpuscles sometimes an increase, sometimes a summation, but usually a decrease of hæmolysis. Bürgi's law on the actions of combinations of drugs receives thus no confirmation. W. D. H.

**Process for Drying Fluids and Tissues of Animal and Vegetable Origin by Anhydrous Sodium Sulphate.** VLADIMIR NJEGOVAN (*Biochem. Zeitsch.*, 1912, **43**, 203—206).—The material is heated to 40°, and then treated with the amount of anhydrous sodium sulphate necessary to combine with the water. The mixture is then rapidly cooled, so that the hydrated salt,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , is formed. It is then powdered and dried over sulphuric acid in a vacuum, whereby practically all the water is extracted. S. B. S.

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## Chemistry of Vegetable Physiology and Agriculture.

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Chemical Composition and Formation of Enzymes. VI. Acid Formation by Certain Micro-organisms. HANS VON EULER and HERMANN MEYER (*Zeitsch. physiol. Chem.*, 1912, 80, 241—252. Compare this vol., ii, 793).—In the alcoholic fermentation, various intermediate products occur, and special interest attaches to the formation of acids by micro-organisms. Harden and Young showed in their work on *Bacterium coli*, that lactic and acetic acids accompany alcohol when this organism acts on dextrose. This result is fully confirmed in the present research. Particulars are also given in regard to acid formation by *Mucor mucedo*. Soorpilz is stated to act specifically on xylose, and not on arabinose (Lindner); this also is confirmed, but the presence of arabinose accelerates its activity. In its action carbon dioxide is liberated, but no fatty acids formed; this is accompanied by a change into a molecule which is either optically inactive or nearly so. W. D. H.

Chemical Action on Dextrose of a Variety of *Bacillus coli communis* (Escherich) Obtained by Cultivation in Presence of a Chloroacetate. ARTHUR HARDEN and WILLIAM J. PENFOLD (*Proc. Roy. Soc.*, 1912, B, 85, 415—417).—Penfold has shown that when *B. coli communis* is plated out on nutrient agar containing 0.5% sodium chloroacetate, a large number of small colonies and a few large ones are produced. The cultures made from some of the large colonies are found to have lost the power of producing gas from dextrose when grown in dextrose peptone water in a test-tube provided with a Durham gas-tube.

Comparative quantitative experiments carried out with the original and selected organisms have shown that the latter grown anaerobically in presence of chalk yield a small quantity of hydrogen, but very much less than that from the original strain. The other main difference is the increased proportion of lactic acid, and the corresponding diminished proportion of other products (acetic acid, alcohol, and carbon dioxide).

The explanation is suggested that the products formed by the normal organism are the result of the action of three enzymes. One of these converts the dextrose into lactic acid, a second forms alcohol, acetic and formic acids, and the third decomposes the formic acid into carbon dioxide and hydrogen. The process of selection has resulted in the survival of an organism containing a large proportion of the lactic acid-forming enzyme and a small proportion of that producing alcohol, acetic and formic acids. It still retains the power of decomposing formic acid (compare Harden, *Trans.*, 1901, 79, 610). W. J. Y.

**Action of Certain Esters of Glycerol on the Tubercle bacillus.** A. T. SALIMBENI (*Compt. rend.*, 1912, 155, 368—370).—The esters studied were the mono-, di-, and tri-chlorohydrins. Preliminary experiments showed that, in the cold, the mono- and di-chlorohydrins dissolve a fatty matter obtained from the bacillus by acetone extraction, but not a waxy substance extracted by chloroform and insoluble in acetone. The trichlorohydrin readily dissolved both fat and wax. The study was then extended to the bacilli in the presence of the esters; for the first two the moist microbe as obtained from cultures being used, and for the third the bacillus dried in a vacuum over sulphuric acid was used. The ethers and microbes were ground together in a mortar, and in a few seconds were changed to an oily paste, which gradually passed through an emulsion to a clear liquid. The action of the trichlorohydrin is more energetic and complete than that of the dichlorohydrin, and this in turn than that of the monochlorohydrin. The bacilli with the trichlorohydrin rapidly lose their power of resisting acids, become granular, and readily take a blue stain. After prolonged action they are transformed into a granular amorphous substance. The microbe mass so treated can be separated into two parts, one soluble in water, precipitated by alcohol, and the other insoluble in water. The insoluble portion contains the nitrogenous part of the bacilli, no nitrogen being detectable in the soluble portion, which is insoluble in alcohol and ether, and when precipitated is only partly redissolved by water. The three ethers have a very marked bactericidal action on the tubercle bacilli, a few seconds sufficing to kill them. W. G.

**Mechanism of the Fertilising Action of Sulphur.** E. BOULANGER and M. DUGARDIN (*Compt. rend.*, 1912, 155, 327—329. Compare this vol., ii, 381).—The favourable influence which very small doses of sulphur exert on vegetation is due to its activating effect on the bacteria, which break down nitrogenous matter in the soil to ammonia, and also to its influence on the nitrification ferments. Larger doses of sulphur, whilst enhancing the first effect, check the second. W. G.

**The Decomposition of Asparagine by Bacteria in Presence of Free Oxygen. II. Respiration Quotient and Proportion of Gaseous Product.** TOR CARLSON (*Medd. K. Vetensk. Nobelinst.*, 1912, 2, No. 19, 1—13. Compare this vol., ii, 191).—In order to determine the relative oxidation capacity of a species of bacteria, the mass of the bacteria has to be determined. This was done indirectly by filtering the culture fluid after an experiment and determining the total carbon in the filtrate and the quantity of carbon dioxide formed, and as practically all the carbon was introduced in the original asparagine, the amount of carbon in the bacteria, and hence the total weight of bacteria, could be determined by difference.

In the detailed experiments the weight of asparagine taken, the carbon dioxide in the culture fluid or given off in the course of the experiment, the combined carbon in the culture fluid, and the volume of oxygen taken up were either known or determined, and hence the respiration quotient and the proportion of carbon given off as carbon dioxide were determined. In all the investigations, one-half and more of the asparagine is converted into gaseous products and not assimilated. The results show that for one and the same species of bacterium  $kf/u = \text{constant}$ , where  $k$  is the rate of growth,  $f$  is the amount of the carbon converted into gas, and  $u$  the proportion assimilated, from which it follows that the smaller the rate of growth of the cells, the more completely is the asparagine converted into gaseous products.

G. S.

**Some Conditions Influencing Nitrogen Fixation by Aerobic Organisms.** W. B. BOTTOMLEY (*Proc. Roy. Soc.*, 1912, B, 85, 466—468).—A simple and efficient nutrient medium for both *Azotobacter* and *Pseudomonas*, or for a mixed culture of the two, may be obtained by adding to distilled water 1% of dextrin, 0.2% of dipotassium phosphate, 0.02% magnesium sulphate, and 0.4% basic slag.

W. J. Y.

**The Fermentation of Cocoa.** GEORGES LAMBERT (*Chem. Zentr.*, 1912, i, 1632; from *Bull. Sci. Pharm.*, 1912, 18, 574—587).—The fermentation of cocoa is due to simultaneous alcoholic fermentation caused by *Saccharomyces Theobromae*, and oxidation of the colouring matter by an oxydase, *theobromase*, the latter existing ready formed in the seed.

C. H. D.

**The Reducing Properties of Yeast. Hydrogenation of Sulphur in Alcoholic Fermentation.** M. A. CHOWRENKO (*Zeitsch. physiol. Chem.*, 1912, 80, 253—273).—Hydrogenation of sulphur during the alcoholic fermentation is a property of several varieties of yeast examined. Increase of sugar in the substrate leads to the production of more hydrogen sulphide. Most gas is evolved in the period preceding the fermentation and in the presence of air. The addition of alcohol, toluene, and thymol greatly diminishes the production of the gas. The preparation known as zymin acts like the yeast, and its power to do so is destroyed by boiling.

W. D. H.

**In What Way is Tartaric Acid Attacked by Yeast?** LASZLÓ KARCZAG (*Biochem. Zeitsch.*, 1912, 43, 44—46).—Amongst the products of yeast action in sterile fermentations were found propionic and butyric acids (volatile acids), together with lactic and succinic acids (etheral extract). The author gives a scheme showing how these acids may be derived from tartaric acid, through malic and glyceric acids as intermediate products. There was also indication of the formation of acetaldehyde. The chief processes taking place during yeast fermentation appear to be reduction processes. S. B. S.

**Fermentations with Yeast in Absence of Sugar. VII. The Formation of  $\beta$ -Hydroxybutaldehyde in the Fermentation of Butyric Acid.** CARL NEUBERG (*Biochem. Zeitsch.*, 1912, 43, 491—493. Compare this vol., ii, 78).—In the fermentative destruction of potassium pyruvate by yeast, potassium carbonate and acetaldehyde are formed, the latter undergoing condensation to  $\beta$ -hydroxybutaldehyde (aldol) according to the equations  $2\text{CH}_3\cdot\text{CO}\cdot\text{CO}_2\text{K} + \text{H}_2\text{O} = 2\text{CH}_3\cdot\text{CHO} + \text{K}_2\text{CO}_3 + \text{CO}_2$  and  $2\text{CH}_3\cdot\text{CHO} = \text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CHO}$ . It was of interest to ascertain whether the latter reaction was due to the yeast or to the alkali. In the former case it was conceivable that an optically active product would be produced. The crude aldol was, therefore, oxidised to the corresponding  $\beta$ -hydroxybutyric acid by silver oxide, and isolated as a silver salt. This was found, however, to be optically inactive. The problem, therefore, remains unsolved.

S. B. S.

**Fermentation with Yeast in Absence of Sugar. VIII. The Formation of Acetaldehyde by Auto-fermentation.** CARL NEUBERG and J. KERB (*Biochem. Zeitsch.*, 1912, 43, 494—499. Compare preceding abstract).—In view of the fact that acetaldehyde is formed by yeast from pyruvic acid, it is conceivable that the latter substance is an intermediary product of change during fermentation. It was of interest to ascertain, therefore, whether acetaldehyde is formed during auto-fermentation, when the yeast acts only on the sugar it contains in its own cells. Acetaldehyde was, in fact, found to be formed as a product of auto-fermentation, carried out under varied conditions, which are discussed by the authors.

S. B. S.

**Action of Uranium on Certain Micro-organisms.** HENRI AGULHON and R. SAZERAC (*Bull. Soc. chim.*, 1912, [iv], 11, 868—872. Compare Kayser, this vol., ii, 860).—Comparative trials of the influence of uranyl nitrate and uranyl acetate on *Aspergillus niger*, yeast, and acetic ferment showed that in solutions containing up to 1 part per 1000 of either salt no effect was produced on the growth of *Aspergillus niger*, but growth ceased in a 1% solution, possibly due to the precipitation of all the soluble phosphates by the salt. In the case of yeast, fermentation diminished in presence of one part of either salt in 50,000, and was stopped by 1 in 10,000, although the yeast was not killed. The activity of acetic acid ferment was increased by uranyl acetate and also by uranyl nitrate so long as the proportion of the latter present did not exceed 1 in 50,000.

T. A. H.

**Is the Bactericidal Action of Radium Emanation due to the Evolution of Ozone?** HANS JANSEN and OVE STRANDBERG (*Chem. Zentr.*, 1912, i, 1668; from *Zeitsch. Hyg. Infekt.-Krank.*, 1912, 71, 223—228).—The quantity of ozone required to kill bacteria is much greater than that required to affect potassium iodide-starch paper, whilst in experiments in which radium emanation killed bacteria, an ozone reaction could not be detected. C. H. D.

**Action of Acids, Bases, and Certain Salts on Bactericidal Sera.** DONATO OTTOLENGHI (*Zeitsch. Immunitätsforsch. exp. Ther.*, 1912, Reprint 30 pp.).—The author has examined the effect of the addition of certain acids, bases, and salts on bactericidal sera, and draws the conclusion that lactic, formic, acetic, oxalic, and hydrochloric acids cause a diminution in bactericidal power, and that similar properties are possessed by bases, such as ammonia and potassium hydroxide, and by salts of certain organic acids, although in a less degree. The inactivating power of acids is connected with their strength, since it appears to be diminished when, presumably, a diminution in their electrolytic dissociation is occasioned by addition of their salts. The bactericidal power of sera which has been diminished by the addition of acids may be partly restored, even after many hours, by the neutralisation of the acid.

In the case of anticholera serum, at any rate, the influence of bases on bactericidal power is attributable entirely, or in part, to specific action on the bacteria. H. W.

**Deodorisation.** KARL KISSKALT (*Chem. Zentr.*, 1912, i, 1669—1670; from *Zeitsch. Hyg. Infekt.-Krank.*, 1912, 71, 273—295).—Ozone in large excess is capable of destroying hydrogen sulphide, but not butyric acid, whilst methylindole is rather masked than destroyed. A combination of water spray and ozone has no advantages. Experiments with charcoal and other absorbents are also described. C. H. D.

**The Artificial Nutrition of Seedlings.** W. ZALESKI and N. TUTORSKI (*Biochem. Zeitsch.*, 1912, 43, 7—9).—Pea seedlings, after sterilisation with bromine water or hydrogen peroxide solution, can grow in the dark in Knop's solution to which various sugars have been added. The sugar which gives the best result is sucrose. Lævulose, dextrose, and maltose have about the same action, whereas in galactose no growth takes place. They can also grow in Knop's solution containing sucrose when the nitrates are replaced by ammonium phosphate or sodium aspartate. S. B. S.

**Assimilation of Nucleic Nitrogen and Phosphorus by the Inferior Algæ.** E. C. TEODERESCO (*Compt. rend.*, 1912, 155, 300—303).—Pure cultures of an inferior algæ was grown in four different solutions: (1) a complete mineral culture liquid; (2) without nitrogen; (3) without nitrogen or phosphorus; (4) similar to (3) but with the addition of sodium nucleate. In (2) and (3) the development was almost inappreciable. In (1) the algæ were well developed, but the

best growth was obtained in (4), although the algæ did not live so long in (4) as in (1). On replacing the soluble sodium nucleate by insoluble nucleic acid, which fell to the bottom, the algæ only developed on the surface of the deposit. At the end of three or four weeks from one-third to one-half of the organic phosphorus originally present in solution (4) was found to have been converted into a mineral salt; thus certain inferior algæ are capable of decomposing nucleic acid and mineralising the phosphorus, the nitrogen and phosphorus in the nucleic acid seeming, in the first stages, to exert a more favourable influence on the rapid and abundant growth of the algæ than mineral nitrogen and phosphorus.

W. G.

**The Law of the Minimum.** ISIDORE POUGET and D. CHOUGHAK (*Compt. rend.*, 1912, 155, 303—306).—A reply to Mazé (compare this vol., ii, 796). The authors quote two further sets of water-culture experiments in support of the law of the minimum, and of the view recently put forward by them that the absorption of a nutritive substance is proportional to the concentration of the solution, provided that the substance can be assimilated by the plant as fast as it is absorbed (compare this vol., ii, 796). They consider that Mazé's law of physiological ratios (*loc. cit.*) and the law of the minimum are not contradictory.

W. G.

**The Physiological Action of Neutral Salts of Alkalis and Alkaline Earths on Green Plants.** THOMAS BOKORNY (*Biochem. Zeitsch.*, 1912, 43, 453—477).—It has been shown that calcium nitrate in 0.1% solution has a particularly favouring action on the growth of *Spirogyra* when kept in the dark. The author has investigated the action of various neutral salts of alkalis and alkaline earths on various plants, including higher plants, such as pea and bean seedlings, cabbages, and on yeast, etc. Calcium nitrate was found to have a more effective action on *Spirogyra* than any other salt. It also has a beneficent action on the growth of seedlings of higher plants. Rubidium sulphate also exerts a special favouring action in 0.2% solution. In 0.5% and higher concentrations, the action is harmful. Cæsium sulphate can also exert a favouring action (on barley), but the concentration in this case is much lower (0.01%). Higher concentrations are toxic. Lithium sulphate in concentrations from 0.005% to 0.01% favourably influences growth. The action of other salts is not so marked as those of rubidium sulphate and calcium nitrate.

S. B. S.

**The Action of Phosphates on the Post-mortal Respiration of Plants.** W. ZALESKI and ELISABETH MARX (*Biochem. Zeitsch.*, 1912, 43, 1—6).—It has been shown that disodium hydrogen phosphate increases the post-mortal respiration of powdered peas and oats, and it is conceivable, from the results of other experiments, that this is due to the stimulation by phosphates of alcoholic fermentation. On the other hand, it may be due simply to the alkaline reaction. Experiments with sodium hydroxide and edestin, which in this case acts as a base, show that alkalis increase the post-mortal respiration,

whereas acids (including casein and other acids) inhibit it. Nevertheless, the experiments are not conclusive, as the objects of experiment contain themselves inorganic phosphates. S. B. S.

**Presence of Arsenic in Plant Parasites and in Plants Supporting Parasites.** F. JADIN and A. ASTRUC (*Compt. rend.*, 1912, 155, 291—293).—The authors have determined the amount of arsenic in a number of plant parasites, and in the plants on which they were growing. From their results they draw the conclusion that plant parasites, like plants growing directly in the soil, normally contain a certain quantity of arsenic, and that the same species of parasite, although growing on different trees in different districts, contains practically the same amount of arsenic. It is, however, impossible to establish any relation between the arsenic content of the parasite and of the plant on which grown. Plants take arsenic from the soil in amounts necessary to them, and independently of the richness of the soil in arsenic. W. G.

**Determination of Manganese in the Vegetable Kingdom.** F. JADIN and A. ASTRUC (*Compt. rend.*, 1912, 155, 406—408).—As a result of eighty determinations of the amounts of manganese present in plants belonging to thirty-two different natural orders, the authors draw the following conclusions: (1) manganese is of constant occurrence in plants; (2) the presence of manganese in vegetable foodstuffs accounts, at least in part, for the occurrence of this element in the animal organism (Bertrand and Medigreceanu, this vol., ii, 459, 662); (3) the aerial portions of plants are usually richer in manganese than the subterranean parts, and (4) in the same species the quantity of manganese present may show great variation. T. A. H.

**Alfalfa Investigation. III. The Colouring Matters in Alfalfa.** C. A. JACOBSON (*J. Amer. Chem. Soc.*, 1912, 34, 1263—1266. Compare this vol., i, 239).—By the extinction method of Malarski and Marchlewski (Abstr., 1910, ii, 362), the alfalfa hay has been found to contain 0.68% of chlorophyll, which closely resembles that from nettle leaves, and by studying the ultra-violet absorption bands according to Jacobson and Marchlewski's method (this vol., i, 285), it was observed that this particular specimen of chlorophyll contained 66% *neo*- and 34% *allo*-chlorophyll. In addition, the yellow colouring matters in the chlorophyll residues were extracted by means of ether and found to compose 0.28% of the dried alfalfa. J. C. W.

**The Invertase of *Aspergillus niger*. The Influence of Carbonaceous Food on the Secretion of Enzymes.** G. GREZES (*Ann. Inst. Pasteur*, 1912, 26, 556—573).—Experiments were carried out to ascertain the effect on the formation of invertase in *Aspergillus niger* of cultivating the mould in media containing either sucrose or sodium succinate. The activity of the enzyme in each case was estimated by macerating a given weight of the dried mycelium with water for two hours at 36°, and determining the inverting power of the filtered liquid to sucrose.

It was found that the enzyme was present in largest quantity in the mycelium of the mould after it had been habituated to sucrose by repeated sub-cultivation in a medium containing sucrose, whereas when sodium succinate was employed instead of sucrose in the medium, much less active preparations were obtained.

Attempts to select an organism with no invertase by repeatedly sub-cultivating the mould on the sodium succinate medium were unsuccessful. After sixty generations it still contained the enzyme, and when further sub-cultured once on sucrose, the original activity was reproduced.

W. J. Y.

**Rennet Ferment of *Calotropis procera* Latex.** C. GERBER and P. FLOURENS (*Compt. rend.*, 1912, 155, 408—410).—The latex of this plant contains a rennet ferment, which, like those present in the fig (this vol., ii, 801), papaw, etc., coagulates boiled milk more rapidly than raw milk and is very resistant to heat. Its action is inhibited by mercuric chloride, but not by salts of the alkali metals.

T. A. H.

**The Inulin Metabolism of *Cichorium Intybus* (L.) (Chicory).**  
I. **The Seedling Metabolism.** VIKTOR GRAFE and V. VOUK (*Biochem. Zeitsch.*, 1912, 43, 424—433).—During the growth of the seedling in the dark on blotting paper, the fat of the seed (originally 18%) sinks in quantity. During the first two days the sucrose also diminishes, but the inulin does not alter greatly; after this period the inulin and sucrose both increase in quantity. When grown in the light, the fat also disappears, and is converted into a reducing sugar. This does not appear, however, to be stored up as inulin, as is the case when the seeds sprout in the dark, but is used up in the building up processes of the plant. There is no simple quantitative relationship between the reducing sugar and the inulin, and in the later growth of the seedling the quantity of inulin increases, whilst that of the sucrose remains constant or diminishes. These researches indicate that the inulin is formed from fat.

S. B. S.

**Chemical Examination of the Bark of *Erythrophloeum Guineense*.** FREDERICK B. POWER and ARTHUR H. SALWAY (*Amer. J. Pharm.*, 1912, 84, 337—351).—The following results were obtained during an investigation of the bark of *Erythrophloeum Guineense*.

A quantity of the bark was completely extracted with hot alcohol, and the resulting concentrated extract distilled in a current of steam, but it yielded no essential oil.

From the portion of the extract which was soluble in water the following substances were isolated: a very small amount of luteolin,  $C_{15}H_{10}O_6$  (the tetra-acetyl derivative of which, m. p. 222—224°, was also prepared), and a small amount of an alkaloid which agreed in its characters and physiological action with erythrophleine. Neither the alkaloid nor its salts could be obtained in a crystalline state. The aqueous liquid also contained indefinite amorphous material, a considerable quantity of tannin, and a sugar which yielded *d*-phenyl-glucosazone, m. p. 210° (decomp.).

The portion of the alcoholic extract which was insoluble in water consisted of a dark brown, brittle resin and represented 13.5% of the weight of the bark. From this product the following substances were obtained: a *phytosterol*,  $C_{27}H_{46}O$ , m. p. 130—133°; possibly a second *phytosterol*, m.p. 135—142°, in quantity too small to allow complete characterisation; cerotic, stearic, palmitic, oleic, and linoleic acids; very small amounts of ipuranol,  $C_{23}H_{38}O_2(OH)_2$ , m. p. 162—163°, and luteolin. A portion of the latter compound was apparently contained in the resin in the form of a glucoside.

Since a preliminary test had indicated the presence of a much larger amount of the alkaloid than could subsequently be isolated, it appeared that some change had taken place during the processes of extraction.

H. W.

**Chemical Constituents of Green Plants. II. The Volatile Acids of Hornbeam Leaves.** THEODOR CURTIUS and HARTWIG FRANZEN (*Sitzungsber. Heidelberger. Akad. Wiss.*, 1912, Reprint 7 pp.).—The presence of  $\Delta^a$ -hexenaldehyde among the components of green plants has already been proved (this vol., ii, 797). For the further examination of the volatile products, hornbeam leaves were distilled in steam and the distillate made alkaline with barium hydroxide. After distillation, the barium salts of the acids remained. Volatile aldehydes were converted into the silver salts of the corresponding acids by means of silver oxide, the silver salts transformed into barium salts, and the solution again distilled, when only the volatile alcohols and ketones were volatilised.

The volatile acids were found to consist mainly of formic and acetic acids; smaller quantities of acids sparingly soluble in water were also found, among which were a hexenoic acid together with one or more of its higher homologues.

H. W.

**Chemical Constituents of Green Plants. IV. Further Volatile Aldehydes of Hornbeam Leaves.** THEODOR CURTIUS and HARTWIG FRANZEN (*Sitzungsber. Heidelberger. Akad. Wiss.*, 1912, Reprint 18 pp.).—The authors have already proved the presence of formaldehyde in plants (this vol., ii, 797). The barium salts of the oxidised aldehydes (see preceding abstract) were employed to obtain further insight into the aldehydes originally present. After liberation of the acids and oxidation of formic acid by yellow mercuric oxide, unsuccessful attempts were made to separate these by fractional precipitation of their silver salts. Finally, fractional distillation was found to be the readiest method of separating them.

The presence of the following aldehydes was ascertained: formaldehyde, acetaldehyde, *n*-butaldehyde, valeraldehyde,  $\Delta^a$ -hexenaldehyde, and higher homologues of the latter, of which the highest member is at least nonenaldehyde. Of these substances,  $\Delta^a$ -hexenaldehyde forms by far the greater part. Considerable quantities of acetaldehyde and *n*-butaldehyde are also present, but formaldehyde, valeraldehyde, and the higher homologues of hexenaldehyde only occur in small amounts.

For the purpose of identifying the acids, an attempt was made to

convert them into the corresponding hydrazides, which should yield benzylidene derivatives. When, however, propionic acid and anhydrous hydrazine were boiled during eight hours, 1-amino-2:5-diethyl-1:3:4-triazole (compare Dedichen, *Abstr.*, 1906, i, 539) was obtained in place of the desired hydrazide. H. W.

**Chemical Constituents of Green Plants. V. Volatile Alcohols of Hornbeam Leaves.** THEODOR CURTIUS and HARTWIG FRANZEN (*Sitzungsber. Heidelberger. Akad. Wiss.*, 1912, Reprint 11 pp.).—The alcohols obtained from hornbeam leaves (see above) were separated by fractional distillation and the fractions analysed. They were found to contain butylene alcohol, amylene alcohol, hexylene alcohol, an alcohol,  $C_8H_{14}O$ , and one or more higher alcohols. The presence of ketones could not be detected by means of semicarbazide.

The authors discuss the probable mode of formation and function of the various products, the presence of which they have proved. For details, the original paper must be consulted. H. W.

**The Formation of "Töre" in Pine Wood.** IVAR NORDENSKJÖLD (*Arkiv. Kem. Min. Geol.*, 1912, 4, No. 28, 1—21).—"Töre" is the Swedish name given to wood obtained from the rooted stumps left from trees which have been felled ten to fifteen years previously. It is rich in resin, containing 15—20% thereof, which is about double the percentage found in ordinary pine wood.

The formation of "töre" is discussed and a summary given of the results hitherto obtained in the investigation of the composition of pine wood, its acid number, specific gravity, etc. Finally, tables are given summarising the authors own results with respect to the amount of resin, acid number, etc., found in a number of different specimens of pine wood. T. S. P.

**The Saponoid of *Primula officinalis*.** GEORGES MASSON (*Chem. Zentr.*, 1912, i, 1628; from *Bull. Sci. Pharm.*, 1912, 18, 699—702).—After removing fat from the powdered root, the acid extract is dialysed, yielding dextrose and volemite, whilst the residue in the dialyser contains primulinic acid, which forms an amorphous powder, decomp. above  $230^\circ$ .

Boiling 5% sulphuric acid resolves this acid into primuligenic acid and a reducing sugar,  $[\alpha]_D + 10.21^\circ$  in 10% solution. Primuligenic acid is a white, amorphous powder, m. p.  $210-211^\circ$ . C. H. D.

**Variations in the Proportion of Nicotine in the Different Organs of the Tobacco Plant During Growth.** ERNEST CHUARD and R. MELLET (*Compt. rend.*, 1912, 155, 293—295. Compare Schloessing, jun., *Abstr.*, 1910, ii, 743).—The tobacco plants were grown and harvested according to the Swiss method, and the amount of nicotine was estimated in the various parts of the plant in the green state at various stages of growth. A table is given showing the percentage of nicotine in the leaves, stems, roots, shoots, and heads at four stages in the plant's life. The by-products, after the leaf harvest, contain amounts of alkaloid not to be neglected.

W. G.

**Injury of Plants by Tobacco Smoke.** THOMAS BOKORNY (*Chem. Zeit.*, 1912, 36, 1050—1051).—The injurious effect of tobacco and other smoke is attributed to the ammonia present combining with the protoplasm. Nicotine has practically no effect in small quantities, and even large amounts of carbon monoxide only retard germination.

N. H. J. M.

**Chemical Means of Protecting Plants from Frost.** N. A. MAXIMOFF (*Ber. Deut. bot. Ges.*, 1912, 30, 293—305. Compare this vol., ii, 476).—The protective action of the various substances is closely connected with the position of the eutectic point of the solution, and diminishes rapidly when this point is reached. Substances, such as mannitol, sodium and potassium sulphates, and sodium oxalate, the eutectic points of which are very high, have no protective action.

Isotonic solutions of substances of varying chemical characters, having very low eutectic points, are almost equal as protective agents. The protective effect is considerably lessened when the substance employed acts injuriously on the protoplasm.

N. H. J. M.

**Action of Monocalcium Phosphate in the Preservation of Green Fodder.** G. SANI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 108—112).—Green fodder, stored alone in silos, loses large proportions of its starch and digestible proteins, whilst the amino-acids increase largely in amount. In presence of 0.3% of calcium monophosphate, the fodder loses little in digestible proteins, and shows proportions of starch and fat in closer correspondence with those of the original fodder. The experiments lasted eleven months.

T. H. P.

**Oryzanin, a Constituent of Rice Husks and its Physiological Significance.** UMETARO SUZUKI, T. SHIMAMURA, and S. ODAKE (*Biochem. Zeitsch.*, 1912, 43, 89—153).—Hens, doves, mice, and other animals readily become ill when fed exclusively with shelled rice, and finally die, after a great loss of body-weight. This effect is due to the absence of a substance which is essential to life, and which has been isolated up to the present only from rice husks. To this the authors give the name of oryzanin. Whenever this substance is absent from a diet, the diet is insufficient to support life. If it be added to an artificial diet of fat, protein, carbohydrate, and salt, in which it is absent, the diet again becomes efficient. Dogs also cannot live without oryzanin, and they rapidly waste when fed on shelled or extracted rice. If they receive 0.3 gram oryzanin daily when in a wasted condition produced by oryzanin-free diet, they rapidly recover. Oryzanin is fairly widely distributed in various foodstuffs. The relationship of these facts, which are illustrated by numerous experiments, to beri-beri is discussed by the authors.

The oryzanin was extracted from fat-free husks (previously extracted with ether) by alcohol. From the alcoholic extract it was precipitated by phosphotungstic acid. From the phosphotungstate

precipitate, after the usual treatment, a still more active preparation was obtained by precipitation with tannic acid, and from this further purified substance, oryzanin was obtained in the form of a crystalline picrate. On hydrolysis with acids it yields two acids of unknown constitution, choline, dextrose, and nicotinic acid. From meat, an alcoholic extract was obtained, which could restore dogs which had been fed on oryzanin-free diet, but not mice. An account is given of attempts to prepare oryzanin from other sources. S. B. S.

**The State of Combination of Sulphuric Acid in Wine.** W. I. BARAGIOLA and CH. GODET (*Chem. Zentr.*, 1912, ii, 139; from *Mitt. Lebensmittelunters. Hyg.*, 1912, 3, 53—73).—The sulphuric acid in wine is shown by physico-chemical experiments to be present as secondary sulphates. Purely analytical tests do not lead to any conclusion. Adulterated wine, containing primary sulphates and probably free sulphuric acid, differs from a normal wine in yielding an ash free from carbonates and chlorides, and containing pyro- and meta-phosphates instead of orthophosphates. The acidity of the adulterated wine is also excessive. It is desirable to express analytical results as  $\text{SO}_4''$ , and not as potassium sulphate, a suitable limiting figure being 1 gram  $\text{SO}_4''$  per litre. C. H. D.

**Chemical and Physical Nature of Red Soils.** DAVID J. HISSINK (*J. Landw.*, 1912, 60, 237—241. Compare Blanck, this vol., ii, 482).—It is shown, from Blanck's results, that whilst the number of mols. of  $\text{SiO}_2$  to 1 mol.  $\text{Al}_2\text{O}_3$  in the hydrochloric extract of the red soils (Roterde) varies from 2.54 to 11.75, the numbers obtained with "rote Erde" are very much higher.

Laterite soils were shown by van Bemmelen to be characterised by high amounts of alumina in the silicates, which are decomposed by dilute hydrochloric acid. Blanck's "Roterde" yielded only small amounts of aluminium, and the results obtained with "rote Erde" were still lower. N. H. J. M.

**Exchange of Bases in Soils.** GEORG WIEGNER (*J. Landw.*, 1912, 60, 197—222).—When neutral salts and amorphous, so-called double silicates containing water interact, the cations of the neutral salts are in part withdrawn from the solution and replaced by cations from the silicate gel in almost equivalent amounts; the anions remain unaffected as long as secondary changes are excluded. The reaction has all the characters of adsorption (Freundlich), and the conclusion is drawn that cations are adsorbed, equivalent amounts of cations being expelled from the gel of the so-called aluminium silicic acid.

In soils, the conditions are the same as in the aluminium hydroxide-silicic acid gel. N. H. J. M.

**The Chemistry of Steam-heated Soils.** OSWALD SCHREINER and ELBERT C. LATHROP (*J. Amer. Chem. Soc.*, 1912, 34, 1242—1259).—The effect of steam heat on two soils of common geological origin and of very similar organic composition, but of widely different fertility, is here described. In harmony with previous experience it

was found that there was an increase in those constituents which dissolve in water and also in the acidity of the soils, even though ammonia and amines were formed. The organic constituents were isolated as far as possible, and, except in the case of nucleic acid, increased amounts were found in the heated soils, whilst, in addition, xanthine, hypoxanthine, guanine, cytosine, and arginine had been formed. These decomposition products of nucleic acid and protein material are beneficial to plant life, but their effect is more than overbalanced by dihydroxystearic acid, which was found in increased amount in the poorer soil after heating, and, although originally absent, was produced in the more fertile soil. Culture tests in the soils and their extracts showed that the heated soils gave a poorer plant growth, the effect being most remarkable with what was originally the better soil, and not until the harmful products are modified by appropriate cultural treatment can the full benefits of steaming be realised.

A consideration of the results and of the origin of the degradation products shows that, although these soils have received the same kind of organic matter, they have been subjected to different biochemical factors, resulting in differences in their organic matter and in their fertility.

J. C. W.

**Guanine from a Heated Soil.** ELBERT C. LATHROP (*J. Amer. Chem. Soc.*, 1912, 34, 1260—1263).—In the mixture of purine bases obtained by Balke's method (Abstr., 1893, i, 535) from one of the steam-heated soils described in the foregoing abstract, a base was found, the solubilities, colour reactions, and characteristic picrate and dichromate of which established it as guanine. This is largely derived from the decomposition of nucleic acids (compare Kossel, Abstr., 1885, 1080), but it has not yet been found in unheated soil. It may be that, like arginine and adenine, which are of infrequent occurrence, it is so subject to the action of micro-organisms and enzymes that it rapidly loses its identity.

J. C. W.

**Degradation of Phosphatic Manures during a Rotation of Crops.** ACHILLE MÜNTZ and HENRI GAUDECHON (*Compt. rend.*, 1912, 155, 257—260).—A test of the advisability of incorporating in the soil at the commencement of a rotation the quantity of phosphatic manure considered necessary for the whole series of crops in the rotation. A series of pot cultures was set up, to one of which the phosphorus was added in the form of superphosphate, to the second as dicalcium phosphate, to the third as basic phosphate, whilst the fourth received no fertiliser. Five sets of these cultures were started, and at the end of three years the total weight of dry matter from the principal and catch crops of each set of five similarly treated pots was estimated for each year, and also the amounts of phosphorus absorbed by the crops. In each set where the phosphorus had been added it was found that the plants absorbed a considerably larger amount of phosphorus and gave bigger crops than the blank in the first year. In the second year the difference was less marked, and in the third year there was practically no difference in the four series. Phosphatic manures should, therefore, not be added to the soil in large amounts at the

beginning of a rotation, but in smaller quantities each year as required. W. G.

The Action of Manganese Dioxide on Nitrogen Compounds, especially Amides, in Reference to the Use of the Dioxide as a Manure. GIOVANNI LEONCINI and COSIMO PIERI (*Chem. Zentr.*, 1912, i, 1635—1636; from *Staz. sperim. agrar. ital.*, 1912, 45, 224—244).—Ammonium compounds are not oxidised by manganese dioxide. Fatty amides are oxidised to nitric acid in boiling aqueous solution, with or without acid or alkali, but not below 30°. Amino-acids and purine derivatives are not oxidised. Manganese dioxide is thus incapable of oxidising organic nitrogen at the ordinary temperature. C. H. D.

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## Analytical Chemistry.

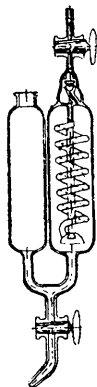
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**A Modified Wiley Extraction Apparatus.** W. D. RICHARDSON and E. F. SCHERUBEL (*J. Ind. Engin. Chem.*, 1912, 4, 220).—A description (with sketches) of two different modifications of the Wiley extraction apparatus (Wiley, *Principles and Practice of Agricultural Analysis*, vol. 3), with one or other of which the author considers any kind of material can be satisfactorily extracted.

The "percolating" form contains an aluminium cup with a perforated base, whilst the "siphon" type is fitted with a nickel-plated brass cup to which a siphon tube is attached; the inner diameter of the siphon tube is one-eighth of an inch, it having been found that larger tubes will not siphon satisfactorily.

F. M. G. M.

**An Absorption Vessel for the Orsat Gas Apparatus.** GEORG PREUSS (*Chem. Zeit.*, 1912, 36, 897\*).—The absorption vessel, which is rapid in action, does not require the reversal of a tap at each passage of the gas, and is easily kept free from bubbles, is constructed as shown in the diagram. The small tube in the upper compartment is provided with a glass valve, ground on to its seal. This valve is closed during the downward passage of the liquid, whilst the gas is brought into intimate contact with the absorbing liquid by means of the spiral and the inverted cup. On reversal the valve closes.



C. H. D.

**An Improvement on the Kjeldahl Distilling Apparatus.** W. L. HADLOCK (*J. Ind. Eng. Chem.*, 1912, 4, 222).—The improvement is essentially a movable support for the flasks, consisting of

\* and *Zeitsch. angew. Chem.*, 1912, 25, 2112.

sheets of galvanised iron containing holes in which the flasks rest ; these can be raised or lowered by means of a lever, and are attached to an iron frame which can be fastened against a wall. F. M. G. M.

**An Apparatus for Automatically Decanting and Washing Precipitates.** ERIC SINKINSON (*Chem. News*, 1912, 106, 49—50).—The funnel is attached to one end of a balanced arm, a sliding weight being adjusted to balance any required quantity of liquid. The arm in falling makes and breaks mercury contacts, which control an electric motor. The beaker holding the liquid to be decanted is held by a tilting table, the raising and lowering of which are effected by a screw, driven by gearing from the motor. A pouring rod is held in position by a spring. The washing arrangement is a glass mercury valve, acting automatically, and provided with a washing jet which is rotated by means of a motor. The action is entirely automatic.

C. H. D.

**Modifications in the Systematic Detection of the Bases.** ATTILIO PURGOTTI (*Gazzetta*, 1912, 42, ii, 58—67).—Those sulphides which are precipitated by hydrogen sulphide and are insoluble in ammonium sulphide are conveniently treated with either a mixture of nitric (2 vols.) and sulphuric acids (1 vol.) and water (7 vols.) or with hydrogen peroxide acidified with sulphuric acid. In either case the sulphides of bismuth, copper, and cadmium are dissolved, whilst the mercuric sulphide remains with the whole of the lead as sulphate ; virtually no nitrous vapours are evolved. Arsenic may be detected rapidly and with certainty by dissolving the sulphide in the least possible quantity of concentrated nitric acid, gradually adding excess of calcium carbonate, heating gently, and adding silver nitrate ; silver arsenate is precipitated in presence of even small amounts of arsenic.

The use of hydrogen sulphide may be avoided by adding, to a solution of about 0.5 gram of the substance in 50—60 c.c. of water, either 1—1.5 gram or, if the sulphide precipitate is large in amount, 3—4 grams of powdered phosphorus pentasulphide and heating to about 60° with frequent shaking until a small portion of the clear solution gives no precipitate with hydrogen sulphide. A little cold water is added and the precipitate collected, washed, and heated in suspension in concentrated ammonia solution. The filtered precipitate is washed with hot ammonia solution twice and then with water, its examination being conducted as described above.

The filtrate is treated with a little nitric acid and concentrated to a small volume, the liquid being then boiled for some time with sufficient saturated sodium carbonate solution to form a precipitate, 10—15 c.c. of 20% sodium hydroxide solution, and excess of sodium hypochlorite solution ; the last should be added to the cooled solution after any ammonia present as ammonium salts has been expelled by the alkalis. If the liquid becomes red or green owing to the presence of manganese, a few drops of alcohol are added to destroy the manganate or permanganate formed. Filtration gives a solution (A) and a precipitate (B).

*A* may contain Zn, Al, Cr (Gl, V, W), a yellow colour indicating Cr. It is tested thus: (*a*) the solution is heated, acidified with sufficient nitric acid to dissolve any precipitate formed, and boiled with excess of ammonium hydroxide solution. A white precipitate indicates Al or Gl; the latter is dissolved in concentrated ammonium carbonate solution, which re-deposits it on prolonged boiling, or Gl may be confirmed by heating with sodium phosphate. Al is tested for in the dry way in the residue insoluble in ammonium carbonate. The filtrate is divided into (*b*), which is treated with ammonium sulphide, a white precipitate indicating Zn; the filtrate from the zinc sulphide will be red or brown, and will give a brown precipitate on acidification with hydrochloric acid, in presence of V or W; and (*c*), which is acidified with acetic acid and treated with one or two drops of lead acetate solution: yellow precipitate shows Cr.

*B* may contain  $\text{Fe}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{Co}_2\text{O}_3$ ,  $\text{Ni}_2\text{O}_3$ ,  $\text{MgO}$ , and Ba, Sr and Ca as carbonates or phosphates (also U, Th, Zr, Ce, etc.). It is washed with boiling water until neutral. (*d*) A small amount of the precipitate is boiled with excess of concentrated nitric acid and lead dioxide, diluted with water, and left; reddish-violet supernatant liquid shows Mn. (*e*) To a small portion of the precipitate dissolved in the minimum quantity of concentrated hydrochloric acid are added 3—4 c.c. of a mixture in equal volumes of amyl alcohol and ether (or the alcohol alone) and 3—4 c.c. of 50% potassium thiocyanate solution. On vigorous shaking the alcohol assumes a green colour in presence of cobalt and a red colour in presence of iron; the red colour may be destroyed, and any green colour revealed by shaking with excess of crystalline sodium acetate. (*f*) The rest of the precipitate is heated with a mixture of 2*N*-solutions of ammonium chloride and carbonate (1:4), which dissolves the Mg, Ni, and any traces of cobalt. Addition of ammonium sodium phosphate and excess of ammonia to the filtered solution gives a white, crystalline precipitate if magnesium is present, whilst a faint, white turbidity soluble in a little ammonium citrate indicates traces of Ba, Ca or Sr. (*g*) The liquid from the magnesium precipitate is boiled, concentrated to expel ammonia, and treated with ammonium sulphide; a black precipitate indicates nickel if cobalt is absent, but may be due to traces of the latter metal when this is present. (*h*) The filtrate from the nickel sulphide is freed from ammonium sulphide by boiling, acidified with hydrochloric acid, and tested for uranium with potassium ferrocyanide. (*i*) The precipitate undissolved by the ammoniacal mixture is dissolved in the minimal quantity of hot hydrochloric acid, and the liquid treated with 1:1 sulphuric acid and at least double its volume of alcohol (denatured); a white precipitate shows Ba, Ca, Sr, or a rare earth metal.

The precipitate is washed with alcohol, gently heated with water, and filtered. The filtrate gives a precipitate with ammonia if rare earths are present. To the filtrate from this, ammonium oxalate is added, the precipitate formed being suspended in water and boiled for some time with excess of crystallised sodium carbonate; the precipitate is then collected, washed, and dissolved in acetic acid. If calcium has been indicated by precipitation occurring with ammonium

oxalate, the acetic acid solution is rendered alkaline with ammonia, heated to boiling, treated with at least an equal volume of saturated potassium ferrocyanide solution, again boiled, and the cooled liquid filtered. The filtrate is boiled with sodium carbonate, the precipitate formed being dissolved in acetic acid, and this solution treated with potassium dichromate; a yellow precipitate indicates Ba. The filtrate from this is neutralised with ammonia and boiled, a precipitate being formed if strontium is present in marked quantity; if not, one-third or one-half of its volume of alcohol is added to the liquid, which is boiled, a voluminous precipitate of strontium chromate being then obtained even with traces of Sr. Where calcium is absent, the above acetic acid solution is treated directly with dichromate.

The alkali metals and ammonia are best detected by the procedure described by Vortmann.

The rare earth precipitate obtained with ammonia (see above) contains almost all the thorium, part of the cerium, and a little zirconium, whilst the alcoholic solution from which the calcium, barium, and strontium are separated contains almost all the zirconium, part of the cerium, and a little thorium. Methods are given for detecting these metals.

T. H. P.

**Benzoic Acid as an Acidimetric Standard.** GEORGE W. MOREY (*J. Washington Acad. Sci.*, 1912, 2, 306—309; *J. Amer. Chem. Soc.*, 1912, 34, 1027—1033).—From the results of experiments on the standardisation of hydrochloric acid solutions by Hulett and Bonner's method (*Abstr.*, 1909, 2, 342), the silver chloride method, against sulphuric acid, sodium oxalate, and benzoic acid respectively, the author is led to the conclusion that the latter constitutes an accurate standard in acidimetry. Its stability, high molecular weight, and lack of hygroscopicity are points in its favour, whilst its bulkiness can easily be reduced by fusion before use.

H. W.

**Application of Ultra-violet Light in Chemical Analysis.** MARC LANDAU (*Compt. rend.*, 1912, 155, 403—406).—Ethylene is slowly polymerised by light from a mercury lamp of 110 volts, but the action is incomplete even after 134 hours. With a 500 volt mercury lamp, polymerisation is eventually complete, both for ethylene and acetylene. Ethane and methane are not affected by ultra-violet light, but in the presence of excess of oxygen the former is eventually completely oxidised to carbon dioxide and water. Carbon monoxide in presence of oxygen is also slowly, but completely, oxidised to carbon dioxide. The author suggests that the analysis of mixtures of hydrogen, ethylene, and ethane might be accomplished by the use of ultra-violet light.

T. A. H.

**Electrolytic Analysis with Platinum Electrodes of Light Weight.** FRANK A. GOOCH and W. L. BURDICK (*Amer. J. Sci.*, 1912, [iv], 34, 107—112).—Owing to the high cost of platinum, the authors have experimented with various electrodes in which the weight of platinum has been cut down to a minimum. Ordinary electrodes of platinised glass (gas-electrodes) are not suitable, as the films flake off during the electrolysis, and are also removed from the glass when the deposited

metal is subsequently dissolved by a suitable reagent. A much more closely adherent film may be obtained when a viscous mixture of glycerol and dry chloroplatinic acid is substituted for the usual plating solution, and on electrodes prepared in this way 0.13 gram of copper may be deposited quantitatively in thirty to forty minutes, using 2 amperes and rotating the cathode. Similarly, 0.07 gram of nickel can be deposited quantitatively in thirty to fifty minutes. This electrode suffers from the disadvantage, however, that there is a tendency of the film to disintegrate when the deposited metal is subsequently dissolved off the electrode, so that after a few successive determinations the film needs to be renewed; also, there is some tendency to the disengagement of particles during the process of electrolysis.

In another form of apparatus the cathode (rotating) consists of a disk of gauze or foil, about 1 cm. square, carried by a rod of lead glass which is fused into the meshes of the gauze or into a central hole in the foil. The cathode rotates in a small cell made from a thistle funnel, through the bottom of which is fused the anode, also 1 cm. square. With such a small cathode the deposited metal lacks compactness, and is likely to be disengaged from the electrode, so that in carrying out the analysis the cell, together with the electrodes, is first weighed, and then, after the electrolysis is complete, the electrodes, cell, and disengaged particles of deposited metal are carefully washed and dried and weighed again. The results obtained with this apparatus were fairly satisfactory, but it was difficult to carry out the washing thoroughly. To obviate this difficulty a platinum sieve, on which a felt of asbestos was deposited, was fused into a small glass tube, so that the washing could be done by applying suction to the end of the tube, which dipped into the cell, and adding water continuously to the cell until the washing was complete. The sieve tube is weighed with the cell and its electrodes, both before and after the electrolysis. The total weight of the cell and its electrodes is 17–18 grams, and the weight of platinum about 1 gram. Very good results were obtained in the quantitative deposition of nickel and copper, the details being the same as those given with the platinised glass electrodes. T. S. P.

**Decomposition Potentials of Certain Double Thiosulphates and their Application to Electro-analysis.** EMILIO JIMENO GIL (*Anal. Fis. Quim.*, 1912, 10, 271–284).—The potential difference between silver and a *N*/100-solution of silver sodium thiosulphate is 0.397 volt, and that between mercury and a *N*/100-solution of mercury potassium thiosulphate is 0.3526 volt.

When these solutions are employed in electro-analysis it is necessary to use a diaphragm of parchment paper or a porous cell between the electrodes in order to prevent sulphuration of the deposited metal. Good results are thus given by ammoniacal solutions, but the method presents no advantages over other well-known processes. G. D. L.

**Estimation of Hydrogen and Methane in Gas Mixtures.** WALTHER HEMPEL (*Zeitsch. angew. Chem.*, 1912, 25, 1841–1845).—An illustrated description of the fractional combustion and absorption of gaseous mixtures occurring in salt mines. L. DE K.

**Detection and Estimation of Haloid Hydrogen in Presence of Hydrogen Cyanide by means of Formaldehyde.** KARL POLSTORFF and HERMANN MEYER (*Zeitsch. anal. Chem.*, 1912, 51, 601—609).—The process is based on the fact that, in dilute solutions, 1 mol. of hydrogen cyanide combines with 1 mol. of formaldehyde, forming a compound not precipitated by silver nitrate. After testing for hydrogen cyanide in the usual way (Prussian-blue test), the alkaline solution is mixed with excess of formaldehyde, and after acidifying the solution with nitric acid the liquid is tested with silver nitrate for its halogen.

For the quantitative estimation about 0.6 gram of the cyanide is dissolved in 100 c.c. of water, the liquid is, if necessary, rendered alkaline with pure sodium hydroxide, and 20—30 drops of 35% formaldehyde are added. After a few minutes, 5 c.c. of 30% nitric acid are added, and the halogen is titrated with standard silver solution (Volhard's thiocyanate method).

L. DE K.

**Detection of Chlorine in Iodine.** H. BOUGE (*Chem. Zentr.*, 1912, ii, 60—61; from *Bull. Sci. Pharm.*, 1912, 19, 72—74).—Two grams of iodine are shaken with 25 grams of benzene for fifteen minutes, the decanted liquid is then shaken with 5 c.c. of water, and the aqueous layer again shaken with benzene to remove iodine. The aqueous layer is then placed in a test-tube with 0.1 gram of potassium permanganate and 1—2 c.c. of sulphuric acid, a cork and delivery tube are fitted, and the vapours evolved on boiling are passed into a few drops of pure sodium hydroxide solution. If chlorine is present, forming chlorobenzene, the alkali solution gives a blue coloration when heated with Denigès' reagent. The reaction fails if the chlorine is less than 0.2%. In this case the aqueous solution is mixed with silver nitrate and nitric acid, and the precipitate of silver halide is tested by its solubility in ammonia and ammonium nitrate for the presence of chloride.

C. H. D.

**Estimation of Chlorous Acid.** G. LASÈGUE (*Bull. Soc. chim.*, 1912, [iv], 11, 884—886).—The method depends on the precipitation of the acid as lead chlorite, which is practically insoluble in 80% alcohol.

Excess of lead nitrate is added to a solution of the chlorite, free from alkali, and the mixture agitated well. Six volumes of alcohol (85° French) is then added, and the whole allowed to remain one hour, after which the precipitate is collected and dried under reduced pressure over sulphuric acid. If alkali is present it is neutralised by adding magnesium nitrate, and the process described above is applied to the filtrate.

Chlorites may be estimated by the above method in presence of hypochlorites and chlorides, and the two latter may be determined in the same solution, the first by titrating the iodine liberated by adding potassium iodide and hydrochloric acid and deducting that due to the action of the chlorite, and the second by reducing the two oxy-salts to chloride by sodium arsenite and then determining the total chloride and deducting that due to the oxy-salts. Chlorates do not affect the

hypochlorite determination unless they are present to a larger extent than 0.6 gram per litre, and they can be determined after the chloride by treating the filtrate from the final estimation with sodium nitrite and estimating the chloride produced by the reduction of the chlorates.

T. A. H.

**Sensitive Reaction for Bromine in Presence of Other Halogens.** ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1912, 47, 696—703).—A trace of bromine gives an intense violet-blue coloration with a solution of magenta previously decolorised by means of sulphur dioxide (Schiff's aldehyde reagent). Under similar conditions iodine gives virtually no colour, and chlorine yields merely a brownish-yellow or red tint. The magenta reagent is best applied on pure filter-paper, quite free from starch, the paper being suspended over the liquid in which the bromine has been liberated by means of chlorine water, etc. When a liquid containing this colouring matter is shaken with ether, the colour collects between the ethereal and aqueous layers. On the other hand, the coloration given by the magenta reagent with formaldehyde or acetaldehyde is reddish-violet, and the colour is not removed from the solution by ether; further, this coloration is produced only in solution, and is not given by the vapour of the aldehyde.

The violet coloration is obtained with as little as 0.00001 gram of potassium bromide in 0.1 c.c. of solution after treatment with 2 c.c. of 25% chromic acid solution.

The reaction is hindered by nitrites, which must be previously removed, whilst thiocyanates give either no reaction or a faint rose coloration.

The colouring matter thus formed by bromine has been obtained as a violet, microcrystalline powder, exhibiting metallic reflexion and containing a large proportion of bromine. It dyes silk, cotton and wool, and, when heated to high temperatures, first assumes an iridescent golden-yellow colour with a bronze-green metallic lustre, then turns green, and finally decomposes. It is probably identical with the tetrabromo-derivative of magenta,  $C_{20}H_{17}ON_3Br_4$ , obtained by Caro and Graebe.

T. H. P.

**Diffusion of Bromine in Nature and its Detection in Organic Substances.** ICILIO GUARESCHI (*Atti R. Accad. Sci. Torino*, 1912, 47, 988—998).—The reaction previously described (preceding abstract) reveals the presence of traces of bromine compounds in many natural and commercial products; the latter are oxidised by means of chromic acid before being tested with the magenta reagent. Human urine, the ash of oak wood, all products derived directly or indirectly from sea salt or from the Stassfurt deposits, etc., contain small proportions of bromine, which is, however, not present in bone ash.

Bromine may be detected in an organic compound by oxidising a fraction of a milligram of the latter by means of chromic acid and suspending a filter-paper moistened with the decolorised magenta in the test-tube. Addition of the magenta solution to 5 c.c. of liquid contain-

ing 0.0000025 gram of potassium bromate results in a distinct reddish-violet coloration; the method may therefore be applied to the detection of bromates (1 part in 20,000) in bromides.

The magenta may be replaced by: magenta-S, rosaniline acetate, pararosaniline hydrochloride, and Hofmann's violet, which reacts more slowly, but gives a more intense coloration.

Magenta decolorised with sulphur dioxide is not coloured by prolonged passage through it of air or carbon dioxide. T. H. P.

**The Estimation of Halogens in Organic Compounds, including a Device for the Combustion of Volatile Substances.** E. EMMET REID (*J. Amer. Chem. Soc.*, 1912, 34, 1033—1039).—The halogens may be readily estimated by a combustion method in which they are absorbed by a weighed mixture of powdered silver and silver oxide, contained in a silver boat, the percentage composition of which is known. The halogen compound is burnt in a stream of oxygen, and the chlorine and hydrogen chloride liberated are absorbed by the above-mentioned mixture, which is kept at a temperature of 250—293°. When the combustion is complete, the unaltered silver oxide is reduced at 170° in a current of hydrogen, after which the boat is again weighed. From the change in weight of the boat, and known composition of the mixture of silver and silver oxide, the percentage of halogen is readily determined. It is safe to burn 0.2—0.25 gram of the substance in twenty minutes.

Details are given of a simple contrivance for the combustion of volatile substances by the above method. T. S. P.

**Detection of Carbon Disulphide, Hydrogen Sulphide, and Other Compounds Containing Sulphur (Albumin) in Fats and Oils.** FRANZ KNORR (*Chem. Zentr.*, 1912, ii, 63; from *Seifensieder-Zeit.*, 1912, 39, 496—497).—The oil is saponified with concentrated sodium hydroxide, salted out, and the liquor from the soap tested with sodium nitroprusside.

Fish oils and American grease contain sulphur in the form of albumin. C. H. D.

**Estimation of Selenium in Pyrites.** PETER KLASON and HJALMAR MELLQUIST (*Arkiv. Kem. Min. Geol.*, 1912, 4, No. 29, 1—10).—In various sulphite-cellulose manufacturing difficulties have occurred which have been traced to the presence of selenium in the pyrites used for burning. Part of the selenium remains in the burnt pyrites and part goes off with the sulphur dioxide, and the authors have found it necessary to determine the relative amounts of this volatile and non-volatile selenium in different pyrites.

The part of the selenium which goes off with the burnt gases was determined by carefully roasting the pyrites in a current of oxygen, using the apparatus previously described (this vol., ii, 201). The contents of the tube were dissolved in warm potassium cyanide, the selenium then being precipitated with hydrochloric acid and sulphur dioxide, and estimated according to the iodometric method (*loc. cit.*). To estimate the total selenium in the pyrites, the method

previously described was used, with the following amplifications. After the selenium has been precipitated with stannous chloride, since it generally contains arsenic and sometimes tellurium, it is collected and completely burned in the sublimation tube. The contents of the tube are then dissolved in hot concentrated hydrochloric acid, and the selenium and tellurium precipitated with sulphur dioxide, the arsenic remaining in solution. The precipitate is again oxidised in the tube, and the contents dissolved in water, whereby the tellurium oxide remains undissolved. The selenious acid in solution is then determined iodometrically.

The investigation of fourteen different pyrites shows that the relative amounts of selenium going off with the burnt gases and remaining in the burnt pyrites varies considerably. When the pyrites contain copper or lead, the selenium is retained by the burnt pyrites to a much greater extent than is otherwise the case.

Grabe and Petrén (*Tekn. Tids. Kem. and Berg.*, April, 1911) have determined the amounts of selenium in different pyrites, but their results are not trustworthy, owing to the fact that they used the thiosulphate method of Norris and Fay (*Abstr.*, 1897, ii, 70; 1900, ii, 272), which does not give accurate results in the presence of arsenic. The present authors show that thiosulphate is oxidised by arsenic acid, the oxidation being one of the causes of the error in the above-mentioned authors' results.

T. S. P.

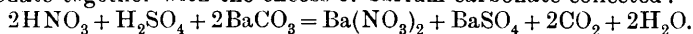
**Colour Reaction of Ammonia.** PIERRE THOMAS (*Bull. Soc. chim.*, 1912, [iv], 11, 796—799).—Berthelot has recorded that ammonia and its salts in presence of phenol give a blue coloration with hypochlorites, and the author suggests the application of this reaction in the colorimetric estimation of ammonia. Tarugi and Lenci have stated (this vol., ii, 397) that a similar coloration is given by all substances containing  $\cdot\text{NH}$  or  $\cdot\text{NH}_2$ , but the author finds that this is not the case. Among the amino-acids, aminoacetic acid is the only one which gives the reaction intensely in dilute solution; alanine and leucine also give it feebly, and glutamic and aspartic acids very feebly.

Acetamide gives no coloration, and carbamide a pale green. The purine bases give characteristic colours; for example, uric acid, reddish-orange, and xanthine, olive-green.

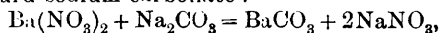
Methylamine and ethylamine give intense blue tints, but amylamine and dimethylamine give feeble blue tints, possibly due to the presence of traces of ammonia.

T. A. H.

**Estimation of Sulphuric, Nitric, and Nitrous Acids in Mixed and Waste Acids.** GEORGE FINCH (*Zeitsch. ges. Schiess Sprengstoffwesen*, 1912, 7, 113—115).—An excess of barium carbonate is added to the mixture of sulphuric and nitric acids, and the barium sulphate together with the excess of barium carbonate collected:



The barium nitrate in the neutral filtrate is decomposed with excess of standard sodium carbonate:



and the amount of nitric acid present then determined by titrating the excess of sodium carbonate left in the solution. The nitrous acid can be estimated by titration with potassium permanganate, whilst the mixed barium sulphate and carbonate precipitate is readily dealt with by known methods.

F. M. G. M.

**Detection and Estimation of Small Quantities of Nitrous Acid.** E. HOLL MILLER (*Analyst*, 1912, 37, 345).—A solution is prepared containing 8 grams of dimethylaniline and 4 grams of hydrochloric acid per 100 c.c., and also a solution of sodium nitrite representing 1 part of nitrous acid per 100,000. The estimation is performed in Nessler tubes or a colorimeter. Fifty c.c. of the solution under examination are acidified with one drop of hydrochloric acid, and, after adding five drops of the dimethylaniline solution, allowed to remain for fifteen minutes or longer, if necessary. The yellow colour is then matched in the usual manner against the standard solution, which is acidified with 1 drop of acid and mixed with 3 drops of the reagent. Nitrates do not interfere.

L. DE K.

**Estimation of Phosphoric Acid in Wine.** KARL VON DER HEIDE and J. SCHWENK (*Zeitsch. anal. Chem.*, 1912, 51, 615—627).—After trying several methods in addition to the official one, the authors arrive at the following conclusions.

The amount of organic-combined phosphoric acid is but small. On adding, according to Phillippe and Duperthuis, barium hydroxide solution, the inorganic phosphoric acid only is precipitated, and may then be determined in the precipitate as usual (preferably by von Lorenz's process). From the filtrate the remaining phosphoric acid is recovered after removing the excess of barium with sulphuric acid and burning off the organic matters, etc. After destroying the organic matters, say, by moist combustion, the total phosphoric acid may be conveniently titrated by means of Grete's molybdate-gelatin process (*Abstr.*, 1909, ii, 936). The official method of adding oxidising mixture to assist the combustion of the carbon is not to be recommended. The best way of obtaining an ash is as follows: 50 c.c. of the wine (previously fermented if necessary) are evaporated and charred. The mass is extracted with hot water, and the char is then burnt completely. The nitric acid solution of the residue is united with the watery liquid, and the phosphoric acid estimated as usual. Grete's process may also be applied to the wine directly if the sugar does not exceed 0.5%.

L. DE K.

**A Trustworthy Method for the Estimation of Phosphoric Acid Soluble in Citric Acid in Thomas Slag.** M. POPP (*Chem. Zeit.*, 1912, 36, 937).—The error due to the precipitation of silica is avoided by the following procedure: 50 c.c. of the citrate extract are mixed with 25 c.c. of a solution prepared from 1 kilogram of citric acid, 30 grams of ferric chloride, and 30 c.c. of water dissolved in 4 litres of 20% ammonia and diluted to 5 litres, and with 10 c.c. of 0.3% hydrogen peroxide and 25 c.c. of magnesia mixture, which has been filtered several days after preparation.

C. H. D.

**Estimation of Phosphoric Acid Soluble in Citric Acid in Thomas Slag.** WILHELM FUCHS and PAUL WAGNER (*Chem. Zeit.*, 1912, 36, 1037—1039. Compare Popp, preceding abstract).—A comparison of the different methods available, with a detailed description of each. Accurate results may be obtained by either of the usual methods. The results are not appreciably affected if a longer time or more rapid rotation is employed in the extraction of the ground slag with citric acid.  
C. H. D.

**Arsenic Xanthate in Analytical Chemistry.** NAZARENO TARUGI and F. SORBINI (*Boll. Chim. Farm.*, 1912, 51, 361—370).—Arsenic xanthate,  $\text{As}(\text{S}\cdot\text{CS}\cdot\text{OEt})_3$ , m. p.  $94\cdot8^\circ$  (corr.), which may be prepared by the action of potassium xanthate (3 mols.) on a solution of any compound of arsenic (1 atom), is absolutely insoluble in hot or cold water or cold acetic acid, and readily soluble in benzene, carbon disulphide, carbon tetrachloride, or chloroform, whilst glycerol, vegetable oils, vaselin, lanolin, etc., also dissolve it, especially in the hot. It is non-volatile in steam.

The precipitation of this compound by potassium xanthate is so completely quantitative that the filtrate shows no trace of arsenic even by Marsh's test.

Various volumes of a solution of arsenious anhydride containing 1 gram of arsenic per litre were measured out, rendered alkaline with sodium hydroxide, mixed with excess of potassium xanthate solution, and acidified with glacial acetic acid. After twelve hours the precipitate was collected on a small filter, washed with water, dried in a vacuum over sulphuric acid, and dissolved in boiling chloroform, the solution being evaporated to dryness in a tared beaker and the latter weighed. In some cases the purity of the precipitate was controlled by the m. p., and in others the precipitate was heated on the water-bath with a few drops of aniline, dried at  $150^\circ$ , and weighed as  $\text{As}_2\text{S}_3$ . By either method very exact results were obtained.

Very small quantities (0·001 milligram) of arsenic may be detected by shaking the solution containing the xanthate precipitate (after twelve hours) with an equal volume of chloroform, separating the latter by means of a narrow pipette, filtering it through a funnel containing a small ball of filter-paper to dry it, and evaporating it to dryness on a watch-glass. A characteristic radiating mass of crystals is thus obtained. If this is touched with the end of a rod moistened with aniline and heated gently, the sulphide is formed. This test only answers well with arsenious compounds, so that if arsenates are present the liquid should be treated previously with sulphurous acid.

In a similar manner the strength of potassium xanthate preparations may be determined by precipitation with an arsenite solution. This estimation may also be carried out volumetrically as follows. Into a graduated cylinder of about 150 c.c. capacity are measured an excess (10 c.c. or more) of a potassium hydroxide solution of arsenious anhydride of known titre towards decinormal iodine solution, and 5 c.c. of the xanthate solution, the whole being well shaken. After about fifteen minutes, the liquid is acidified with glacial acetic acid, a little water and about 20 c.c. of benzene being then added. The cylinder is

vigorously shaken until the aqueous liquid remains clear, and the volume of this aqueous layer made up exactly to 100 c.c. with water. Part of this liquid is then removed by means of a pipette, the point of which has been sealed with sodium carbonate fused in its water of crystallisation so as to prevent the entry of benzene. After filtration through a dry filter, 10 c.c. are neutralised with sodium hydrogen carbonate and titrated with the iodine solution. The difference between the numbers of c.c. of the latter corresponding with the arsenite solution before and after the precipitation is multiplied by 0.024 gram to obtain the amount of potassium xanthate in the solution taken.

Carbon disulphide may be estimated as follows: The liquid containing the disulphide is added to, or the air containing vapour of the disulphide passed through, a cooled potassium hydroxide solution of arsenic trioxide mixed with a little alcohol. After about fifteen minutes the liquid is acidified with glacial acetic acid, left for twelve hours, and so on. The estimation may also be carried out volumetrically as described above for xanthate solutions.

All these methods give very accurate results.

T. H. P.

**Further Applications of the Precipitation of Iodides in Sulphuric Acid.** GIUSEPPE BRESSANIN (*Gazzetta*, 1912, 42, ii, 97—101. Compare Abstr., 1911, ii, 1133, 1134; this vol., ii, 638).—In solution in sulphuric acid of 50° Bé, tin in either state of oxidation gives, with potassium iodide, a canary-yellow precipitate readily soluble in hydrochloric acid. Stannic compounds are precipitated as stannic iodide, and are hence quite different in behaviour from arsenates and antimonates, which are precipitated as  $AsI_3$  and  $SbI_3$  with liberation of iodine. Arsenic and antimony may hence be estimated in presence of tin by the method previously described if the liquid is first oxidised.

Arsenic in commercial copper may be estimated as follows: About 0.5 gram of the copper, in chips, is dissolved in 5 c.c. of aqua regia in a porcelain dish at a gentle heat, the solution being evaporated to dryness until all acid fumes disappear, and the residue dissolved by heating with about 250 c.c. of sulphuric acid of 50° Bé. The cold solution is treated with 25 c.c. of 30% potassium iodide solution, and left for about twenty minutes for the precipitate to settle. The supernatant liquid and finally the precipitate are passed on to a very fine asbestos filter, washed with 30—40 c.c. of sulphuric acid containing 5% of 30% potassium iodide solution, and treated with about 100 c.c. of dilute sulphurous acid solution, which dissolves the arsenious iodide and reduces any remaining traces of iodine. To the clear solution are added a little starch paste and sufficient iodine solution to give a faint blue colour, the liquid being then titrated with iodine solution to determine the amount of arsenic present. This method is found to yield accurate results.

T. H. P.

**Estimation of Soluble Arsenic in Commercial Lead Arsenates.** B. E. CURRY and T. O. SMITH (*J. Ind. Eng. Chem.*, 1912, 4, 198—200).—The standard American process for estimating soluble arsenic in commercial lead arsenate requires eleven days for

completion, during ten of which the sample remains in contact with water and receives eighty shakings to ensure complete solution of free arsenic oxide. The author considers that this can be satisfactorily achieved by continual stirring during eighteen hours at 20°, when results are obtained only 0.65% lower than those by the more prolonged process, and suggests that this method be adapted and the necessary correction applied.

For 2 grams of the sample, 500 c.c. of water are employed, and the arsenic subsequently estimated in the filtrate by known volumetric methods.

F. M. G. M.

**Estimation of Carbon in Steel.** ARTHUR G. LEVY (*Analyst*, 1912, 37, 392—395).—Attention is again called to the influence of dissolved carbonaceous gases in iron or steel when estimating the carbon by the combustion process; the plus error may amount to 0.03%, or even more. In delicate work it is safer to apply the "solution" method.

L. DE K.

**Construction of a Toximeter for Carbon Monoxide.** A. GUASCO (*Compt. rend.*, 1912, 155, 282—284).—Various methods have been devised for detecting the presence of small quantities of carbon monoxide in the air or in other gases. These have either not been sufficiently sensitive or have been open to the criticism that other gases would give the same reaction. The author has devised a toximeter which is sensitive to one part of carbon monoxide in ten thousand of air. It consists of a U-tube ending in two bulbs, one of which is coated with platinum black. These bulbs are hermetically enclosed in an envelope, which isolates them from the air and into which the gases penetrate by endosmosis through a porous medium. The presence of carbon monoxide is shown by alteration in the level of a coloured liquid with which the U-tube is one-third filled, the alteration being approximately proportional to the percentage of carbon monoxide in the air. By replacing the coloured liquid with mercury and fixing a platinum contact, the apparatus can be made to give an automatic warning.

W. G.

**Carbon Dioxide: its Volumetric Estimation.** LEON T. BOWSER (*J. Ind. Eng. Chem.*, 1912, 4, 203—205).—The volumetric estimation of carbon dioxide has been previously advocated by Mims (*Bull.* 65, 156, *U.S. Bureau of Chemistry*), whose method with a few modifications is found to give accurate results, whilst in simplicity of apparatus and reduction of time considerable advantage is claimed.

The carbon dioxide is released with hydrochloric acid, distilled with water vapour into a concentrated solution of alkaline hydroxide, and the absorbed gas estimated by titration with standard acid primarily in the presence of phenolphthalein; as soon as the pink colour disappears, indicating that all the hydroxide has been neutralised and the normal carbonate converted into a hydrogen carbonate, one drop of methyl-orange is added and the titration continued until the

reaction is complete, the amount of acid used in the second titration being half that required to release the total carbon dioxide present.

Absorption takes place in a tower containing glass beads, and from which the carbonated solution can be readily washed, it being found that merely passing carbon dioxide through an unbroken column of alkaline hydroxide gives imperfect absorption. Any difficulty in reading the phenolphthalein end-point is remedied by the addition of a little alcohol, and care should also be taken not to add any excess of methyl-orange beyond that required to indicate that the reaction is complete.

Sulphuric acid should not be employed to release the carbon dioxide from the material, it being found to give incomplete decomposition, whereas hydrochloric acid reacts satisfactorily and it is immaterial if a little is carried over into the receiver; likewise potassium hydroxide is a more satisfactory absorbent than sodium hydroxide, and barium hydroxide is too insoluble. The reaction is carried out in a corked flask fitted with a dropping funnel, and connected to a Liebig condenser, through which the carbon dioxide passes into the absorption tower.

F. M. G. M.

**The Estimation of Free Carbon Dioxide in Water by Trillich's Method.** FRIEDRICH AUERBACH (*Zeitsch. angew. Chem.*, 1912, 25, 1722—1723).—The titration of carbon dioxide by means of sodium carbonate can only be carried out with accuracy in very dilute solutions, and with a very dilute solution of phenolphthalein (compare Noll, this vol., ii, 685). In making a series of experiments, it is desirable to determine the error by means of a blank titration with an artificial water of approximately the same concentration (compare Auerbach and Pick, Abstr., 1911, ii, 1078).

C. H. D.

**Estimation of Potassium. Potassium Sodium Cobalt Nitrite Method.** EILHARD A. MITSCHERLICH and HERMANN FISCHER (*Landw. Versuchs-Stat.*, 1912, 78, 74—86. Compare this vol., ii, 204).—The composition of potassium sodium cobalt nitrite is not constant. As, however, the reduction factor alters only within the limits of the experimental error of the potassium estimation, and it is practically immaterial how great an excess of reagent is employed, the method can be recommended. Examples of analyses are given, showing that the method is suitable both with small and large amounts of potassium in manures as well as other substances.

The factor 0.000161 should be employed instead of 0.000157 as previously stated.

N. H. J. M.

**The Characterisation and Estimation of Potassium and Sodium.** P. J. GÉRARD (*Chem. Zentr.*, 1912, ii, 149; from *Bull. Sci. Pharm.*, 1912, 19, 214—231).—The following method is suitable for animal organs. The dried material is incinerated in a muffle at 350—400°, and the powdered ash extracted with 1000 times its weight of water. After addition of ammonia and ammonium phosphate, the liquid is filtered and exactly neutralised, and the phosphate is precipitated by means of ferric chloride and ammonium acetate. The

filtrate and washings are evaporated to dryness, converted into sulphates, and the mixed sodium and potassium sulphates weighed after fusion. The dissolved mass is then precipitated with lead acetate and alcohol, the lead precipitated by hydrogen sulphide from hydrochloric acid solution, and the chlorides weighed. The two chlorides are separated by platinum chloride, and the potassium platinichloride decomposed by magnesium, the platinum being weighed. The filtrate is reduced by formic and sulphurous acids, and the sodium converted into sulphate. C. H. D.

**Valuation of Fluorspar.** E. BIDTEL (*J. Ind. Eng. Chem.*, 1912, 4, 201—202).—There is no practical method of separating fluorine from silica suitable for the commercial analysis of ores, whilst the practice of determining the total calcium and the carbonate and calculating the fluorine from these indicates too high a percentage of carbonate and too low of fluoride, because lead, zinc, and iron carbonates are frequently present, and, moreover, the whole of the calcium present is not usually in the form of carbonate or fluoride. The following method is suggested. One gram of the sample is heated with 10 c.c. of 10% acetic acid, washed, dried, and ignited at a low temperature, when the loss of weight minus 0.0015 gram (the amount of calcium fluoride found to dissolve under these conditions) indicates the calcium carbonate. The residue is then treated in a platinum crucible with an aqueous emulsion containing about 1 gram of mercuric oxide (to oxidise lead sulphide), evaporated to dryness, heated at a dull red heat, cooled, and weighed, and subsequently again evaporated three times to dryness with hydrofluoric acid. A few drops of hydrofluoric acid and macerated filter-paper (as recommended by Dittrich) are then added, together with some ammonium hydroxide, the mixture evaporated, and heated to a dull red heat, when the loss in weight indicates silica. The contents of the crucible are then digested on the water-bath with a mixture of nitric and hydrofluoric acids during half an hour and evaporated to dryness; if the residue is coloured, it is digested with a mixture of aqueous ammonium acetate and citrate (to remove any zinc, lead, or iron) and hydrofluoric acid, filtered, washed, and the residue subsequently ignited in the same crucible, when a colourless residue of pure calcium fluoride should be obtained.

As none of the ores employed contained either gypsum or heavy spar, the influence of their presence has not been considered in these experiments. F. M. G. M.

**Differentiation of the Magnesium Hardness in Carbonate and Non-Carbonate Hardness; Detection of Alkali Carbonates in Waters.** HERMANN NOLL (*Chem. Zeit.*, 1912, 36, 997—998).—The usual process, boiling the water for half an hour with constant replenishing, fails to precipitate all the magnesium carbonate, but if 1000 c.c. of water are evaporated to 250 c.c., the magnesium carbonate is practically all precipitated. If alkali carbonates [acid carbonates] are present, the precipitation is less complete, and the remaining calcium and magnesium, after titrating with *N*/10-sulphuric acid, must be estimated and allowed for; calcium, however, is but rarely present. L. DE K.

**Estimation of Zinc in Ferruginous Minerals.** EDGAR BEYNE (*Bull. Soc. chim. Belg.*, 1912, 26, 355—362).—The estimation of zinc in ferruginous minerals according to Schaffner's method generally yields somewhat low results, owing to adsorption of zinc by ferric hydroxide. The author shows that this adsorption can be completely avoided if sufficient ammonium chloride is added before precipitating the iron with ammonium hydroxide. H. W.

**Estimation of Lead in Tinplate as Lead Chloride.** E. CRATO (*Chem. Zentr.*, 1912, i, 1927—1928; from *Veröff. Geb. Militärsanitätswesens*, 1912, 72—78).—One gram or more of the material is dissolved in 20 c.c. of 25% hydrochloric acid and a little nitric acid, cooled, diluted with 60 c.c. of alcohol, and cooled with ice. If in twenty-four hours no lead chloride, or only a few isolated needles have separated, the material contains less than 1% of lead. If more is present, the mixture is allowed to remain for two days; the crystals are collected, washed with alcohol, dissolved in boiling water, filtered, evaporated, dried at 100°, and weighed. The precipitation of small quantities of lead takes place much more favourably when an excess of tin is present. C. H. D.

**Detection and Estimation of Small Quantities of Copper in Plants.** B. GUÉRITHAULT (*Chem. Zentr.*, 1912, i, 1639; from *Bull. Sci. Pharm.*, 1912, 18, 633—639).—The ash, obtained by incineration in a muffle, is repeatedly extracted with hot dilute hydrochloric acid, and the solution is concentrated, partly neutralised, and precipitated with hydrogen sulphide. The precipitate is collected after twenty-four hours, washed, ignited, and dissolved in nitric acid. The copper is then estimated electrolytically or colorimetrically. The copper found in a large number of different plants amounts to 0·0171—0·0046% of the dried substance. C. H. D.

**The Electrolytic Estimation of Copper in Pyrites.** W. D. TREADWELL (*Chem. Zeit.*, 1912, 36, 961).—In order to avoid the tedious removal of aqua regia by evaporation, ammonia is added to the solution until just turbid, and 8 to 12 grams of Rochelle salt are added for 3 to 4 grams of pyrites, followed by 5 grams of ammonium sulphate and 20 c.c. of concentrated ammonia. The cold solution is then electrolysed with a rotating gauze cathode and a cylindrical anode. The cathode must be completely covered, as air causes the copper to redissolve. With two Edison accumulators, a resistance is unnecessary until the end of the process to maintain the potential at 2 volts. Deposition is complete in one to one and a-quarter hours. For rapid estimations the iron is reduced with hydrazine sulphate, and the solution is then electrolysed with a rotating cathode in thirty minutes with 1·8—2 volts. In this case the deposit always contains a little iron. It is, therefore, redissolved in nitric acid and again deposited. Lead is also removed by this second treatment. A reducing agent must not be used if arsenic is present. C. H. D.

**Estimation of Total Mercury in Official Mercury Salicylate.** ERWIN RUPP and K. KROPAT (*Apoth. Zeit.*, 1912, Reprint 4 pp).—The gravimetric estimation of mercury in official mercury

salicylate is tedious. The authors therefore recommend the following volumetric method, the results by which agree well with those obtained gravimetrically.

The preparation is dissolved in sodium carbonate solution and treated with finely ground potassium permanganate. Concentrated sulphuric acid is cautiously added, the solution diluted with water, and treated with pure 3% hydrogen peroxide until all manganese dioxide is dissolved. Potassium permanganate is now cautiously added until in slight excess, and the excess removed by means of ferrous sulphate. The solution is then titrated with thiocyanate solution, iron alum being used as indicator.

H. W.

**Rare Earth Reactions in Non-Aqueous Solvents.** O. L. BARNEBEY (*J. Amer. Chem. Soc.*, 1912, 34, 1174—1189).—A number of the reactions of the common acids and bases, including the alkaloids, with the yttrium group, neodymium, lanthanum, and cerium have been studied, utilising acetone and in some cases alcohol as the solvent. The iodides and nitrates of the earths, and to a limited extent the bromides, were found to be appropriate solutes. The reactions are of the same general order as those in aqueous solutions, but the solubilities vary so much that the results are vitally different in many cases. The earths form more compounds insoluble in acetone than in aqueous solution, especially in the case of the compounds with acids and with the alkaloids. A scheme for the separation of the rare earths based on the fractionation of the basic nitrates by acetone was found to work well; cerium is very quickly obtained in a high degree of purity from the first fraction, and didymium concentrates in the last. Another scheme for the separation of the yttrium group, depending on the fractional precipitation by tartaric acid in acetone solutions, was also found effective.

J. C. W.

**The Quantitative Separation of Lanthanum from Yttrium.** CHARLES JAMES and T. O. SMITH (*Chem. News*, 1912, 106, 73—74; *J. Amer. Chem. Soc.*, 1912, 34, 1171—1174).—The separation of yttrium from lanthanum by means of potassium sulphate is incomplete, much yttrium potassium sulphate being carried down with the lanthanum salt. With sodium sulphate, on the other hand, the lanthanum is not precipitated completely, even when an excess of sodium sulphate is used. The formates may be separated by means of 95% alcohol, but some lanthanum accompanies the soluble yttrium salt. The cacodylates are unsatisfactory, owing to the formation of colloidal solutions. The best results are obtained by Urbain's method, mixing the nitrates with bismuth magnesium nitrate in large excess, together with magnesium nitrate and nitric acid. The lanthanum is found in the insoluble portion, together with a very small quantity of yttrium.

C. H. D.

**Estimation of Manganese in Steel.** JAMES J. BOYLE (*J. Ind. Eng. Chem.*, 1912, 4, 202).—A discussion of different methods employed in the estimation of manganese in steel; the following modification of the ammonium persulphate-sodium arsenite titration is

considered satisfactory, and to give results closely approaching the bismuthate method in accuracy. One gram of steel is dissolved in 100 c.c. of nitric acid (D 1.20), cooled, and diluted to 500 c.c. with water; 100 c.c. of the solution are removed, warmed, treated with 15 c.c. of silver nitrate solution (0.133% solution), and about 1.5 grams of ammonium persulphate, followed after some minutes' warming by 6 c.c. of a 0.14% solution of sodium chloride, which precipitates all the silver; the solution is then cooled, and titrated with standard sodium arsenite until the pink colour disappears; the end-point is very sharp, and re-oxidation of the reduced permanganic acid cannot occur if the titration is carried out at 0°.

F. M. G. M.

**A New Spectrophotometer and its Application in Analytical Chemistry.** CH. FÉRY and EUGÈNE TASSILLY (*Chem. Zentr.*, 1912, ii, 173—174; from *Bull. Sci. Pharm.*, 1912, 19, 11—27).—The Féry spectrophotometer has a scale proportional to the concentration of an absorbing layer of constant thickness, the measurements being made by means of thin wedges of smoked glass moving across the two halves of the slit until the intensities are equal.

In the estimation of iron as thiocyanate in potable water by means of the spectrophotometer, a curve showing the absorption as a function of the quantity of thiocyanate per gram-atom of iron has three breaks, corresponding with the proportions  $\text{FeCl}_3.3\text{KCNS}$ ;  $\text{FeCl}_3.2\text{KCNS}$ , and  $\text{FeCl}_3.11\text{KCNS}$ . The maximum of absorption lies in the bluish-violet, that of sensitiveness in the green. If the thiocyanate is in large excess, the readings are proportional to the iron present. Acids are without influence on the result; sulphates exert an influence, which is, however, prevented by the presence of hydrochloric acid.

A 250 c.c. flask is used, and 100 c.c. of the water are heated to boiling with 20 c.c. of hydrochloric acid. After the addition of 0.5—1 gram of potassium chlorate, heating is continued until chlorine is no longer evolved. After cooling, 20 c.c. of a 1.7% solution of potassium thiocyanate are added, and the absorption is determined. The method may also be used for the spectrophotometric estimation of copper in foods as ferrocyanide in sulphuric acid solution. The maximum sensitiveness lies in the green.

C. H. D.

**Estimation of Titanium in the Presence of Iron.** WILLIAM M. THORNTON, jun. (*Amer. J. Sci.*, 1912, [iv], 34, 214—217).—The iron in the solution is separated as follows: tartaric acid, in quantity equal to three times the aggregate weight of the oxides to be held by it in solution, is added; the iron is then reduced to the ferrous condition by hydrogen sulphide, ammonium hydroxide added to slight alkalinity, and hydrogen sulphide again passed in until the iron has been completely precipitated and the solution left faintly alkaline. The ferrous sulphide is collected and washed with very dilute colourless ammonium sulphide, when all the titanium will be in the filtrate. The tartaric acid in the filtrate is then destroyed by oxidation with potassium permanganate, the solution being first boiled with sulphuric acid in order to expel the hydrogen sulphide. The titanium is then precipitated by the basic acetate process. Owing to the amount of

manganese present in the solution, it is necessary to precipitate the titanium twice, since some manganese is carried down in the first precipitation.

A better method of procedure is the following: the filtrate is evaporated down to incipient charring of the tartaric acid. The basin containing it is then covered with a clock glass, and the heating continued as long as charring and frothing can take place without any loss. After cooling somewhat, 5 c.c. of fuming nitric acid are added, and the heating continued until all the organic matter is destroyed and a pale syrupy liquid is left. This is poured into cold water, filtered, and the titanium estimated by the basic acetate method, only one precipitation being necessary.

T. S. P.

**Analysis of Ferrozirconium.** S. PIÑA DE RUBIES (*Anal. Fis. Quim.*, 1912, 10, 267—271).—The method of Wunder and Jeanneret (this vol., ii, 96) for the analysis of ferrozirconium based on the insolubility of zirconia in fused sodium carbonate is shown to yield good results by filtering the zirconia through hardened filter-papers and washing with boiling water containing ammonium nitrate. During the fusion the crucible should be left open in order to facilitate the oxidation of the zirconium.

G. D. L.

**Reactions of Gold Salts with *m*-Phenylenediamine.** J. A. STREMSSEN (*Chem. Zeit.*, 1912, 36, 934).—Very dilute solutions of gold chloride, down to 0.005%, give a yellow or brown coloration with a 0.5% solution of *m*-phenylenediamine sulphate. Should the latter have become coloured, it is first decolorised by means of charcoal.

C. H. D.

**Elementary Analysis.** ALBIN KURTENACKER (*Zeitsch. anal. Chem.*, 1912, 51, 639—640).—A reply to Dohrt (this vol., ii, 92), who, contrary to the experience of the author and of other investigators, holds that metallic silver is fit to replace the metallic copper in organic combustions.

Two nitrogenous substances, *p*-nitroaniline and *m*-dinitrobenzene, analysed by Epstein and Dohrt (*Abstr.*, 1908, ii, 132) in order to prove the efficacy of metallic silver, were found by the author to yield accurate carbon and hydrogen results without using any reducing agent whatever. On the other hand, carbamide nitrate gave copious fumes of nitric peroxide, which were not acted on by red-hot silver spirals and so vitiated the results.

L. DE K.

**The Estimation of Carbon in the Wet Way.** HUGO SIMONIS and F. H. THIES (*Chem. Zeit.*, 1912, 36, 917—918).—Phenylacetaldehyde always gives about 4% too low carbon on combustion with copper oxide. The method of wet combustion gives good results. It is best to heat the substance in a 200 c.c. flask with potassium dichromate and sulphuric acid, the vapours passing first through a vertical cylinder packed with glass wool and then through a heated tube packed tightly with copper oxide. A current of oxygen is passed through the apparatus. The substance (0.2 gram) is weighed in a

small platinum boat, covered with potassium dichromate, and allowed to slide into the flask, followed by 15—20 grams of potassium dichromate. The copper oxide tube is heated, and oxygen is passed until all air is expelled, when 60 c.c. of pure sulphuric acid are allowed to flow into the flask, the flow being regulated by the passage of gas bubbles through the absorbing apparatus. The combustion occupies thirty to forty minutes.

C. H. D.

**The Detection of Hydrocarbons in Turpentine.** K. UTZ (*Chem. Zentr.*, 1912, i, 1641; from *Farbenzeit.*, 1912, 17, 1208—1209).—A method proposed by Mennechet consists in shaking the turpentine with magenta and a little nitric acid, which gives a red colour with pure turpentine, but more or less brown in the presence of hydrocarbons. The colorations with pure hydrocarbons are now found to be quite characteristic, but the test fails when the liquids are mixed, unless the adulterant amounts to at least 30%.

C. H. D.

**Estimation of Caoutchouc as Tetrabromide.** K. UTZ (*Gummi Zeit.*, 1912, 26, 968—970. Compare Abstr., 1911, ii, 545).—The author discusses the methods employed by Hübener, Budde, Spence, Galletly, and Scott for this estimation, and advocates one based on that of Baubigny and Chavaune (Abstr., 1903, ii, 510; 1904, ii, 203).

F. M. G. M.

**Direct Estimation of Nitrogenous By-products and Impurities in Raw Caoutchouc.** FRITZ FRANK and EDUARD MARCKWALD (*Gummi Zeit.*, 1912, 26, 936—937).—In consequence of the publication of experiments by Beadle and Stevens (*Analyst*, 1911, 37, 13—16) on this subject, the authors draw attention to their communication (*Gummi Zeit.*, 1908, 22, 1344) in which they describe the estimation of mineral and other impurities in caoutchouc.

F. M. G. M.

**Detection and Estimation of Methyl Alcohol.** FERDINAND WIRTHLE (*Zeitsch. Nahr. Genussm.*, 1912, 24, 14—26).—The presence of methyl alcohol in spirits is detected by collecting 50 c.c. of distillate from 100 c.c. of the spirit, twice fractionally distilling this distillate, and oxidising the final distillate obtained (which should measure about 3 c.c.) with potassium permanganate in the presence of dilute sulphuric acid. The mixture is then filtered, 1 c.c. of the filtrate is mixed with 5 c.c. of sulphuric acid, and 5 mg. of morphine hydrochloride are added. A violet coloration develops if methyl alcohol was present in the spirit examined. The temperature at which the alcoholic solutions commence to distil is an indication of the presence, or absence, of methyl alcohol. For instance, a mixture containing 10% of methyl alcohol begins to distil at 75°. For the estimation of methyl alcohol, 100 c.c. of the spirit (containing, say, 40% of alcohol) are distilled, and the residual solution in the distillation flask is twice treated with quantities of ethyl alcohol and distilled. A quantity of the mixed distillates, corresponding with 10 c.c. of alcohol (as ascertained from the sp. gr.), is then boiled in a reflux apparatus with

iodine and amorphous phosphorus in order to convert the alcohols into their iodides, the latter are separated by distillation, washed with 10% potassium hydroxide solution, and weighed. Ten c.c. of methyl alcohol yield 31.35 grams of methyl iodide, whilst 10 c.c. of ethyl alcohol yield 23.72 grams of ethyl iodide. The methyl iodide may also be identified by its saponification value, 394.3, that of ethyl iodide being 358.9 (compare this vol., ii, 607). W. P. S.

**The Estimation of Methyl Alcohol in Mixtures with Ethyl Alcohol, Especially in Brandy.** W. KOENIG (*Chem. Zeit.*, 1912, 36, 1025—1027).—The dichromate method has been modified as follows: A litre flask is fitted with a double-bored rubber cork, through which pass a tap-funnel closed by a soda-lime tube, and a reflux condenser. The flask contains some pumice which has been boiled with potassium permanganate and sulphuric acid and then ignited. The absorption apparatus, connected to the condenser, consists of U-tubes containing sulphuric acid, calcium chloride, and soda lime. After removing carbon dioxide from the apparatus by means of air, the soda-lime tubes are attached, and the alcohol (1—3 grams) to be tested is introduced, followed by a mixture of 30 grams of potassium dichromate, 500 c.c. of water, and 50 c.c. of concentrated sulphuric acid, which has been boiled and cooled to 5°. After at least four hours at the ordinary temperature, the flask is gently heated, so that the gas bubbles slowly through the absorption apparatus. Air is then passed through the apparatus. Satisfactory results are obtained with artificial mixtures of methyl and ethyl alcohols, and with brandy. C. H. D.

**A Gas-volumetric Method for Estimation of Ether and Chloroform Vapour in Atmospheric Air.** MARTIN KOCHMANN and WILHELM STRECKER (*Biochem. Zeitsch.*, 1912, 43, 410—417).—The analysis is carried out in a Bunte burette. The organic substances are absorbed by alcohol, and the alcohol vapours by water. By measuring the diminution of volume, the amount of alcohol or chloroform in the air is ascertained. S. B. S.

**Estimation of Dextrose in the Presence of Other Substances by Bertrand's Method.** M. ROSENBLATT (*Biochem. Zeitsch.*, 1912, 43, 478—480).—In view of the fact that a large number of methods have been recently suggested for removing amino-acids, peptones, and other substances which interfere with the estimation of sugars by Fehling's solution, the author shows, by many examples, that this removal is unnecessary when Bertrand's method is employed. S. B. S.]

**Detection of Sucrose in the Presence of Other Sugars, Especially its Detection in Musts and Wines.** S. ROTHENFUSSE (*Zeitsch. Nahr. Genussm.*, 1912, 24, 93—104).—For the removal of other sugars and substances which interfere with the detection of sucrose by the test described previously by the author (compare Abstr. 1910, ii, 463; 1911, ii, 665), it is recommended that hydrogen peroxide

in alkaline solution (preferably barium hydroxide) be used. In the case of musts, 5 c.c. of the sample are added to a mixture consisting of 6 grams of barium hydroxide, 25 c.c. of hot water, and 25 c.c. of 3% hydrogen peroxide solution; the whole is heated on a water-bath for twenty minutes (more hydrogen peroxide is added if a yellow coloration develops), then filtered, and 5 c.c. of the filtrate are tested with the diphenylamine reagent as described (*loc. cit.*). When testing dry wines, 10 c.c. of the latter are heated with 50 c.c. of a 5% barium hydroxide solution and 10 c.c. of 3% hydrogen peroxide. Sweet wines require a somewhat different treatment; 10 c.c. of the wine are shaken with 50 c.c. of acetone for about thirty seconds, and again after the addition of a small quantity of kieselguhr. The mixture is now filtered, 30 c.c. of the filtrate are diluted with water, heated on a water-bath until the acetone has been removed, and the residual solution treated with 6 grams of barium hydroxide and 25 c.c. of 3% hydrogen peroxide.

W. P. S.

**The Influence of Fish Gelatin on Sugar Estimations by Fehling's Solution.** ALESSANDRO BERNADI (*Biochem. Zeitsch.*, 1912, 43, 275—279).—In continuation of his other investigations on the influence of colloids on the amount of cuprous oxide precipitated from Fehling's solution by dextrose, the author now finds that in the presence of fish gelatin, the amount is too large, but that the corrected amount can be found if the oxide is converted into thiocyanate. Furthermore, the gelatin can be removed satisfactorily from solution by precipitation with mercuric chloride or ammonium molybdate. This last-named reagent can also be used for precipitation of peptones.

S. B. S.

**Estimation of Sucrose in Condensed Milk.** H. NOWAK (*Zeitsch. anal. Chem.*, 1912, 51, 610—614).—An application of Jolles's method (*Abstr.*, 1911, ii, 74) to the analysis of condensed milks, etc. Twenty-five grams of milk (or 5 grams of condensed milk) are diluted in a 250 c.c. flask with 200 c.c. of water, and 10 c.c. of copper sulphate solution (34.639 grams per litre) are added. The liquid is then rendered neutral with sodium hydroxide and diluted to the mark. From the filtrate, 50 c.c. are taken for the gravimetric estimation of the lactose (by means of alkaline copper solution), and another portion is then examined for sucrose after first removing the excess of copper by cautious addition of powdered potassium ferrocyanide (about 0.5 gram).

After destroying the rotatory power of the lactose by heating 50 c.c. of the filtrate with 1.3 c.c. of sodium hydroxide (so as to obtain a *N*/10-alkaline solution) for forty-five minutes in a pressure flask placed in a boiling-water bath, the liquid, when cold, is clarified by addition of 3.7 c.c. of basic lead acetate and then examined polarimetrically in a 22 cm. tube.

L. DE K.

**Estimation of Sucrose in Urine in the Presence of Other Sugars.** ADOLF JOLLES (*Biochem. Zeitsch.*, 1912, 43, 56—64).—The author has already shown that dextrose, lævulose, etc., on treatment

with *N*/10-sodium hydroxide rapidly lose their optical activity, whereas sucrose under these conditions remains unchanged (Abstr., 1911, ii, 74). He now shows that advantage can be taken of this fact for estimating sucrose in urine. One hundred c.c. of urine are treated with 2.5 c.c. of 4*N*-sodium hydroxide solution for twenty-four hours at 37°. In the presence of dextrose alone, the rotation sinks to an average value of about  $-0.3^{\circ}$  V, whatever the initial value. There is a possible source of error in certain urines which contain a large amount of ammonium salts, in that the addition of alkali hydroxide sets free ammonia, which acts only very weakly on the sugars. This error may be obviated by diluting the urines before addition of the sodium hydroxide, so that the latter is always in excess. S. B. S.

**Estimation of Cellulose in Woods and Textile Fibres.** JOSEF KÖNIG and FR. HÜHN (*Zeitsch. Farb.-Ind.*, 1911, 10, 297—300, 326—330, 344—348, 366—370; 1912, 11, 4—9, 17—29, 37—46, 57—64, 77—81, 102—109).—A comprehensive study of various cellulose-containing materials, with a bibliography of, and discussion on, the work of others. The different materials examined included the bark and wood of beech, oak, and fir trees, together with cotton, flax, hemp, and jute fibres, and the results of drying these under different conditions before examination are described.

The occurrence, distribution, or preparation of cellulose, ligno-cellulose, pectocellulose, mucocellulose, adipocellulose, cutocellulose, hemicellulose, pectin, hemilignin, cutin, hydrocellulose, oxycellulose, hexosanes, and pentosanes are discussed with methods of identification or estimation.

The results obtained are compared with those of other workers and demonstrated in curves and tabular form. F. M. G. M.

**Estimation of Lactic Acid in Wine by the Methods of Möslinger and Kunz.** THEODOR ROETGEN (*Zeitsch. Nahr. Genussm.*, 1912, 24, 113—124. Compare Abstr., 1901, ii, 700; 1902, ii, 180).—A critical examination of these two methods yielded results which show that both processes are trustworthy. Möslinger's method may be slightly improved by taking care that the volatile acids are removed completely from the wine, and it is recommended that 5 c.c. of 10% barium chloride solution be added to the distillation residue. In the case of Kunz's method, barium hydroxide solution should be used in place of solid barium hydroxide for neutralising the wine previous to the evaporation, and the extraction with ether should be carried out in a Parthiel's apparatus for twenty-four hours. This method is more tedious than that described by Möslinger. W. P. S.

**Modification of the Processes for the Estimation of Succinic and Malic Acids in Wines.** KARL VON DER HEIDE and ERW. SCHWENK (*Zeitsch. anal. Chem.*, 1912, 51, 628—638).—The original process (Abstr., 1909, ii, 444—445) has been much improved. Instead of neutralising the crude succinic acid with alkali before resorting to the silver titration, it is rendered alkaline with barium hydroxide,

the excess of which is then removed by a current of carbon dioxide and subsequent warming.

Malic and succinic acid may be estimated jointly by first removing the tartaric acid, and then treating the filtrate as follows: after diluting to 100 c.c., 50 c.c. are evaporated almost to dryness after adding 5 c.c. of 10% barium chloride. After neutralising the residue with barium hydroxide and removing the excess by carbon dioxide, the whole is evaporated to dryness and then dissolved in 15 c.c. of water, when 85 c.c. of 96 vol. % alcohol are added. The precipitate is collected and washed with about 100 c.c. of 80 vol. % alcohol; it is then returned to the basin by a jet of hot water, and the whole is again evaporated to dryness. The residue is then moistened with a few c.c. of 40% sulphuric acid, and, after trituration, 1 or 1.5 c.c. of sulphuric acid is added drop by drop while continuing using the pestle. In order to obtain a dry mass, 20—30 grams of anhydrous sodium sulphate are added in small portions, and, after remaining in a desiccator overnight, the mass is powdered and extracted with ether in a Soxhlet tube. The malic and succinic acids are recovered from the ethereal solution by distillation, and then converted into neutral barium salts in the manner described. The barium salts are converted by ignition into carbonate, which is titrated in the usual manner with standard acid and alkali.

The tartaric acid is removed (and estimated) as follows: 100 c.c. of the wine are evaporated to 20 c.c., 3 grams of potassium chloride are added, also 0.5 c.c. of glacial acetic acid, 0.5 c.c. of 20% potassium acetate, and 6 c.c. of 96 vol. % alcohol. The potassium hydrogen tartrate is collected on a Gooch crucible containing filter-paper fibre, and washed with 20 c.c. of a mixture composed of 15 grams of potassium chloride, 20 c.c. of alcohol and 100 c.c. of water, and may then be titrated as usual with standard alkali. L. DE K.

**General Method for the Estimation of Tartaric Acid.** ANDRÉ KLING and D. FLORENTIN (*Bull. Soc. chim.*, 1912, [iv], 11, 886—895).—The process is a generalised form of that already described (Abstr., 1911, ii, 666). It has been found that the precipitation of calcium racemate may be made complete, even in presence of considerable amounts of iron, aluminium, antimony or copper, by effecting it in presence of ammonium citrate. Where large quantities of the interfering elements are present, they must be eliminated first, the aluminium as ammonia alum, and the other metals as sulphides. A detailed description of the method of carrying out the estimation in its new form is given. T. A. H.

**The Detection of Benzoic Acid in Foods.** O. BIERNATH (*Chem. Zentr.*, 1912, i, 1928—1929; from *Veröff. Geb. Militär-sanitäts-wessens*, 1912, 59—71).—The ferric chloride and hydrogen peroxide test proposed by Jonescu (Abstr., 1909, ii, 627) is very delicate and convenient. Mineral and volatile organic acids and alcohol hinder the reaction. If salicylic acid is also present, it may be destroyed in the distillate from the acidified material by means of alkaline potassium permanganate. C. H. D.

**Detection of Benzoic Acid in Milk.** CECIL REVIS (*Analyst*, 1912, 37, 346).—Not less than 100 c.c. of milk are diluted with an equal volume of water, and, after adding 5 c.c. of 10% sodium carbonate solution, heated in boiling water for two or three minutes; 10 c.c. of 20% calcium chloride are added, and the heating continued until complete coagulation has taken place. When cold the liquid is filtered and the filtrate neutralised with hydrochloric acid, 10 c.c. of copper sulphate solution (34.6 grams per half-litre) are added, followed by 10 c.c. of potassium hydroxide (31.18 grams per litre), and the liquid is again filtered. The filtrate is poured into a separating funnel, acidified with hydrochloric acid, and extracted with 50 c.c. of ether. After washing the ether three times with a little water, 10 c.c. of water are added, also a drop of phenolphthalein solution, and then barium hydroxide solution until, after shaking, the watery layer remains pink. After evaporating this to about 5 c.c., the liquid is filtered into a test-tube and dilute acetic acid is dropped in until the pink colour is discharged, when another two drops are added. The solution is then tested for benzoic acid with a drop of a 10% neutral ferric chloride solution.

When testing cream, 50 c.c. are diluted to 200 c.c. and treated as just directed. L. DE K.

**Volumetric Estimation of Phenol-*p*-sulphonic Acid.** CARL E. SMITH and HENRY C. FREY (*J. Amer. Chem. Soc.*, 1912, 34, 1040).—A quantity of the sample corresponding with 0.18–0.2 gram of phenol-*p*-sulphonic acid is dissolved in 50 c.c. of water in a stoppered, long-necked, 250 c.c. flask. To this are added 50 c.c. of an aqueous solution containing 2.7833 grams of potassium bromate and about 40 grams of potassium bromide per litre. Five c.c. of hydrochloric acid (D 1.18) are then added, the flask stoppered to prevent loss of bromine, and the mixture allowed to remain at 20–25° for not less than ten and not more than fifteen minutes, during which time a turbidity should not be produced. Dibromophenolsulphonic acid is formed by the action of the free bromine, the excess of which is determined by titration with standard thiosulphate after the addition of potassium iodide. The method is accurate to  $\pm 0.5\%$ . T. S. P.

**Estimation of Hippuric Acid in Urine.** THEODOR HRYNTSCHAK (*Biochem. Zeitsch.*, 1912, 43, 315–322).—The urine is heated with sodium hydroxide to hydrolyse the hippuric acid. It is then oxidised with excess of permanganate, the excess is removed by sodium hydrogen sulphite, and sulphuric acid in excess is added, care being taken to prevent superheating during neutralisation. The liquid is then extracted several times with ether, the ethereal extract is dissolved in dry chloroform, and the chloroform is then evaporated off. From the weight of practically pure benzoic acid thus obtained, the amount of hippuric acid can be calculated.

S. B. S.

**The Naphthenic Acids and their Reaction with Ferrous Salts.** E. PYHÄLÄ (*Chem. Zeit.*, 1912, 36, 869–870).—Salts of

naphthenic acids yield dark brown colorations with ferrous salts. It is shown that this reaction is due to the formation of ferric salts by oxidation, and that it is only given when sodium naphthenate is present, the free acids not giving a coloration. The sodium salt is commonly present in a colloidal form in the technical naphthenic acids.  
C. H. D.

**Estimation of the Fat Content of Milk by the Aid of Trichloroethylene.** D. P. ROSS VAN LENNEP and J. D. RUYS (*Chem. Weekblad*, 1912, 9, 654—657).—The authors give a number of results of extractions of milk fat with trichloroethylene. They recommend it as a fat solvent on account of its non-inflammability and lack of explosive tendency.  
A. J. W.

**Quantitative Estimation of Aliphatic Amino-groups.** DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1912, 12, 275—284. Compare Abstr., 1910, ii, 751; 1911, ii, 779—780).—The author describes various improvements which have been effected in the apparatus devised by him for the determination of aliphatic amino-groups. The chief of these is a device by which the "deaminising" bulb and the Hempel pipette can be shaken mechanically, which greatly increases the rapidity and trustworthiness of the determinations, whilst another advantage of the newer apparatus is that the necessity of disconnecting the "deaminising" vessel from the gas burette between analyses has been abolished. He further recommends the replacement of amyl alcohol, recommended in the original description to prevent the foaming of viscous solutions, by octyl alcohol.  
H. W.

**Gasometric Estimation of Free and Conjugated Amino-acids in the Urine.** PHOEBUS A. LEVENE and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1912, 12, 301—312. Compare Abstr., 1911, ii, 944).—For the determination of total (free and conjugated) amino-acid nitrogen in the urine, the author heats the specimen with sulphuric acid during one and a-half hours at 175°, drives off free ammonia by boiling the solution with lime, and determines the total amino-nitrogen gasometrically (see previous abstract). He finds the total amino-nitrogen in normal urines to be between 1.5% and 2.5% of the total nitrogen, and considers this method of estimation to be more accurate than the Sørensen formol titration.

The determination of free amino-acid nitrogen by this method is complicated by the fact that carbamide slowly evolves nitrogen when heated with nitrous acid. Under the conditions of experiment, however, this nitrogen is found to be fairly regularly evolved, and a correction can be applied. Free ammonia must first be removed. This can be conveniently accomplished, with simultaneous estimation of the ammonia, by mixing the urine with alcohol and milk of lime, and distilling under diminished pressure. After distillation, excess of lime and calcium salts are dissolved by glacial acetic acid. In one portion of the solution, the amino-acid nitrogen is determined, the duration of the reaction being the shortest time in which, at the

prevalent temperature, amino-acids will completely react. Immediately thereafter the determination is repeated under precisely the same conditions, except that the reaction is continued for exactly twice as long. The increase in volume obtained by doubling the reaction time represents the amount of nitrogen evolved from the carbamide during half the time of the second reaction, or the entire duration of the first. It is, therefore, the correction which must be subtracted from the first result in order to leave only the nitrogen obtained from the amino-acids. The free amino-nitrogen never exceeded 1.5% in the limited number of cases in which it was determined.

H. W.

**Application of the Formaldehyde Titration Method to the Estimation of Amino-acids in Plants.** O. BAILLY (*Chem. Zentr.*, 1912, i, 1640; from *Bull. Sci. Pharm.*, 1912, 18, 702—711).—The plant extract is clarified by adding solutions of silicotungstic acid and quinine hydrochloride, and removing the precipitate by centrifugation. The filtrate is shaken with animal charcoal, followed by the addition of barium chloride in alkaline solution to remove phosphates. The filtrate is acidified with *N*/10-hydrochloric acid, and exactly neutralised with *N*/10-potassium hydroxide after addition of *p*-nitrophenol. Neutral formaldehyde solution is then added, and the amino-acids are titrated with potassium hydroxide and phenolphthalein. Another portion of the filtrate is distilled with magnesia, and the ammonia in the filtrate titrated. The proportion of amino-acid may then be calculated. The results are usually accurate within 3% with tyrosine, but with histidine only to 10%. Some estimations are recorded.

C. H. D.

**Extractives of Muscles. XIII. The Precipitability of Certain Nitrogenous Extractives by Phosphotungstic Acid and Mercuric Salts.** S. DEMJANOWSKI (*Zeitsch. physiol. Chem.*, 1912, 80, 212—217. Compare Gulewitsch, *Abstr.*, 1911, i, 815).—Analytical data which, however, are regarded as only approximate, are given in reference to free creatinine, free carnosine, and methylguanidine nitrate in muscle extracts.

W. D. H.

**Separation and Estimation of Pyridine and Ammonia.** ALEXANDER BAYER (*J. Gasbeleuchtung*, 1912, 55, 513—514).—Ferric thiocyanate is found to be a more satisfactory indicator than methyl-orange or ferric chloride in the titration of pyridine in solutions of ammonium salts. The mixed bases are acidified with *N*/10-hydrochloric acid, treated with a drop of ferric chloride and ammonium thiocyanate solution, and titrated with *N*/10-sodium hydroxide until the brownish-red colour is destroyed. A partial separation can be effected by distilling the neutral solution of the mixed salts, when the pyridine passes over accompanied by a very small amount of ammonia; the latter is titrated with hydrochloric acid in the presence of litmus, excess of acid is then added, and the pyridine estimated as above.

F. M. G. M.

**The Methods Employed for the Estimation of Nicotine in Tobacco and Tobacco Extracts.** JULIUS TÓTH (*Chem. Zeit.*, 1912, 36, 937—938. Compare Abstr., 1911, ii, 345, 943).—A reply to Koenig (Abstr., 1911, ii, 1143). The silicotungstate method (Bertrand and Javillier, Abstr., 1909, ii, 450) gives good results, both with tobacco and its extracts, especially when it is necessary to estimate nicotine in presence of ammonia and pyridine bases. C. H. D.

**Detection of Pilocarpine in Presence of Quinine.** G. MEILLERE (*J. Pharm. Chim.*, 1912, [vii], 6, 108—109).—The method depends on the fact that quinine chromate is soluble in chloroform, whilst the pilocarpine salt is insoluble in this solvent, the solubilities in water being reversed.

Potassium dichromate is added to a slightly acid solution containing the two alkaloids. Quinine chromate is precipitated if much of this alkaloid is present. The filtrate is shaken with chloroform until the latter is no longer coloured yellow, and the liquid is then tested for pilocarpine by adding hydrogen peroxide. T. A. H.

**Detection of Yohimbine in Medicinal Tablets.** C. VIRCHOW (*Ber. Deut. Pharm. Ges.*, 1912, 22, 380—383).—Five grams of the powdered material are shaken with 10 c.c. of saturated barium hydroxide solution and 40 c.c. of ether. The ethereal solution is separated and acidified with a few drops of dilute hydrochloric acid; crystals of yohimbine hydrochloride form almost immediately, and, after the lapse of one hour, are separated from the ethereal solution, washed twice with ether, dried at the ordinary temperature, and examined microscopically. The shape of the crystals is characteristic, and somewhat resembles that of uric acid crystals. When dissolved in sulphuric acid, the crystals yield a coloration on the addition of a trace of potassium dichromate; this reaction is not, however, characteristic of yohimbine. W. P. S.

**The Application of Adsorption to the Detection and Separation of Certain Dyes.** A. CHASTON CHAPMAN and ALFRED SIEBOLD (*Analyst*, 1912, 37, 339—345).—Ten c.c. of coal-tar dye solution (1 gram per litre) are stirred for several minutes with 5 grams of kaolin previously mixed with 10 c.c. of water, and the mixture is filtered through a Büchner funnel with the aid of a pump. In this manner it was found that the various dyes could be divided into three classes: (a) those which are entirely adsorbed; (b) those which are partly adsorbed, and (c) those that are not appreciably adsorbed.

In many cases alcoholic solutions may be used, but they are not affected by kaolin to the same extent. For instance, safranin, which is completely removed from water, is only partly adsorbed from a solution in 90% alcohol. In some cases, however, although a dye is very soluble in alcohol, it cannot be extracted from kaolin by that solvent. The dried kaolin containing the adsorbed dyes can then be tested by the application of reagents similar to those employed for the detection of dyes on wood or other fibres.

For details the three tables in the original paper should be referred to.  
L. DE K.

**A Delicate Method for Determining Minute Quantities of Chlorophyll.** C. A. JACOBSON (*J. Amer. Chem. Soc.*, 1912, 34, 1266—1269).—The ultra-violet absorption spectra for a series of standard solutions representing 0.0004 to 0.000005 gram of chlorophyllan per c.c. have been photographed. Since in these dilutions the yellow colouring matters do not interfere with the chlorophyllan bands (compare Jacobson and Marchlewski, *Abstr.*, 1912, i, 285), the amount of chlorophyll in a leaf the green weight of which is only 0.2 gram can be determined by comparing the intensity of the bands with these standards.  
J. C. W.

**Comparison of the Forensic Value of Hæmin and Hæmochromogen Crystals.** HEINE (*Chem. Zentr.*, 1912, i, 2079—2080; from *Vjschr. ger. Med. öffentl. Sanitätswesen*, 1912, 53, 268—281).—The hæmochromogen test is best carried out by using a reagent composed of two parts of pure pyridine and three parts of concentrated aqueous hydrazine sulphate. The test gives positive results much more readily than the hæmin test in the case of old and putrid blood. Iron rust prevents the formation of crystals, but not of dissolved hæmochromogen, which is readily detected by means of the microspectroscope. It has been proposed to distinguish hæmin crystals from indigo by reduction with hydrazine hydrate, but this becomes unnecessary if the hæmochromogen test is used.  
C. H. D.

**Coagulation of Albumin by Heat and its Precipitation by Potassium Mercuric Iodide. Consequences in Connexion with its Gravimetric and Volumetric Estimation.** LUCIEN VALLERY (*Compt. rend.*, 1912, 155, 417—420).—The incomplete precipitation of albumin from organic liquids heated in presence of acids (this vol., ii, 212) is now shown to be due to partial hydrolysis of the albumin by the acid when this is dissociated in aqueous solution. In presence of an undissociable acid, such as *n*-hexoic acid, heat induces complete coagulation.

In estimating serum- or egg-albumin by Tautet's reagent, a definite quantity of mercury is adsorbed by the precipitate in accordance with the following equation:  $1/x \log H/H - h = K$ , where  $x$  is the quantity of albumin,  $H$  the initial amount of mercury,  $h$  the quantity of mercury adsorbed, and  $K$  a constant. When  $H = 0.2$  gram and the mixture is diluted to 200 c.c. after precipitation,  $K = 0.54$  for serum-albumin and 0.52 for egg albumin. The adsorption is affected by the presence of phosphates, but not by sodium chloride or carbamide.  
T. A. H.

**Phosphotungstic-Phosphomolybdic Compounds as Colour-Reagents.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1912, 12, 239—244).—Two new reagents are described: the first, termed the *uric acid reagent*, does not react with monohydric phenols or their derivatives, such as tyrosine; the second, the *phenol reagent*, is far more delicate than any colour reagent for phenol groups. The first is pre-

pared by adding 100 grams of sodium tungstate and 80 c.c. of 85% phosphoric acid ( $H_3PO_4$ ) to 750 grams of water. These are boiled together for two hours, cooled, and diluted to 1 litre. Two c.c. gives the maximum colour with 1 mg. of uric acid. The second is prepared by boiling 750 grams of water with 100 grams of sodium tungstate, 20 grams of phosphomolybdic acid, and 50 c.c. of 85% phosphoric acid for two hours, cooling, and diluting to 1 litre. Two c.c. of this gives the maximum colour with 1 mg. of tyrosine or uric acid. The reagents used must be free from nitrates.

W. D. H.

**Tyrosine in Proteins Estimated by a New Colorimetric Method.** OTTO FOLIN and W. DENIS (*J. Biol. Chem.*, 1912, 12, 245—252).—The reaction referred to in the preceding abstract may be used colorimetrically for the estimation of tyrosine in proteins. The percentages so determined are given in tabular form, and are in every case greater than those reported in the literature, which, however, vary a good deal. The reasons for this are discussed, and the general conclusion reached is that the colorimetric method is the only one which approaches accuracy.

W. D. H.

**Estimation of Caffeine [in Coffee].** G. COSTES (*Anal. Chim. anal.*, 1912, 17, 246—249).—The process is devised more in particular for those brands of coffee which have been deprived to a large extent of caffeine. Twenty (or more) grams of the sample are gradually moistened with 15 to 20 c.c. of sulphuric acid, and then heated on the boiling water-bath for ten to fifteen minutes. The mass is then exhausted thrice in succession with 200, 150, and 100 c.c. of boiling water, boiling for ten and fifteen minutes respectively in the first two extractions; the flask in which the filtrates are collected contains sodium hydroxide, but not sufficient to completely neutralise the acid. After rendering alkaline with sodium carbonate, the liquid is rapidly concentrated to 250 c.c. When cold, the solution is, if necessary, filtered through a quick filter.

The caffeine is now removed by three successive extractions with chloroform (200, 150, 100 c.c.). If the acid had not been neutralised, a much larger volume of the solvent would have been required. The chloroform is then recovered by distillation, and when about 4 c.c. are left, this is transferred to a glass spouted capsule and the flask is rinsed twice with 2 c.c. of chloroform. In order to remove foreign matters, 2 c.c. of sulphuric acid are added, and the capsule heated for ten minutes on the water-bath. The residue is then dissolved in a little water, and the filtrate, after being made alkaline with ammonia, is extracted thrice with chloroform, using 25, 20, and 10 c.c. respectively.

The chloroform on evaporation yields the caffeine. In delicate analyses this should be tested as to its purity by the Kjeldahl process; it generally has a 93% caffeine content.

L. DE K.

## General and Physical Chemistry.

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**Optical Properties of Substances at the Critical Point.**  
CLARENCE SMITH (*Proc. Roy. Soc.*, 1912, *A*, 87, 366—371).—According to Traube's measurements, the magnitude  $b$  of van der Waals' equation and the molecular refractivity are connected by the equation  $b = 4.03(n^2 - 1)M/(n^2 + 2)d$ . Assuming that the specific refractivity is constant for all temperatures up to the critical point, then after dividing both sides by the value of the molecular weight  $M$ , the equation may be written  $b = 4.03(n_c^2 - 1)/(n_c^2 + 2)d_c$ , where  $n_c$  is the critical refractive index and  $d_c$  the critical density. Since  $1/d_c = 3b$ , this equation leads to  $n_c = \text{constant} = 1.126$ . According to this, all substances have the same refractive index at the critical point.

This deduction has been tested by reference to the experimental data for a number of gases and vapours, for inorganic liquids and condensed gases, and for organic liquids, the value of  $n_c$  being obtained by substitution of the values of  $n$ ,  $d$ , and  $d_c$  in the equation  $(n_c^2 - 1)/(n_c^2 + 2) = (n^2 - 1)d_c/(n^2 + 2)d$ . In the majority of cases, the percentage difference between the value so obtained and the theoretical value (1.126) is well within 1%, whilst the largest divergence is only 2.2%. There are, however, a number of substances which appear to be exceptions. These are either aromatic substances or halogen compounds, and their anomalous refraction at the critical point cannot as yet be explained.  
H. M. D.

**Spectro-chemistry of Unsaturated Organic Compounds.**  
**Influence of Alkyl Groups in Conjugated Systems.** KARL VON AUWERS (*Ber.*, 1912, 45, 2764—2781. Compare *Abstr.*, 1911, ii, 781).—It is known that the exaltation of refraction and dispersion, characteristic of conjugated systems, is reduced by the introduction of alkyl groups, and the present investigation was made to determine the influence of structure, weight, and position of the substituent groups on this optical exaltation. In general, the effect of an ethyl group is a little greater than that of a methyl group when the position is the same, but the introduction of still heavier groups causes no further marked change in refraction or dispersion, although in some cases the introduction of branched alkyls causes a further fall. The introduction of alkyl groups at two different points causes a slight fall in refractive index and a considerable fall in dispersion, so that in certain cases doubly substituted compounds can be distinguished from singly substituted substances by this means. These conclusions are drawn from the results of a study of compounds of the types  $C_6H_5 \cdot CR : O$ ,  $C_6H_5 \cdot CH : CH \cdot CR : O$ , and  $C_6H_5 \cdot CH : CR' \cdot CR : O$ .

Comparison of the effects of substitution in such systems as  $C : C \cdot CH : O$  and  $C : CH \cdot C : O$  exhibiting the same initial exaltation, shows that the change in exaltation due to the substitution of either hydrogen atom by an alkyl group is the same, and that, in general, no

specific change occurs, unless the conjugated system is altered. These rules only hold for "active" conjugated systems; in the case of "neutral" systems, alkylation may even cause an increase in exaltation, thus in styrene the introduction of methyl in the  $\beta$ -position causes no change, in the  $\alpha$ -position a fall ensues, and in the para-position an increase in exaltation occurs. This special influence of para-substitution is not confined to styrene, and in general  $E\Sigma_a$  and  $E\Sigma_p$  is about +3 for such substitution. The effect in increasing dispersion is less regular. Tables illustrating all these phenomena are given in the original.

The following new data are recorded :

Phenyl ethyl ketone, b. p. 124°/41 mm.;  $D_4^{16.3}$  1.0131,  $D_4^{15.9}$  1.0134,  $D_4^{20}$  1.010;  $n_a$  1.52375,  $n_D$  1.52900,  $n_B$  1.54223,  $n_\gamma$  1.55403 at 15.9°. The semicarbazone has m. p. 176°. Phenyl isopropyl ketone, b. p. 125.5°/32 mm.;  $D_4^{16.9}$  0.9863,  $D_4^{16.6}$  0.9865,  $D_4^{20}$  0.984;  $n_a$  1.51445,  $n_D$  1.51919,  $n_B$  1.53172,  $n_\gamma$  1.54286 at 16.6°. Phenyl isobutyl ketone, b. p. 137—138°/38 mm.;  $D_4^{16.4}$  0.9701,  $D_4^{15.3}$  0.9710,  $D_4^{20}$  0.967;  $n_a$  1.50917,  $n_D$  1.51385,  $n_B$  1.52574,  $n_\gamma$  1.53611 at 15.3°. The semicarbazone has m. p. 208—209°. Phenyl *tert*-butyl ketone, b. p. 110—111°/18 mm.;  $D_4^{15.9}$  0.9681,  $D_4^{19.2}$  0.9678,  $D_4^{20}$  0.967;  $n_a$  1.50427,  $n_D$  1.50857,  $n_B$  1.51971,  $n_\gamma$  1.52964 at 19.2°. This ketone was purified through the oxime, m. p. 165—166°. Phenyl undecyl ketone, m. p. 46°, b. p. 222—223°/21 mm.;  $D_4^{22.2}$  0.8969;  $n_a$  1.48149,  $n_D$  1.48503,  $n_B$  1.49425 at 52.4°.

Styryl methyl ketone,  $D_4^{45.2}$  1.0097;  $n_a$  1.57466,  $n_D$  1.58359,  $n_B$  1.60999 at 45.9°. Styryl ethyl ketone,  $D_4^{43.9}$  0.9926,  $D_4^{50.3}$  0.9875;  $n_a$  1.55991,  $n_D$  1.56838,  $n_B$  1.59237 at 50.3°. Styryl propyl ketone, b. p. 158—159°/14 mm.;  $D_4^{23.5}$  0.9915,  $D_4^{20}$  0.994;  $n_a$  1.55998,  $n_D$  1.56797,  $n_B$  1.59062,  $n_\gamma$  1.61337 at 23.95°. Styryl isopropyl ketone, b. p. 153°/14 mm.;  $D_4^{24.5}$  0.9859,  $D_4^{20}$  0.990;  $n_a$  1.55870,  $n_D$  1.56693,  $n_B$  1.59000,  $n_\gamma$  1.61338 at 24.6°. Styryl *n*-butyl ketone,  $D_4^{46.2}$  0.9584,  $D_4^{20}$  0.979;  $n_a$  1.54416,  $n_D$  1.55181,  $n_B$  1.57293 at 44.7°. Styryl *tert*-butyl ketone,  $D_4^{46.2}$  0.9509,  $D_4^{20}$  0.972;  $n_a$  1.53954,  $n_D$  1.54732,  $n_B$  1.56847 at 45.7°.  $\alpha$ -Methylstyryl methyl ketone, b. p. 142.5—144°/17—19 mm.;  $D_4^{18.4}$  1.0274;  $n_a$  1.57426,  $n_D$  1.58234,  $n_B$  1.60453 at 18.1°.  $\alpha$ -Ethylstyryl methyl ketone, b. p. 136—138°/12 mm.;  $D_4^{21.75}$  1.0005;  $n_a$  1.55786,  $n_D$  1.56503,  $n_B$  1.58503 at 21.6°.  $\alpha$ -Methylstyryl ethyl ketone, b. p. 144—147°/13 mm.;  $D_4^{20.5}$  1.0058;  $n_a$  1.55812,  $n_D$  1.56539,  $n_B$  1.58520 at 20.2°.  $\alpha$ -Propylstyryl methyl ketone, CHPh:CPra·COMe, b. p. 144.5—145°/12 mm.;  $D_4^{19.3}$  0.9833;  $n_a$  1.54981,  $n_D$  1.56672,  $n_B$  1.57573,  $n_\gamma$  1.59411 at 19.2°, obtained by condensing methyl butyl ketone with benzaldehyde by means of hydrogen chloride, is a colourless oil, and gives a semicarbazone, m. p. 157°.  $\alpha$ -Ethylstyryl propyl ketone, CHPh:CEt·COPra, b. p. 157—158°/13 mm.;  $D_4^{23.9}$  0.9718,  $D_4^{20}$  0.975,  $n_a$  1.54116,  $n_D$  1.54761,  $n_B$  1.56514,  $n_\gamma$  1.58203 at 23.9°.

$\alpha$ -Methylcinnamaldehyde, b. p. 156—157°/33 mm.;  $D_4^{16.3}$  1.0397,  $D_4^{20}$  1.037;  $n_a$  1.59596,  $n_D$  1.60575,  $n_B$  1.63313 at 16.7°.

*p*-Methylstyrene, b. p. 77—79°/33 mm.;  $D_4^{16.2}$  0.9011;  $n_a$  1.53820,  $n_D$  1.54474,  $n_B$  1.56208,  $n_\gamma$  1.57797 at 16.3°. *ap*-Dimethylstyrene, b. p. 101.5°/29 mm.;  $D_4^{18.5}$  0.9024;  $n_a$  1.52870,  $n_D$  1.53447,  $n$  1.54944,

$n_\gamma$  1.56306 at  $18.7^\circ$ , was obtained by treating *p*-methylacetophenone with magnesium methyl iodide.

*p*-Tolualdehyde, b. p.  $203.6-204.6^\circ$ ;  $D_4^{128}$  1.0261,  $D_4^{20}$  1.020;  $n_a$  1.54372,  $n_D$  1.55027,  $n_\beta$  1.56761,  $n_\gamma$  1.58369 at  $11.9^\circ$ .

*p*-Methylacetophenone, b. p.  $112.5^\circ/11$  mm.;  $D_4^{178}$  1.0058,  $D_4^{20}$  1.004;  $n_a$  1.52976,  $n_D$  1.53533,  $n$  1.55018,  $n_\gamma$  1.56369 at  $17.4^\circ$ . 3:4-Dimethylacetophenone, b. p.  $250.6-251.2^\circ$ ;  $D_4^{144}$  1.0090,  $D_4^{20}$  1.005;  $n_a$  1.53563,  $n_D$  1.54218,  $n_\beta$  1.55603,  $n_\gamma$  1.56944 at  $15.0^\circ$ . 2:4:5-Trimethylacetophenone, b. p.  $247-248^\circ$ ,  $D_4^{147}$  1.0039,  $D_4^{20}$  1.000;  $n_a$  1.53572,  $n_D$  1.54111,  $n_\beta$  1.55525,  $n_\gamma$  1.56815 at  $14.9^\circ$ .

Ethyl *p*-toluate, b. p.  $122^\circ/22$  mm.,  $D_4^{182}$  1.0269,  $D_4^{20}$  1.0255;  $n_a$  1.50418,  $n_D$  1.50888,  $n_\beta$  1.52106,  $n_\gamma$  1.53183 at  $18.2^\circ$ . Ethyl *p*-cinnamate, b. p.  $158-159^\circ/17$  mm.;  $D_4^{164}$  1.0336,  $D_4^{20}$  1.031;  $n_a$  1.55503,  $n_D$  1.56302,  $n_\beta$  1.58531,  $n_\gamma$  1.60748 at  $15.9^\circ$ .

T. A. H.

**Spectro-chemistry of Chloro-compounds.** KARL VON AUWERS (*Ber.*, 1912, 45, 2781—2808. Compare preceding abstract).—From an investigation of the refraction and dispersion of a large number of chloro-compounds, the conclusion is drawn that in compounds belonging to such systems as  $\cdot\text{C}:\text{C}:\text{C}:\text{C}:\text{Cl}$  or  $\text{CO}:\text{C}:\text{C}:\text{Cl}$ , the latent valencies of the chlorine atoms exert little or no influence on the spectrochemical properties, and the group  $\text{C}:\text{C}:\text{Cl}$  is spectrochemically "indifferent."

The optical exaltation shown by some chloro-derivatives of benzene homologues is not due to the chlorine, but usually to the effect of several side-chains. The optical exaltation shown by acid chlorides is probably not due, as Eisenlohr supposed (this vol., ii, 2), to the influence of conjugation between the carbonyl group and the latent valencies of the chlorine atom, but to the loose state of combination of the chlorine to carbon already united to oxygen. In a conjugated system the entry of chlorine has about the same effect as that of an alkyl group. The following new experimental data are given.

$\beta$ -Chlorostyrene, b. p.  $79.5^\circ/11$  mm.;  $D_4^{179}$  1.1095;  $n_a$  1.57039,  $n_D$  1.57736,  $n_\beta$  1.59582,  $n_\gamma$  1.61279 at  $17.8^\circ$ . The substituted  $\beta$ -chlorostyrenes examined have been described already (*Abstr.*, 1907, i, 400, 401). Hydratropaldehyde, b. p.  $112-114^\circ/33$  mm.;  $D_4^{181}$  1.0025;  $n_a$  1.51310,  $n_D$  1.51762,  $n_\beta$  1.52894,  $n_\gamma$  1.53878 at  $17.9^\circ$ .

$\alpha$ -Chlorostyrene, b. p.  $83.5-84^\circ/23$  mm.;  $D_4^{1755}$  1.1016;  $n_a$  1.55617,  $n_D$  1.56226,  $n_\beta$  1.57845,  $n_\gamma$  1.59311 at  $16.55^\circ$ .  $\alpha$ -Chloro- $\beta$ -methylstyrene, b. p.  $90.5^\circ/9$  mm.;  $D_4^{148}$  1.089,  $D_4^{20}$  1.085;  $n_a$  1.55753,  $n_D$  1.56352,  $n_\beta$  1.57913,  $n_\gamma$  1.59334 at  $14.55^\circ$ .  $\alpha$ -Chloro- $\beta$ -ethylstyrene, b. p.  $102-102.5^\circ/9$  mm.;  $D_4^{148}$  1.0604,  $D_4^{20}$  1.056;  $n_a$  1.54709,  $n_D$  1.55277,  $n_\beta$  1.56765,  $n_\gamma$  1.58112 at  $14.85^\circ$ . Other compounds used in this investigation are described already (*Abstr.*, 1911, i, 298).

$\beta$ -Bromostyrene. Data are given for four different preparations, all of which gave slightly different results.

Ethyl crotonate, b. p.  $48-50^\circ/21$  mm.;  $D_4^{15}$  0.9223,  $D_4^{20}$  0.918;  $n_a$  1.42378,  $n_D$  1.42675,  $n_\beta$  1.43448,  $n_\gamma$  1.44113 at  $15^\circ$ . Methyl  $\alpha$ -chlorocrotonate, b. p.  $161.5-161.7^\circ/762$  mm.;  $D_4^{237}$  1.157;  $n_a$  1.45357,

$n_D$  1.45689,  $n_B$  1.46516,  $n_\gamma$  1.47243 at  $23.1^\circ$ . Ethyl  $\alpha$ -chlorocrotonate, b. p.  $72^\circ/14$  mm.;  $D_4^{20.3}$  1.1084;  $n_a$  1.44985,  $n_D$  1.45303,  $n_B$  1.46099,  $n_\gamma$  1.46778 at  $20.1^\circ$ .

Methyl  $\beta$ -chlorocrotonate, b. p.  $64-67^\circ/14$  mm.;  $D_4^{22.3}$  1.1555;  $n_a$  1.45905,  $n_D$  1.46275,  $n_B$  1.47166,  $n_\gamma$  1.47959 at  $21.4^\circ$ . Ethyl  $\beta$ -chlorocrotonate, b. p.  $76-77^\circ/14$  mm.;  $D_4^{19.9}$  1.1062;  $n_a$  1.45550,  $n_D$  1.45888,  $n_B$  1.46754,  $n_\gamma$  1.47498 at  $19.6^\circ$ .

$\beta$ -Chloroisocrotonic acid,  $D_4^{63.2}$  1.1969;  $n_a$  1.46625,  $n_D$  1.47039,  $n_B$  1.48156,  $n_\gamma$  1.49094 at  $66^\circ$ . Methyl ester, b. p.  $42-43^\circ/13$  mm.;  $D_4^{18.8}$  1.1362;  $n_a$  1.45355,  $n_D$  1.45733,  $n_B$  1.46650,  $n_\gamma$  1.47472 at  $18.9^\circ$ . Ethyl ester, b. p.  $56-57^\circ/13$  mm.;  $D_4^{17.4}$  1.0898;  $n_a$  1.45119,  $n_D$  1.45467,  $n_B$  1.46951,  $n_\gamma$  1.47137 at  $17.7^\circ$ .  
T. A. H.

**Anomalous Dispersion in Sodium Vapour.** D. ROSCHDESTWENSKY (*Ann. Physik*, 1912, [iv], 39, 307-345).—The dispersion produced by sodium vapour has been examined in the immediate neighbourhood of the lines  $D_1$  and  $D_2$ . The experimental data indicate that Sellmeier's formula for the dispersion in the spectral region where no absorption occurs is also applicable to the immediate neighbourhood of the absorption lines with an accuracy of  $\pm 2.5\%$ . There appear to be, however, certain systematic deviations from the formula, which cannot be accounted for by errors of observation.

The ratio of the constants  $a_1/a_2$  in the dispersion formula  $n-1 = a_1\lambda^2/(\lambda^2-\lambda_1^2) + a_2\lambda^2/(\lambda^2-\lambda_2^2)$ , is found to remain unaltered when the density of the sodium vapour is altered in the ratio of 1:50.

H. M. D.

**Wave-lengths from the Arc Spectrum of Iron in the International System.** F. GOOS (*Zeitsch. wiss. Photochem.*, 1911, 11, 305-316. Compare this vol., ii, 404).—Accurate measurements have been made of the wave-lengths of iron lines between  $\lambda = 5328$  and  $\lambda = 6495$  from observations in the grating spectrum of the fifth order. In the yellowish-red portion of the spectrum, where the number of suitable iron lines is rather limited, supplementary measurements were made for nickel lines.

The data obtained are compared with the international normal wave-lengths and with Kayser's results. Although the agreement is, in general, quite satisfactory, there are a number of lines in this region for which the divergences are appreciably greater than can be attributed to errors of observation. The explanation of these differences appears to be that the structure of many iron lines depends on the length of the arc which is employed as the source of light. Since this is the case, it would appear to be necessary to define more exactly the nature of the source of light before the requisite accuracy of a few thousandths of an Ångström unit is obtainable over the entire range of the visible spectrum.  
H. M. D.

**Series Lines in the Arc Spectrum of Mercury.** JOHN C. McLENNAN (*Proc. Roy. Soc.*, 1912, A, 87, 256-268).—Of various means employed to obtain the mercury spectrum, the best results were found to be given by a Cooper-Hewitt glass lamp provided with a side-

tube closed by a thin plate of crystalline quartz. The spectrum thus produced extends from  $\lambda = 7000$  to  $\lambda = 2150$ .

The following members, indicated by the order number  $m$  of Ritz's formula, have been identified in the triplet series—in the first and second groups of the principal series up to  $m = 18$  and 10 respectively, in the first, second, and third groups of the first subordinate series to  $m = 20$ , 17, and 16 respectively, and in the first, second, and third groups of the second subordinate series to  $m = 20.5$ , 17.5, and 14.5 respectively.

The members identified in the single line series are—principal series up to  $m = 9$ , first subordinate series to  $m = 16$ , and second subordinate series to  $m = 12.5$ .

Examples are also given of combination series formed from elements supplied by the triplet and single series formulæ. H. M. D.

**Constitution of the Mercury Green Line  $\lambda = 5461$  and the Magnetic Resolution of its Satellites by an Echelon Grating.** JOHN C. McLENNAN (*Proc. Roy. Soc.*, 1912, A, 87, 269—276).—By means of a thirty-plate echelon, the line  $\lambda = 5461$  has been resolved into a main line, which is probably a doublet, together with three satellites of greater and three of smaller wave-lengths. The structure of the green line, observed when the mercury arc is first formed, undergoes a change when the lamp becomes heated. This change, also noticed by other observers, is attributed to a reversal of the main line in consequence of absorption and to a widening and intensification of the satellites arising from an increase in the temperature and pressure of the mercury vapour.

The satellites  $-0.243$  and  $+0.090$  have both been resolved by a magnetic field into four components. H. M. D.

**Structure of the Mercury Line  $\lambda = 5461$ .** L. JANICKI (*Ann. Physik*, 1912, [iv], 39, 439—443).—The green mercury line emitted by an Arons-Lummer lamp has been examined for different intensities of the electric current. At 4.5 amperes, the appearance presented was that of an incompletely separated double line; at 3.5 amperes, indications of a more complex structure were obtained, and by lowering the current to 2.5 amperes, the "principal" line was found to consist of five distinct lines. Apart from this resolution, the components of the composite green line observed by the author are in agreement with von Baeyer's results (*Ber. Deut. Physikal. Ges.*, 1907, 9, 84). From this it appears that the line  $\lambda = 5461$  consists of twelve real components.

Under similar conditions, the mercury lines  $\lambda = 5791$ , 5770, 4078, and 4047 did not exhibit any indication of structure differing from that which has been found by previous observers. H. M. D.

**Magnetic Resolution of the Spectrum Lines of Niobium.** ROBERT JACK (*Proc. Roy. Irish Acad.*, 1912, A, 30, 42—90).—A detailed investigation has been made of the influence of a magnetic field on the lines in the spectrum of niobium. The results show that there are two lines which have ten components, three with eight,

five with six, nine with five, eighty-nine with four, and six hundred and three lines with three components. The application of Ritz's formula to the multi-component lines appears to be very satisfactory in many cases, but in others the agreement is not very close, and it is necessary to assume that many components have not been recorded on account of lack of intensity. In regard to its general applicability, Runge's formula would appear to be preferable to that of Ritz.

H. M. D.

**Resonance Spectra of Iodine by Multiplex Excitation.**  
ROBERT W. WOOD (*Phil. Mag.*, 1912, [vi], 24, 673—693. Compare Abstr., 1911, ii, 82, 169, 950).—The absorption spectrum of iodine has been examined with the aid of a spectrograph of very high resolving power, with the result that the visible region is found to contain a vast number of lines, which is estimated at more than 50,000. A comparison of the photographs obtained for a part of the spectrum ( $0.8\mu$  in width) with the corresponding portion of Hasselberg's spectral map, indicates that the lines in the map can only be regarded as showing roughly the position of a small number of the groups of lines which actually occur. The sodium and bromine absorption spectra are equally complex, and it would appear that a large number of lines in the bromine and iodine spectra are coincident. This may be due to the occurrence of identical systems of electrons in the two elements, giving rise to the same series of frequencies.

The resonance spectra of iodine which are produced by excitation with the green and the two yellow lines of mercury have been further examined. The spectrum excited by the green line consists of a series of twenty-five doublets, which are characterised by a constant difference between the frequencies of the two components. The frequency differences between the first members of the successive doublets show a slight increase as the frequency itself increases. No regularity is found, on the other hand, when the frequencies of the doublets excited by each of the yellow mercury lines are examined.

Since the spectral region occupied by the green mercury line contains seven sharp and clearly resolved iodine absorption lines, whilst the spaces occupied by the two yellow mercury lines contain fourteen and twelve absorption lines respectively, it is evident that excitation by such lines is multiplex in character, the breadth of the lines being such as to excite a number of adjacent frequencies. To this is to be attributed the fact that the resonance spectrum of iodine is quite different when excited by the green line of the Cooper-Hewitt mercury lamp (commercial glass lamp) from that obtained when the same line yielded by the mercury arc in quartz (high temperature arc) is used as the exciting agent. In other words, the resonance spectrum is considerably modified when such changes occur in the structure of the exciting line.

The question as to which lines in the resonance spectrum are associated with the several lines in the absorption group, which are called into action by the multiplex excitation represented by the mercury lines, is under examination. A comparison of the spectra obtained with mercury lamps operated under different conditions and

those obtained by the interposition of suitable filters, such as bromine vapour, has shown that valuable results may be expected from the further application of these methods of modifying and resolving the exciting rays.

H. M. D.

**Absorption of Light by Solutions of Benzene and Some of its Derivatives at Low Temperature.** JOSEPH DE KOWALSKI and E. BANASINSKI (*Arch. Sci. phys. nat.*, 1912, [iv], 34, 216—233).—An examination has been made of the absorption of light by ethyl-alcoholic solutions of aromatic hydrocarbons in the region  $\lambda = 210$  to  $\lambda = 800$ , and at temperatures ranging from  $-190^\circ$  to  $15^\circ$ . In the case of benzene, the photographic records show the existence of fifteen bands which may be classified in three groups. The principal group consists of six bands which are equally well defined over the entire range of temperature. The second group consists of two bands, only one of which is seen easily at room temperature, whilst the second band only is observed at  $-190^\circ$ . The third group of seven bands is found at  $-190^\circ$ , but traces only are visible at  $15^\circ$ .

The frequencies of the heads of the bands in the principal group are connected by the linear relation  $1/\lambda = 3852 + 91n$ , where  $n$  represents an integer. At  $-190^\circ$ , the bands are displaced towards the red end of the spectrum as compared with the corresponding vapour bands. The displacement measured in terms of the frequency difference is the same for all bands of the group. In regard to the third group of bands, it has been found that these are characteristic of alcohol solutions, for observations made with pentane solutions show no trace of this group.

The bands given by toluene are more sharply defined at  $-190^\circ$  than at the ordinary temperature, and two groups may be distinguished, each of which is characterised by an approximately constant difference between the frequencies of the successive members. At the low temperature the bands are slightly displaced towards the ultra-violet end.

The absorption spectra of the three isomeric xylenes have also been observed, and these are described with reference to the tabulated wave-length measurements.

H. M. D.

**A Spectro-polariscopic Method for the Investigation of the Absorption of Light and of the Nature of Dyes.** NICOLAI A. UMOFF (*Physikal. Zeitsch.*, 1912, 13, 962—971).—The method described depends on the relationship which exists between the absorption and the polarisation of the scattered light rays. For those regions of the spectrum where considerable absorption occurs, the polarisation of the scattered light has the highest values. This effect is due to the partial depolarisation of the rays which are scattered at the surface by rays which have penetrated below the surface layer and emerge again at the surface.

In applying the polarisation method to the determination of the absorption bands, use is made of a Savart's polariscope. The nature of the pattern, which is observed on looking through the polariscope at the surface of a coloured substance illuminated by the light falling on its surface through a collimator tube, varies in a marked manner with

the extent to which the scattered rays are polarised, and the pattern thus affords a means of locating the position of the absorption bands. The manner in which the spectro-polariscopic method is actually applied can be varied to some extent according to the nature of the coloured substance to be examined. A large number of absorption spectra have been thus obtained, and the results are recorded in diagrammatic form. H. M. D.

**Fluorescence in the Terephthalic Acid Series.** HUGO KAUFFMANN and LEOPOLD WEISSEL (*Annalen*, 1912, 393, 1—29).—See this vol., i, 863.

**Specific Rotation of Certain Optically Active Esters of Triphenylacetic Acid.** LEO A TSCHUGAEFF and S. GLININ (*Ber.*, 1912, 45, 2759—2764).—The menthyl esters of colourless, optically inactive acids are generally levorotatory and possess normal dispersion coefficients. *Menthyl triphenylacetate*, m. p. 100—101°, obtained by heating triphenylacetyl chloride with menthol at 125—130° or by the action of sodium menthoxide upon triphenylacetyl chloride in toluene solution, exhibits an abnormal behaviour. Optical investigation gave the following results: in toluene solution ( $c = 26.17$ ),  $[\alpha]_D^{20} - 3.04^\circ$ ,  $[\alpha]_D^{20} - 3.44^\circ$ ,  $[\alpha]_E^{20} - 3.67^\circ$ ,  $[\alpha]_F^{20} - 3.63^\circ$ ;  $[\alpha]_F/[\alpha]_C$  1.20 (compare Abstr., 1911, ii, 450); in carbon disulphide solution ( $c = 25.36$ ),  $[\alpha]_D^{20} + 9.51^\circ$ ,  $[\alpha]_D^{20} + 13.25^\circ$ ,  $[\alpha]_E^{20} + 18.82^\circ$ ,  $[\alpha]_F^{20} + 24.86^\circ$ ;  $[\alpha]_F/[\alpha]_C$  2.61; in the same solvent ( $c = 19.22$ ),  $[\alpha]_C^{20} + 9.94^\circ$ ,  $[\alpha]_D^{20} + 13.79^\circ$ ,  $[\alpha]_E^{20} + 19.65^\circ$ ,  $[\alpha]_F^{20} + 25.97^\circ$ ;  $[\alpha]_F/[\alpha]_C$  2.61; in chloroform solution,  $[\alpha]_C^{20} - 3.81^\circ$ ,  $[\alpha]_D^{20} - 4.39^\circ$ ,  $[\alpha]_E^{20} - 4.88^\circ$ ,  $[\alpha]_F^{20} - 5.18^\circ$ ;  $[\alpha]_F/[\alpha]_C$  1.36; in acetone solution ( $c = 12.89$ ),  $[\alpha]_C^{20} - 1.58^\circ$ ,  $[\alpha]_D^{20} - 1.58^\circ$ ,  $[\alpha]_E^{20} - 1.28^\circ$ ,  $[\alpha]_F^{20} - 0.70^\circ$ ;  $[\alpha]_F/[\alpha]_C$  0.44°.

*l-Bornyl triphenylacetate*, on the other hand, behaves normally. It has m. p. 104—105°,  $[\alpha]_C^{20} - 15.11^\circ$ ,  $[\alpha]_D^{20} - 19.15^\circ$ ,  $[\alpha]_E^{20} - 24.37^\circ$ ,  $[\alpha]_F^{20} - 29.52^\circ$ ;  $[\alpha]_F/[\alpha]_C$  1.95° in toluene solution ( $c = 17.07$ ) and  $[\alpha]_C^{20} - 18.78^\circ$ ,  $[\alpha]_D^{20} - 23.95^\circ$ ,  $[\alpha]_E^{20} - 30.55^\circ$ ,  $[\alpha]_F^{20} - 37.02^\circ$ ,  $[\alpha]_F/[\alpha]_C$  1.97 in carbon tetrachloride solution ( $c = 15.84$ ).

*Fenchyl triphenylacetate*, m. p. 80—81°, has  $[\alpha]_C^{20} - 13.55^\circ$ ,  $[\alpha]_D^{20} - 17.30^\circ$ ,  $[\alpha]_E^{20} - 22.45^\circ$ ,  $[\alpha]_F^{20} - 27.82^\circ$ ,  $[\alpha]_F/[\alpha]_C$  2.05 in toluene solution ( $c = 13.24$ ). *Amyl triphenylacetate* also exhibits a normal behaviour.

The slight optical activity of the menthyl ester is probably connected with the selective absorption in the ultra-violet and with the superposition of the partial rotations in the molecule (compare Abstr. 1911, ii, 787). H. W.

### Examination of the Purity of Optically Active Compounds.

II. ERNST DEUSSEN (*J. pr. Chem.*, 1912, [ii], 86, 425—429).—The author gives further examples of his method of examining the purity of optically active compounds by the determination of their rotatory dispersion (compare this vol., ii, 510). F. B.

**Glycerol as Sensitiser.** CHARLES W. BENNETT (*J. Physical Chem.*, 1912, 16, 614—615).—When glycerol is exposed to a bright light in

presence of air, an aldehyde is formed. Methylene-blue, safranin, and Biebrich-scarlet are bleached in the dark by acetaldehyde or by a solution of glycerol which has been exposed to light. The sensitising action of glycerol on the above dyes, discovered by Hübl (*Phot. Mittheil.*, 1909), is explained by the formation of aldehyde. The sensitising action ascribed to arsenates in presence of glycerol is held to be actually due to formation of arsenite, but no experiments were made on this point.

R. J. C.

**The Photochemical Oxidation of Benzene.** WILDER D. BANCROFT (*J. Physical Chem.*, 1912, 16, 556—563).—Hydrogen peroxide is known to be formed by the action of bright sunlight or the silent discharge on water and air. Ozone is also produced by wave-lengths less than  $300\mu\mu$ , but is decomposed by wave-lengths greater than  $300\mu\mu$ .

At Manila the minimum wave-length in sunlight was found to be about  $291\mu\mu$ , a value in agreement with results obtained at Assuan, Berlin, Monte Rosa, and elsewhere. The proportion having wave-length less than 300 is small, however. Hence at the surface of the earth bright sunlight tends to destroy ozone and diminishes the yield of ozone from the oxidation of moist phosphorus, but increases the yield of hydrogen peroxide.

When benzene is oxidised by ozone, the chief product is oxalic acid, whereas with hydrogen peroxide phenol is also produced. These facts explain the observations of Leeds (1881) on the oxidation of benzene by moist phosphorus. In diffused daylight oxalic acid only was produced, but in direct sunlight a considerable proportion of phenol was formed.

The paper contains no new experimental matter.

R. J. C.

**The Changes Produced by Light on Certain Pharmaceutical Products.** CARL NEUBERG and OMER SCHEWKET (*Biochem. Zeitsch.*, 1912, 44, 495—501).—The preparations *ferrum saccharatum* and *ferrum mangani saccharatum* on exposure to light undergo a change which is indicated by a diminution of the rotatory power of the solution produced by the precipitation of the preparation with dialysed iron and an electrolyte. *Ferrum kalium tartaricum* on exposure yields a substance capable of reducing Fehling's solution even after a six hours' exposure. The same phenomenon was observed in the case of *ferrum malicum*, *ferrum glycerophosphoricum* (in this case phosphoric acid is set free after prolonged exposure), and *ferrum ammonium citrate*. In the case of *ferrum lacticum*, aldehyde is set free, and can be isolated in the form of the *p*-nitrophenylhydrazone.

S. B. S.

**Photographic Registration of  $\alpha$ -Particles.** HANS GEIGER and ERNEST RUTHERFORD (*Phil. Mag.*, 1912, [vi], 24, 618—623).—With the old apparatus, in which the entrance of an  $\alpha$ -particle into the ionisation chamber is recorded by a sudden jerk of the electrometer needle, it was not possible to count more than 10  $\alpha$ -particles a minute, as the ordinary electrometer only responds slowly. By means of a

string electrometer, designed by Laby (and made by the Cambridge Scientific Instrument Co), under suitable conditions 1000  $\alpha$ -particles a minute have been recorded. To ensure the rapid return of the electrometer needle to zero, a comparatively low resistance, made of a capillary tube filled with xylene and alcohol, is employed, which cuts out slow secondary electrical disturbances and enables only the rapid large effects due to the  $\alpha$ -particles to be registered. To avoid scattering, instead of a cylindrical ionisation vessel, with mica-covered opening, a hemispherical metal vessel with central spherical electrode was employed. The  $\alpha$ -particles entered through a mica window at the pole of the hemisphere, their paths in the vessel and the throws of the needle being sensibly constant. The vessel was filled with helium, purified by charcoal in liquid air, at one-third atmospheric pressure, this gas having many advantages over air. The path in the helium was 3 cm., corresponding in stopping power, at 20 cm. pressure, with a layer of air only 2 mm. thick, and even at 5 mm. pressure the entrance of  $\alpha$ -particles was easily detectable. Eye observations are useless above about 50 throws of the fibre per minute, but by a photographic method of registration 1000 throws a minute can be recorded. Edelman's registration apparatus, in which the speed of the moving film, on which the light from the electrometer mirror was received, could be varied over a wide range, was employed. The films reproduced are remarkably clear, and the simultaneous entrance of two and even three  $\alpha$ -particles into the apparatus can readily be distinguished by the magnitude of the throws.

The recoil-atoms have a range of about 0.1 mm. of air at atmospheric pressure, and it seems likely that the apparatus is sufficiently sensitive to detect a single recoil atom. Experiments are in progress, but the results are difficult to interpret, owing to the necessity of doing away with the mica window.

F. S.

**The Ranges of the  $\alpha$ -Particles from the Thorium and Actinium Products.** HANS GEIGER and J. M. NUTTALL (*Phil. Mag.*, 1912, [vi], 24, 647—654).—A redetermination of the ranges of the  $\alpha$ -rays of actinium and thorium by the method used with uranium (this vol., ii, 408) shows that in these series the rule of the authors, that when the logarithms of the ranges are plotted against the logarithms of the transformation constants the points lie on a straight line, also holds good. The slopes of the three lines in the three series uranium, thorium, and actinium are similar, but the lines do not coincide. The range of the  $\alpha$ -rays of thorium itself as determined is somewhat longer than the rule indicates, but the deviation is within the experimental error, which is the largest in this case owing to the difficulty of determination. The only other exception is radio-actinium, which should have a period, judged from the range of its  $\alpha$ -rays, less than, instead of greater than, that of actinium-*X*. The indicated period of average life of ionium is about 200,000 years, of radium-*C*,  $10^{-6}$  second, and of thorium-*C*,  $10^{-11}$  second.

The collected results are given in the table. The range for thorium-*X* has not previously been determined.

*Ranges of  $\alpha$ -Particles.*

Substance.	Ranges in cm. at		Initial velocity $\times 10^9$ cm./sec.
	0°.	15°.	
Uranium I .....	2.37	2.50	1.47
Uranium II .....	2.75	2.90	1.54
Ionium .....	2.85	3.00	1.56
Radium .....	3.13	3.30	1.61
Radium emanation .....	3.94	4.16	1.74
Radium- <i>A</i> .....	4.50	4.75	1.82
Radium- <i>C</i> .....	6.57	5.94	2.06
Radium- <i>F</i> (Polonium) ...	3.58	3.77	1.68
Thorium .....	2.58	2.72	1.51
Radiothorium .....	3.67	3.87	1.70
Thorium- <i>X</i> .....	4.08	4.30	1.75
Thorium emanation.....	4.74	5.00	1.85
Thorium- <i>A</i> .....	5.40	5.70	1.93
Thorium- <i>C</i> <sub>1</sub> .....	4.55	4.80	1.82
Thorium- <i>C</i> <sub>2</sub> .....	8.16	8.60	2.21
Radioactinium .....	4.36	4.60	1.80
Actinium- <i>X</i> .....	4.17	4.40	1.77
Actinium emanation .....	5.40	5.70	1.93
Actinium- <i>A</i> .....	6.16	6.50	2.02
Actinium- <i>C</i> .....	5.12	5.40	1.89

F. S.

**The Period of Radio-thorium and the Number of  $\alpha$ -Particles given by Thorium and its Products.** MAY S. LESLIE (*Le Radium*, 1912, 9, 276—277).—A repetition of the previous measurements (Abstr., 1911, ii, 1048) with a different mineral, thorite, indicates that the usually accepted value of the half-period of radio-thorium, namely, about two years, is probably correct, the previous results being ascribed to contamination. The ratio between the activities of thorium and its various products are in accord with the view of other observers that six  $\alpha$ -particles are given by the series in equilibrium.

F. S.

**The Absorption and Reflexion of Homogeneous  $\beta$ -Particles.** W. WILSON (*Proc. Roy. Soc.*, 1912, A, 87, 310—325).—A homogeneous beam of  $\beta$ -rays produced by magnetic sorting of the  $\beta$ -rays from radium-*B* and -*C*, when caused to traverse thin sheets of aluminium, copper, and tin, is not absorbed according to an exponential law. On the contrary there is for the quickest rays examined a slight but perceptible increase in ionisation for the first 0.04 cm. of aluminium traversed, and after 0.05 cm. the ionisation produced is 95% of the initial value, whereas for the original rays more than 50% would have been absorbed by this thickness. The explanation advanced is that initially none of the  $\beta$ -particles are stopped, but their average velocity is diminished, with increased ionising power in consequence, but that after a certain thickness has been traversed actual stoppage of the  $\beta$ -particles occurs, the beam becomes heterogeneous, and a final steady state is reached in which the distribution of velocity among the particles does not further alter with the amount of matter penetrated. If the homogeneous  $\beta$ -rays are first passed through platinum, absorption

in aluminium now occurs according to an exponential law, and this is shown to be due, not merely to a scattering of the  $\beta$ -rays, but to an alteration in respect of homogeneity, whereby the velocities of the particles are distributed in such a way as to be not further altered by subsequent passage through the aluminium.

The reflexion of homogeneous  $\beta$ -rays by aluminium gave results that indicate that it is the slower rays which suffer reflexion. The evidence is in favour of the view that there is no real production of secondary  $\beta$ -rays during absorption, apart from the scattering of the primary rays. For rays of high velocity the number of  $\beta$ -rays emerging from both sides of a thin aluminium sheet is approximately equal to the number which strike it.

F. S.

**The Number of  $\beta$ -Particles Emitted in the Transformation of Radium.** H. G. J. MOSELEY (*Proc. Roy. Soc.*, 1912, A, 87, 230—255).—The number of  $\beta$ -particles evolved per atom disintegrating is of importance on account of the great complexity of the  $\beta$ -rays and the view of Rutherford that the radiation is initially homogeneous and is modified by passage through the disintegrating atom itself. The number was determined by measuring the charge transported from the active deposit of radium under conditions in which the numbers of atoms of radium-*B* and -*C* disintegrating in unit time could be deduced. The sources of  $\beta$ -rays were either radium emanation in thin glass tubes covered with just sufficient paper to stop the  $\alpha$ -particles, or a deposit initially of radium-*B*, obtained by recoil from radium-*A*, on the inner surface of India paper tubes. The numbers of  $\beta$ -particles escaping were determined for different thicknesses of paper and extrapolated to zero thickness. The general result was to indicate that each atom of radium-*B* and of radium-*C* emits one  $\beta$ -particle, although the measurements gave 1.10, whilst each atom of radium-*E* appeared to emit less than one  $\beta$ -particle. In the latter case there is considerable uncertainty, due to the period of radium-*D* and other causes.

Measurements of the ionisation produced by the  $\beta$ -particles, coupled with the data obtained for their absorption, after passage through various thicknesses of materials, gave as the result that the number of ions per cm. of path varied from 82 to 160, when  $\mu$  (cm.<sup>-1</sup> of aluminium) varied from 15 to 100. This enables the data of Geiger and Kovarik (*Abstr.*, 1911, ii, 954) to be recalculated, with the result that uranium-*X*, thorium-*D*, and actinium-*D* are estimated to give respectively 1, 0.8, and 1.4  $\beta$ -particles per atom disintegrating.

From the number of secondary  $\beta$ -particles emitted under the action of  $\gamma$ -rays, it seems likely that 2  $\gamma$ -rays are emitted per atom of radium-*C* disintegrating. A new secondary radiation from surfaces penetrated by  $\beta$ -rays has been observed. It resembles the  $\delta$ -rays produced by  $\alpha$ -rays in similar circumstances, and cannot leave the surface unless assisted by an electric field, the velocity of the rays corresponding with a difference of potential of only about 2 volts.

F. S.

**The Origin of  $\beta$ - and  $\gamma$ -Rays from Radioactive Substances.** ERNEST RUTHERFORD (*Phil. Mag.*, 1912, [vi], 24, 453—462).—In spite

of the great complexity of the  $\beta$ -rays it seems clear that each atom on disintegrating emits on the average about one  $\beta$ -particle. The hypothesis is developed that the disintegration of the atom producing the  $\beta$ -ray takes place in exactly the same way, but that the energy of the  $\beta$ -ray is decreased by definite but different amounts in passage through the atom in which it originates, and that this loss of energy is connected with the origin of the  $\gamma$ -rays which accompany in most cases the expulsion of the  $\beta$ -rays. By extrapolation of Barkla's results on characteristic secondary  $X$ -rays produced by primary  $X$ -rays in different elements, it can be calculated that an element of atomic weight 214 (that of radium- $C$ ) should give a characteristic  $X$ -radiation closely according in penetrating power with the  $\gamma$ -rays observed.

The results of Danyasz on the thirty groups of homogeneous  $\beta$ -rays given by radium- $B$  and - $C$  together (Abstr., 1911, ii, 840; 1912, ii, 113) are shown to be connected by a simple relation. The differences of energy between the successive beams of  $\beta$ -rays are expressed by  $pE_1 + qE_2$ , where  $p$  and  $q$  are integers, and  $E_1$  and  $E_2$  represent different quantities of energy. The relation holds best for the rays known to be due to radium- $C$ , for which  $E_1$  and  $E_2$  have the values 0.456 and 1.556 ( $\times 10^{13}e$ ), and  $p$  and  $q$  have values between 0 and 4. A similar relation obtains for the rays of radium- $B$ , but the agreement is less perfect. If the  $\beta$ -ray before escaping from the atom passes through two regions where the energy required to excite a  $\gamma$ -ray is  $E_1$  and  $E_2$  respectively, the energy of the emergent  $\beta$ -ray is  $E_0 - (pE_1 + qE_2)$ , where  $E_0$  is the initial energy, and  $p$  and  $q$  are the number of  $\gamma$ -rays excited in each region. According to this view the transformation of an atom gives rise to only one  $\beta$ -ray, but to  $p$   $\gamma$ -rays of one kind and  $q$   $\gamma$ -rays of another kind.

These results are connected with the author's hypothesis of atomic structure, in which the positive charge is concentrated at the centre, and is surrounded by rings of electrons, rotating in a plane (Abstr., 1911, ii, 453). Instability of the central nucleus leads to expulsion of an  $\alpha$ -particle, whilst instability of the electronic distribution leads to expulsion of a  $\beta$ -particle, which in traversing each ring of electrons external to it may or may not lose part of its energy in exciting one or more  $\gamma$ -rays of definite energy.

F. S.

**The  $\gamma$ -Rays Excited by the  $\beta$ -Rays of Radium.** J. CHADWICK (*Phil. Mag.*, 1912, [vi], 24, 594—600).—In order to settle definitely whether the  $\beta$ -rays of radium- $C$  can excite  $\gamma$ -rays in the same way as the  $\beta$ -rays of radium- $E$  can, and the magnitude of the  $\gamma$ -rays if so excited, a method was employed which magnified the ratio of the effect produced by the excited radiation to that produced by the primary  $\gamma$ -rays. A converging magnetic field concentrated about one-half of the total  $\beta$ -radiation, from a tube containing radium emanation, on to a plate of given material. Rays from this plate could enter an ionisation vessel unimpeded, whereas the effect in the vessel of the primary  $\gamma$ -rays from the emanation tube were reduced to 5% by suitable lead screens. The balance method (Rutherford and Chadwick) of measuring the ionisation was employed, an auxiliary source of radiation being moved to obtain a balance. In

this way secondary  $\gamma$ -radiation generated by the  $\beta$ -rays was put in evidence. It decreased in amount with the atomic weight of the material bombarded by  $\beta$ -rays, and when that given by a plate containing 87% of metallic uranium is termed 100, lead, tin, zinc, and aluminium had the relative values, 92, 82, 79, and 75. The value of the absorption coefficient,  $\mu_1(\text{cm.})^{-1}$ , for a lead plate 1.3 cm. thick varied for these materials from 1.2 to 1.8, and of  $\mu_2$ , when a further iron plate of the same thickness was added, from 0.8 to 1.0. Under identical conditions the values of  $\mu_1$  and  $\mu_2$  for the primary  $\gamma$ -rays were 0.340 and 0.314. The secondary  $\gamma$ -rays are on the whole much softer than the primary, but some small proportion may attain to an equal degree of penetrating power, for it is evident that they are heterogeneous. The secondary  $\gamma$ -rays produce only 0.16% of the effect produced by the primary rays, whereas in the case of radium-*E* the greater part probably of the  $\gamma$ -radiation is secondary. Apparently  $\alpha$ -rays can also generate secondary  $\gamma$ -rays, but details are reserved.

F. S.

**The Initial Velocity of the  $\delta$ -Rays.** FR. HAUSER (*Physikal. Zeitsch.*, 1912, 13, 936—940).—The hypothesis of N. Campbell (this vol., ii, 221, 411) as to the initial velocity of  $\delta$ -rays is criticised, and the following conclusions are arrived at. With surfaces of carbon and soot, and with rough surfaces in general, an electric field is necessary to remove the secondary rays emitted by the electrode, and a very strong field to remove them entirely, but with polished surfaces, whether a polonium-coated plate or a metal bombarded by  $\alpha$ -rays, the greater part, if not all, of the secondary radiation escapes from the surface without the action of a field. The velocity distribution appears to obey Maxwell's law for gas molecules, and the maximum velocity cannot be determined because of the small number of rays of maximum velocity. With a polonium plate, some have a velocity corresponding with 33 to 43 volts, and with secondary radiation from 15 to 20 volts, whilst in the latter case the average is from 4 to 10 volts, the most frequent being 6 volts.

F. S.

**$\delta$ -Rays.** FR. HAUSER (*Physikal. Zeitsch.*, 1912, 13, 979—984, Compare Abstr., 1911, ii, 685).—Polemical against Campbell (Abstr., 1911, ii, 959).—Certain points, relating to the author's previous work, are described in greater detail.

H. M. D.

**The Emission of Electrons by Metals under the Influence of  $\alpha$ -Rays.** HENRY A. BUMSTED and A. G. MCGOUGAN (*Phil. Mag.*, 1912, [vi], 24, 462—483; *Amer. J. Sci.*, [iv], 34, 309—328).—The curves obtained by plotting the number of  $\delta$ -rays emitted from a metal plate struck by  $\alpha$ -rays against the range of the  $\alpha$ -rays, which have the same general character as the ionisation-range curves, have exactly the same form for aluminium, copper, gold, lead, and platinum. This is unexpected, as different gases give ionisation-range curves markedly different in form, and supports the view that the whole of the  $\delta$ -rays may have their origin in surface layers of adsorbed gas. An experiment, in which a platinum strip was heated to redness in a high vacuum, did not, however, reduce the  $\delta$ -rays much further than when

the foil was not heated, but merely kept for some hours or days in the exhausted vessel, which treatment reduced the  $\delta$ -rays by about 30%, but did not affect the form of the  $\delta$ -ray-range curves.

It was noticed that when there is no absorbing foil between the  $\alpha$ -rays and the plate struck, the  $\delta$ -radiation from the plate is more than twice as great as when one aluminium foil, of thickness  $0.64 \times 10^{-1}$  cm., intervenes. The air equivalent of this foil is only 0.58 cm., and it appears that polonium, and also the thorium active deposit, emit a new radiation, completely absorbed by  $0.64 \times 10^{-4}$  cm. of aluminium, and causing the emission of electrons from the metals it strikes. Part of it is primary and unaffected by a magnetic field, and may be due to recoil atoms (Wertenstein, this vol., ii, 222). The other is secondary and consists of electrons of far greater velocity than that ascribed to  $\delta$ -rays, and ranging from less than  $3.8 \times 10^8$  to more than  $24.4 \times 10^8$  cm. per. sec. These secondary rays are emitted by any object on which  $\alpha$ -rays are incident and a part at least, if not the whole, of the  $\delta$ -rays, and possibly also of the ionisation produced by  $\alpha$ -rays in gases, is to be ascribed to them.

F. S.

**Further Experiments on  $\delta$ -Rays.** NORMAN CAMPBELL (*Phil. Mag.*, 1912, [vi], 24, 527—540. Compare Abstr., 1911, ii, 841; 1912, ii, 221, 411).—The relation between the current carried by  $\delta$ -rays from metals struck by  $\alpha$ -rays and the potential difference between the electrodes is independent of temperature, and is determined, when the distance between the electrodes is altered, rather by the  $PD$ , between the electrodes than by the electric held in the space between them. Hence the  $\delta$ -rays must originate with a finite velocity, which is not due, as previously suggested, to secondary causes. New experiments confirm adequately the view that the speed of the  $\delta$ -ray is independent of the nature of the metal in which it originates, and of the velocity of the exciting  $\alpha$ -ray, and are against the view that all materials appear to behave in the same way because of a layer of condensed gas on the surface. The velocity of the  $\delta$  rays is very heterogeneous. Most have speeds below that corresponding with 3 volts, but for some the speed is as high as 10 to 20 volts. In a note the announcement is made that  $X$ -rays liberate  $\delta$ -rays precisely similar to those liberated by  $\alpha$ -rays. [Many of the effects described in the paper appear to be connected with the existence of the new radiation referred to in the preceding abstract.]

F. S.

**Nature of the Chemical Action Produced by  $\alpha$ -Particles and the Probable Rôle Played by Ions.** S. C. LIND (*J. Physical Chem.*, 1912, 16, 564—613. Compare this vol., ii, 513).—The number of molecules of oxygen transformed into ozone by the  $\alpha$ -rays from a quantity of radium emanation sealed up in a glass bulb was found to be of the same order as the number of ions produced in the gas by the  $\alpha$ -rays. In order to make a similar comparison by means of existing data in other cases in which the emanation has been directly mixed with the reacting gases, the author has developed a method of calculating the average path of the  $\alpha$ -particles in small spherical and cylindrical containers. The average path  $p = 0.427 \sqrt[3]{V}$ , where  $V$  is the volume of the container. When the length of the average path is

known, the number of ions produced per second per Curie of emanation can be calculated from Bragg's specific ionisation constants for the various gases.

According to the author's view, the ratio of the number of ions,  $N$ , to the number of molecules undergoing change,  $M$ , should be unity. The value of  $M$  was calculated from the volume change on the basis of  $2.69 \times 10^{19}$  molecules per c.c. Actually, the values of the ratio  $N/M$  obtained from the experiments of Cameron and Ramsay, Usher, Lind, and others are as follows: synthesis of water 0.68 to 2.07, of ammonia 4.25, of hydrogen bromide 2.0, and of ozone 5.1; decomposition of carbon monoxide 0.58, of carbon dioxide 2.86, of hydrogen chloride 1.42, and of ammonia 2.74 to 4.28. These figures are held to justify the view that the primary agents of reaction are the ions. The action of  $\alpha$ -particles is certainly not a catalytic one, since it is of the same order whether the chemical action be endothermic or exothermic.

When radium emanation induces chemical action in a liquid system it may be assumed that the emanation is distributed between gaseous and liquid phases according to Henry's law, and that all  $\alpha$ -particles liberated within the liquid or received from the gas phase are completely absorbed. There is no evidence as to the number of ions produced in a liquid by an  $\alpha$ -particle. The author therefore assumes that the same number is produced as would be produced if the absorbent were in the gaseous state, ionisation along the entire path of an  $\alpha$ -particle in a gas being independent of the pressure.

In experiments such as those of Usher on the decomposition of water and of Lind on the decomposition of anhydrous hydrogen bromide and aqueous potassium iodide by emanation, the gaseous phase was practically absent, and the calculated amount of ionisation agrees well with the amount of chemical action. In other cases where a gaseous phase was present, the calculation of the ionisation is not so satisfactory.

The rate of change in gaseous systems under the influence of radium emanation is subject to a kinetic law  $\kappa\mu/\lambda = \text{constant}$ , where  $\kappa$  is an ionisation coefficient proportional to  $i^3/V$ ,  $i$  being the specific ionisation of the gas,  $\mu$  is the efficiency factor of the ions, and  $\lambda$  is the velocity constant for the rate of decay of the emanation. In experiments where  $i^3/V$  remained fairly constant, a satisfactory constancy was shown by  $\kappa\mu/\lambda$ .

The author combats Cameron and Ramsay's conclusion that each particle of emanation as it disintegrates produces the same amount of change, and argues that the effect produced by a molecule of emanation depends on the length of the path that its  $\alpha$ -particle happens to take. If the  $\alpha$ -particle goes straight into the glass wall it will produce no effect at all.

The author disregards the possible chemical action of  $\beta$ -rays in his calculations, as the amount of ionisation produced by them is relatively small (compare, however, Usher, this vol., ii, 6). The combination of hydrogen with chlorine, in which the ionic efficiency is abnormally high, may be an exceptional case in which  $\alpha$ - and  $\beta$ -rays act catalytically.

R. J. C.

**Analogies in the Behaviour of Moving Electrons and Atoms towards Stationary Atoms.** CARL RAMSAUER (*Jahrb. Radioaktiv. Elektronik.*, 1912, 9, 515—533).—The variation of the ionising power of  $\alpha$ - and  $\beta$ -rays with the velocity has been examined. It is shown that the curve obtained by Geiger (compare Abstr., 1909, ii, 782; 1910, ii, 473) showing the relationship between the ionising power and the velocity of  $\alpha$ -rays can be deduced quantitatively from the curve which represents the connexion between the corresponding quantities in the case of  $\beta$ -rays. The conclusion to be drawn from this is that the nature of the ionisation process is the same for both kinds of rays, the atoms of the gas being penetrated by both the  $\alpha$ - and  $\beta$ -particles.

If the velocity of the particles is greater than  $10.10^8$  cm. per second, every collision results in the penetration of the atom, whereas particles with velocities smaller than  $2.10^8$  cm. per second cannot act in this way. For this reason, the close analogy between the phenomena of ionisation produced by  $\alpha$ - and  $\beta$ -rays no longer holds when the velocity falls below this lower limit. The maximum effect is produced when the velocity of the particles is sufficiently great for the majority of the particles to penetrate the atoms and yet slow enough to allow the contact between the moving particles and the atoms to extend over a sufficiently long period of time.

The formula given by Thomson (compare this vol., ii, 410) for the ionisation produced by  $\alpha$ -rays is shown to be at variance with experimental facts. From the nature of the discrepancies it is inferred that the  $\alpha$ -particles cannot be regarded as simple positively charged masses, but must be considered as systems of corpuscles. Thomson's formula for the ionisation produced by  $\beta$ -rays is also inconsistent with observations of Lenard and Kossel. Whereas the maximum effect, according to Thomson's theory, is to be expected when the velocity of the particles is equal to  $2.83 \times 10^8$  cm. per second, the actually observed maximum corresponds with a velocity of  $8.4 \times 10^8$  cm. per second. The calculated maximum is, moreover, about thirty times as large as that which has been found experimentally. It is shown, however, that the theory may be brought into line with experiment if it is assumed that a portion of the space occupied by the atom is impenetrable, the size of this impenetrable region depending on the velocity of the  $\beta$ -rays.

H. M. D.

**Multiply-charged Atoms.** SIR JOSEPH J. THOMSON (*Phil. Mag.*, 1912, [vi], 24, 668—672. Compare Abstr., 1911, ii, 457; this vol., ii, 410).—The parabolic bands which are obtained when the positive rays, passing through a discharge tube containing mercury vapour, are subjected to the influence of superposed magnetic and electric fields and then allowed to fall on a photographic plate, have been examined in greater detail. Photographs obtained with large electrostatic deflexions exhibit seven distinct parabolic bands, and measurements of  $m/e$  for each of these indicate that the bands are due to mercury atoms with 1, 2, 3, 4, 5, 6, and 7 charges respectively. In general, the bands get less distinct as the charge on the atom increases.

By measuring the electrostatic displacement of the head of the mercury band in very intense fields, it has been found that this is only one-eighth of the normal displacement. From this, it follows that the atoms which give rise to the head of the band must have eight times the maximum amount of energy possessed by normal positive atoms, and this would indicate that some of the mercury atoms have lost eight corpuscles.

The mode of production of the differently charged mercury atoms is discussed in reference to the photographic records, and evidence is brought forward in support of the view that there are only two kinds of ionisation, in one of which the mercury atom loses one corpuscle, and in the other eight corpuscles. The mercury atoms with two to seven charges are therefore produced by the re-combination of the most highly charged atoms with one or more corpuscles.

The singly charged atoms are supposed to be generated by the action of the cathode rays, whilst the production of the atoms with eight charges is attributed to the collision of the mercury atoms with positive rays.

In no case have charges approaching those acquired by mercury atoms been observed with other elements. The atoms of most of these acquire only two charges, but triply charged atoms have been found in the case of nitrogen and argon.

The production of the helium parabolic band affords a means of detecting the presence of very small quantities of helium in a discharge tube. It is estimated that the helium in 1 c.c. of air can be recognised in this way.

H. M. D.

**Influence of the Nature of the Gas on Pulverisation by Canal Rays.** VOLKMAR KOHLSCHÜTTER (*Zeitsch. Elektrochem.*, 1912, 18, 837—844. Compare this vol., ii, 719).—Cadmium vapour was passed into a glass vessel containing two cylindrical aluminium electrodes between which a luminous electric discharge was passed, and the effect of variations of pressure and of the nature of the gas in the vessel on the distribution of the condensed metallic vapour was observed.

At very low pressures the metal collects most largely in the cathode compartment, and occurs partly as a lustrous coating on the walls, partly on the electrode. As regards the amounts on the two electrodes, the proportion on the cathode increases at first and then diminishes as the pressure is gradually increased. At equal pressures it is greater in hydrogen than in nitrogen, and greater in the latter than in argon. From 0.8 mm. pressure upwards more metal condenses on the anode than on the cathode, but the excess diminishes at equal pressures with increasing density of the gas; thus for a pressure of 1.2 mm., where the excess on the cathode side in hydrogen is 27.8%, the distribution in argon is equal. At  $p = 0.3$  mm. there is an excess of 6.1% on the cathode, but in argon and nitrogen there is finally more metal on the anode than the cathode. The explanation given is that in these circumstances a cathodic pulverisation (conversion into fine powder) of the cadmium takes place, which is more marked in argon than in nitrogen.

The factors concerned in bringing about the above results are discussed in detail. There is a close parallelism between the viscosity of the gases and their effect on the distribution of the metal. G. S.

**Positive Rays.** WILHELM WIEN (*Ann. Physik.*, 1912, [iv], 39, 519—544. Compare Abstr., 1910, ii, 475).—The action of mercury vapour on a beam of oxygen and hydrogen canal rays passing through the vapour has been further examined. The apparatus employed was similar to that described in the previous paper (*loc. cit.*). In the case of the oxygen canal rays, the data show definitely that the ratio of negative to positive ions is increased when the rays are passed through mercury vapour. By extending the lateral dimensions of the magnetic field so as to subject the rays for a longer time to its action, it has been found that the introduction of a layer of mercury vapour has also an appreciable influence on the ratio between the ions and the atoms in the hydrogen canal rays.

A theory of the ionisation phenomena in the canal rays is put forward, and on the basis of this, a method by which the mean free path of the canal rays may be determined has been worked out. Measurements of the mean free path of both the charged and uncharged atoms in the hydrogen and oxygen canal rays have been made.

By comparing the frequency of collision of the positively charged hydrogen atoms with the light energy emitted by a hydrogen atom per centimetre of its path, and assuming that the smallest quantity of energy emitted by an atom is represented by Planck's elementary quantum, it is calculated that only one out of 275 collisions of the positively charged atoms gives rise to the emission of light corresponding with the line  $H_{\beta}$ . H. M. D.

**The Mass and Mobility of the Positive Ions of a Flame.** GEORGES MOREAU (*Le Radium*, 1912, 9, 273—276).—The mass of the positive ion may be determined by the same method as that of the negative if the platinum cathode in the pure flame is covered with lime, the ions diffusing into this flame through a gauze from a neighbouring flame charged with the vapour of an alkali or alkaline-earth salt. The lime renders the distribution of potential in the flame more nearly uniform and permits of a precise measure of the diffusion current. From this the mobility, the velocity of agitation, and the mass of the ion are deduced by means of the law of equipartition of molecular energy. The mean value for the mobility at  $1400^{\circ}$  for the salts of the alkali and alkaline-earth elements is 12 cm./sec. for 1 volt/cm., and its value is nearly independent of the nature of the salt and its concentration. The same is true of the mass of the ion between  $1250^{\circ}$  and  $1400^{\circ}$ , which is  $8 \times 10^{-22}$  gram, and corresponds to an assemblage of from three to ten molecules. From previous measurements the mass is deduced at  $443^{\circ}$ ,  $343^{\circ}$ , and  $288^{\circ}$  to be respectively  $6 \times 10^{-20}$ ,  $4 \times 10^{-19}$ , and  $6 \times 10^{-18}$ . At  $15^{\circ}$  the assemblage would contain 70,000 molecules, whilst at  $1900^{\circ}$  it would be reduced to a single molecule of the salt or atom of the metal. F. S.

**The Supply of Radium Emanation from the Soil to the Atmosphere.** LOUIS B. SMYTH (*Phil. Mag.*, 1912, [vi], 24, 632—637).—In continuation of previous experiments (Abstr., 1911,

ii, 1048) two series of experiments from Aug. 16th, 1911, to March 5th, 1912, on the emanation content of the ground gas from a depth of 50 cm. below the surface and on the escape of emanation from the surface at an adjacent spot, have been carried out on a lawn at Trinity College, Dublin where the soil is calcareous, well drained, and several metres thick. The average amounts of emanation found were : ground gas (102 experiments),  $163 \times 10^{-12}$  curie per litre, and exhaled gas (98 experiments),  $2673 \times 10^{-12}$  curie per sq. metre of surface per hour. No seasonal factor appears to be involved. A strong wind increases the exhalation and decreases the amount of emanation in the ground gas, probably by exerting suction on the soil capillaries. Frost and rain cause an accumulation of emanation beneath the surface. The fluctuation of the barometer does not exert any direct influence on the results, apart from the accompanying effects of storm and rain.

F. S.

**A Comparison of the Coefficients of Diffusion of Thorium and Actinium Emanations with a Note on their Periods of Transformation.** MAY S. LESLIE (*Phil. Mag.*, 1912, [vi], 24, 637—647).—A source of the emanation was placed at the bottom of a long tube, and the distribution of active deposit measured on a metal strip fixed in the axis of the tube. If the active deposit settles at the place where it is produced, the distribution of the active deposit along the tube should be proportional to  $e^{-\sqrt{\lambda/D}x}$ , where  $x$  is the distance from the source,  $D$  the diffusion coefficient of the emanation, and  $\lambda$  the radioactive constant of the emanation. The distribution of the active deposit was, however, not exponential with this disposition, but became so when two parallel metal plates, 2 or 3 mm. apart, with an electric field between them due to a P.D. of 160 volts, were employed. The value of  $D$  for the thorium emanation at  $15^\circ$  varied from 0.085 to 0.115 according to the quantity of emanation employed, the higher value corresponding with the largest amounts of emanation obtained from an active radiothorium preparation. Under conditions as near as possible comparable for the two emanations, the value for that of thorium was 0.111 and of actinium 0.107, indicating that the molecular weights are probably very nearly equal. The real diffusion coefficient of thorium emanation is not greater, and probably less than, 0.085, and of actinium emanation, 0.098. The half-periods of the thorium and actinium emanations, determined by a new method, were found to be 54.3 and 3.92 seconds respectively, as the mean of several not very concordant determinations.

F. S.

**Radioactivity of Terrestrial Surface Materials.** JOHN JOLY (*Phil. Mag.*, 1912, [vi], 24, 694—705).—The fusion method (Abstr., 1911, ii, 685) is more trustworthy than the solution method of estimating the radium content of rocks, and gives results differing from it, rendering revision of older measurements by the new method desirable. Undifferentiated materials have alone been dealt with, the question of magmatic differentiation being reserved. Individual specimens are not examined, but samples composed of a large number of mixed powdered materials. The mean results are expressed in the table (in  $10^{-12}$  gram of radium per gram of rock).

*Igneous Rocks.**Acid.*

63 granites .....	2·7	} Mean, 3·01 for 86 rocks
23 intrusive and volcanic .....	3·9	

*Intermediate.*

12 syenites .....	2·4	} Mean, 2·57 for 48 rocks
8 diorites .....	1·6	
18 trachytes .....	3·0	
10 "porphyries" .....	2·8	

*Basic.*

5 gabbros and norites .....	1·3	} Mean, 1·28 for 31 rocks
8 diabases and dolerites .....	1·0	
14 basalts and melaphyres {chiefly Dec- can and Antarctic}.....	2·0	
11 basalts (chiefly Hebridean) .....	0·5	
18 basalts (generally representative) ...	1·4	

*Additional.*

7 Vesuvian lavas .....	12·6
14 Gneisses (various) .....	2·1

The means of the determinations of other observers by the solution method are: acid (33 rocks) 2·17, intermediate (43 rocks) 1·28; and basic (26 rocks) 0·58. The author provisionally rejects in these means his own solution results, which are inexplicably high compared with those of others, and often are above his own fusion results. Taking  $2 \times 10^{-12}$  as the quantity of radium and  $2 \times 10^{-5}$  as the quantity of thorium in the average rocks of the crust of the earth, the total heat development is  $25 \times 10^{-14}$  calorie per gram per second, and a depth of 17 kilometres (10·6 miles) accounts for all the heat reaching the earth's surface from below. At the base of the 17 kilometre layer the temperature due to radioactive heat would be only  $246^\circ$ , which indicates that the rocks of the same degree of radioactivity as those at the surface do not extend downwards to this depth, but that the radioactive layers are at once deeper and less rich than assumed in the calculation.

The fusion method gives for the mean of fifty-nine secondary rocks a radium content of 1·5, whereas the solution method indicates lower results. The amount of thorium is  $1·16 \times 10^{-5}$  gram per gram, and the total heat development is  $16·6 \times 10^{-14}$  calories per gram per second. There is no doubt that there is a substantial difference in radioactive content between igneous and sedimentary materials. F. S.

**Conductivity of Gases in the "Electrodeless Ring Discharge."** RICHARD WACHSMUTH (*Ann. Physik*, 1912, [iv], 39, 611—624).—Experiments are described which show that the electrical conductivity of a gas, subjected to the action of the electrodeless discharge, varies with the pressure in a definite and characteristic manner. The form of the curve showing the relation between the conductivity and the pressure is the same for oxygen, hydrogen nitrogen, carbon dioxide, and air. As the pressure is reduced below about 2 mm., the conductivity increases slowly to a maximum, then falls to a minimum, and on further reduction of pressure rises very quickly to a second maximum. These changes in conductivity are

accompanied by variations in the character of the luminosity emitted by the contents of the discharge tube. If the pressure is reduced below the point at which the second maximum is observed, the luminosity disappears and the conductivity falls to zero.

In so far as the first portion of the curve corresponding with the higher pressures is concerned, it is shown that the curve is similar to that which is obtained when a gas is ionised by Röntgen rays. In this region of pressure, where there is no luminosity effect, the number of ions produced by the electrode-less discharge is proportional to the pressure of the gas. The behaviour at lower pressures is shown to be due to the ionisation of the mercury vapour in the tube, the second increase in conductivity with falling pressure being due to the fact that the pressure of the mercury vapour remains sensibly constant.

H. M. D.

**Conductivity Measurements on Alloys as a Method of Determining their Constitution.** W. GUERTLER (*Zeitsch. Elektrochem.*, 1912, 18, 601—615. Compare Abstr., 1907, ii, 65, 524; *J. Institute of Metals*, 1911, 6, 150).—The paper is mainly theoretical, and is concerned with the conclusions which may be drawn from measurements of the electrical resistance of alloys and the temperature-coefficient of the conductivity. Some of the results have already been published (*loc. cit.*). Emphasis is laid on the fact that besides the equilibrium of the different phases, as represented by the equilibrium diagram, the equilibria of the molecules inside the single phases is also of importance, and no information on these points is afforded by the equilibrium diagram. Further, any system in which two independent crystalline individuals are present is necessarily unstable. The insufficiency of the thermal analysis method of Tammann is pointed out.

The law of Matthiessen, that the diminution of conductivity in an alloy (expressed as a percentage of the conductivity calculated from the mixture rule) is equal to the diminution of the absolute temperature-coefficient of conductivity is shown to hold for alloys of iron and gold (iron with 1, 3, 5, 10, and 20% of gold), and holds both for homogeneous and heterogeneous systems. There are certain exceptions to the rule, however, and a possible explanation of these exceptions is suggested.

The significance of the breaks in the isotherms in dependence on the concentration and of the breaks on the resistance-temperature curves is discussed, with special reference to the change from a homogeneous to a heterogeneous structure.

G. S.

**The Electrical Conductivity of Metallic Alloys in the Liquid State.** KARL BORNEMANN and G. VON RAUSCHENPLAT (*Metallurgie*, 1912, 9, 473—486, 505—515. Compare Bornemann and Müller, Abstr., 1910, ii, 924).—The method previously described has been extended to temperatures as high as 1500° by the use of magnesia tubes. Carbon electrodes are used, but in cases in which the metal dissolves carbon, copper electrodes cooled internally by water have

been employed. Attempts to avoid electrodes by measuring the induction in a secondary circuit consisting of an annular vessel filled with the molten alloy have proved unsuccessful.

Whether the conductivity of a liquid metal is raised or lowered by the addition of a second metal does not depend on the conductivity of the added metal. The evidence from amalgams and alloys of lead tends to show that the determining factor is the tendency to form compounds. The alkali metals, with a strong tendency to combine, always lower the conductivity, whilst indifferent metals may either raise or lower it.

The liquid alloys of copper and nickel give a conductivity curve which is continuous, with a distinct minimum, whilst copper and antimony show a break at the composition  $\text{Cu}_3\text{Sb}$ . This discontinuity is still more strongly marked in the curve of temperature-coefficients. Some alloys of this series have a temperature-coefficient which is either negative throughout or negative at low and positive at high temperatures. This may be due to thermal dissociation of the compound  $\text{Cu}_3\text{Sb}$ . Similarly, the negative coefficient of fused cuprous sulphide may be due to thermal, and not to electrolytic, dissociation of the sulphide.

C. H. D.

[Dissociation Constants of Sulphuric Acid.] KARL DRUCKER (*Zeitsch. physikal. Chem.*, 1912, 80, 630).—In connexion with the recent paper of Enklaar on this subject (Abstr., 1911, ii, 1071), the author points out that he used *E.M.F.* as well as electrical conductivity measurements in arriving at the value 0.018 for the second dissociation constant of sulphuric acid (compare Abstr., 1911, ii, 687), and, further, the value for the migration velocity of the  $\text{HSO}_4'$  ion given in his latest communication is about half that ascribed to the  $\frac{1}{2}\text{SO}_4''$  ion, and corresponds fairly closely with the value given by Noyes (Abstr., 1910, ii, 937).

G. S.

Conductivity and Dissociation of Certain Organic Acids at 35°, 50°, and 65°. E. P. WIGHTMAN and HARRY C. JONES (*Amer. Chem. J.*, 1912, 48, 320—352).—In earlier papers (White and Jones, Abstr., 1910, ii, 821; Wightman and Jones, Abstr., 1911, ii, 689) an account has been given of the conductivity and dissociation of a large number of organic acids at temperatures between 0° and 35°. A good many of these acids have now been studied at 50° and 65°, and the work done on them at 35° has been repeated.

The results obtained at the higher temperatures confirm the conclusions drawn from the previous investigations. It is shown, however, that the statement that the temperature-coefficients of conductivity increase with dilution is not always true. The irregularities in the percentage temperature-coefficients are probably the result of many varying factors which are closely related to one another. The dissociation of the organic acids decreases in all cases on passing from 50° to a higher temperature. The values of  $\mu_\infty$  for the organic acids, plotted against the number of atoms in the anion, do not give a very even curve. This is probably due to the fact that the sodium salts, from the  $\mu_\infty$  values of which the  $\mu_\infty$  values of the

acids are obtained, are more or less hydrated, and the rising temperature produces varying effects. E. G.

**The Influence of Absorbed Gases on the Electrical Resistance of Metallic Wires.** ADOLF SIEVERTS (*Internat. Zeitsch. Metallographie*, 1912, 3, 36—60).—The resistance of wires of platinum, copper, nickel, and iron is not appreciably affected by the presence of hydrogen under atmospheric pressure up to 920°. Carbon monoxide is also without influence on the resistance of nickel. The resistance of silver is increased by heating in hydrogen, although silver does not absorb hydrogen (Abstr., 1907, ii, 741). A permanent alteration of the metal occurs, as the resistance does not return to its original value after heating in a vacuum or in oxygen. On the other hand, the resistance of palladium is increased proportionally to the concentration of the absorbed hydrogen. The relative alteration is less at high than at low temperatures. The increase of resistance is so great relatively to the concentration of the dissolved hydrogen as to point to the existence of a solid solution. Hydrogen absorbed at the palladium cathode has at low concentrations a greater, and at higher concentrations (20 volumes : 1) a less, influence than molecular hydrogen. The temperature-coefficient of such solid solutions is equal to that of pure palladium. C. H. D.

**Properties of Oil Emulsions. II. Stability and Size of the Particles.** RIDSDALE ELLIS (*Zeitsch. physikal. Chem.*, 1912, 80, 597—616. Compare this vol., ii, 13).—The stability of a pure oil-water emulsion is greatest when the contact potential reaches its maximum, that is, in dilute alkaline solution. The stability is diminished by the addition of acid or alkali in concentrations exceeding 0.001*N* to an extent corresponding with the simultaneous lowering of the contact potential. The stability of the emulsion does not depend on the surface tension at the oil-water boundary.

The diminution of stability of the emulsion with diminishing contact potential is due to a diminution in the strength of the electric double layer. As the latter is in these circumstances more easily ruptured, the particles in an emulsion or suspension colloid can unite more readily.

The concentration of salts of univalent, bivalent, and tervalent metals required to reduce the charge on the particles to zero is in the same ratio as the minimum concentration of the same salts necessary to cause immediate coagulation of a colloidal solution. The stability of a suspension colloid depends almost entirely on the contact potential at the surface of the particles, and scarcely at all on alterations of surface tension; when the contact potential becomes zero, the stability of the system is also zero, and coagulation takes place immediately. G. S.

**A Constant Form of a Galvanic Element with Carbon Anode (Brennstoff Element).** FRANZ FISCHER and RICHARD LEPSIUS (*Ber.*, 1912, 45, 2316—2317. Compare Bechtereff, Abstr., 1911, ii, 1054).—The element consists of fused sodium hydroxide contained in a nickel or iron crucible, the one electrode being a carbon

rod, the other a rod of fused ferrosiferrous oxide as made by the Fabrik Griesheim-Elektron. The voltages, on open circuit, are 0.6, 0.7, and 0.8 volt at 350°, 450°, and 550° respectively. When closed through a resistance of 10 ohms the voltage falls to 0.6 volt at 550°, the current strength being 60 milliamperes and remaining constant for hours. The constancy of the *E.M.F.* thus obtained distinguishes this cell from others. By blowing air on to the iron oxide electrode, its depolarising action is somewhat improved. T. S. P.

**Influence of Colloidal Sulphur on the Electrical Conductivity of Certain Electrolytes.** M. RAFFO and G. ROSSI (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 121—124; *Gazzetta*, 1912, 42, ii, 326—331).—If the sulphur contained in a colloidal solution, prepared by Raffo's method (Abstr., 1908, ii, 683), is precipitated by the action of sunlight, the electrical conductivity of the resulting aqueous solution containing sodium sulphate and sulphuric acid is found to be very much larger than that of the original colloidal solution.

When further quantities of the sulphates are added to the colloidal sulphur solution, the observed increase in conductivity agrees, however, with that calculated on the assumption that the sulphur is without influence on the added electrolytes. These facts seem to show that the sulphates originally present in the colloidal solution are in some way associated with the sulphur. This condition cannot be attained by the subsequent addition of the salts to the colloid.

When other electrolytes, such as lithium chloride, potassium chloride, sodium nitrate, and sodium chloride, all of which tend to coagulate the sulphur, are added to the colloidal solution, the observed increase in conductivity agrees with that calculated on the above assumption.

H. M. D.

**Influence of the Acid Content of the Electrolyte on the Chemical Polarisation of the Reversible Electrode Cu|Cu.** DAVID REICHSTEIN [with A. BÜRGER and A. ZIEREN] (*Zeitsch. Elektrochem.*, 1912, 18, 850—864. Compare Abstr., 1911, ii, 249).—The influence of the acid concentration of the electrolyte on the anodic and cathodic polarisation of the reversible electrode Cu|CuSO<sub>4</sub> has been investigated, and it is shown that in both cases the polarisation diminishes with increasing acid concentration. The same rule holds for the cathodic polarisation of the electrode Cd|CdSO<sub>4</sub>.

The quotient of the current density and the acid concentrations ( $J/c=y$ ) represented in terms of the concentrations ( $c=x$ ) is a hyperbola of the form  $y - a = b/x$ ; the constants  $a$  and  $b$  have been determined by the method of least squares. There is a linear relationship between the current density and the acid concentration of the form  $J=ac+b$ . The magnitude of  $b$  is greater than zero, and a kinetic interpretation of this fact is given. G. S.

**Electrolytic Formation of Dichromate from Chromate.** ERICH MÜLLER and EBERHARD SAUER (*Zeitsch. Elektrochem.*, 1912, 18, 844—847).—In the electrolytic preparation of dichromate from chromate with a diaphragm, sodium hydroxide solution being used as anolyte and sodium chromate as catholyte, the yield in alkali in the

cathode compartment falls behind that of the dichromate in the anode compartment. This result is due to the formation in the diaphragm of a more concentrated alkali solution than in the cathode compartment, and it is shown that this result can be accounted for in terms of the various chemical changes taking place and the different migration velocities of the ions concerned.

G. S.

**Reduction of Potassium Dichromate in Solution by Alternating Currents.** PAUL WENGER and D. MIDHAT (*Ann. Chim. anal.*, 1912, 17, 321–323).—The reduction of potassium dichromate in dilute sulphuric acid solution (2 c.c. of *N*/1 acid per 200 c.c. of solution) by an alternating current of 110 volts and 2.5 amperes is dependent on the time of action when platinum electrodes are employed; with rotating electrodes, 100% of the dichromate is reduced in one hour and forty-five minutes, whilst in the same time only 51.6% is reduced when stationary electrodes are used. The reduction is also a function of the kind of electrode, the following proportions of the quantity of salt present being reduced in one hour by different rotating electrodes: copper, 95.4%; aluminium, 7.3%; lead, 76.4%; nickel, 45.8%; silver, 95.4%; platinum, 66.8%. In the case of aluminium and lead, the reduction proceeded more rapidly with stationary electrodes.

W. P. S.

**Electrolytic Reduction of Difficultly Reducible Organic Substances at Thallium Cathodes.** GEORG ZERBES (*Zeitsch. Elektrochem.*, 1912, 18, 619–632).—The electrolytic reduction of caffeine, pyridine, and succinimide with cathodes of thallium has been investigated. The results correspond closely with the corresponding experiments of Tafel and his co-workers (compare Abstr., 1905, ii, 224; 1906, ii, 216) with lead and mercury cathodes. The super-tension at thallium electrodes is of the same magnitude as at lead, mercury, and cadmium cathodes, and therefore reductions take place readily with thallium electrodes. One peculiarity of the reductions with thallium is that the yield does not reach its maximum at the commencement of electrolysis, and, corresponding with this, the potential at which hydrogen is evolved only gradually reaches the final value.

During the electrolytic reduction of caffeine, the yield of the reduction product falls gradually from its maximum value as observed by Tafel with lead cathodes, a result ascribed to the formation on the cathode of a layer of some of the products resulting from the decomposition of deoxycaffeine. The formation of this layer on the cathode also probably accounts for the rise of potential at a thallium cathode caused by the addition of deoxycaffeine. During the reduction of pyridine the rate of yield remains constant for a long period, and, corresponding with this, the reduction product, piperidine, does not influence the cathode potential.

When a solution of thallium in hydrofluosilicic acid was electrolysed with the object of obtaining thallium in thick plates, thallosilico-fluoride,  $\text{Tl}_2\text{SiF}_6$ , separated in transparent, octahedral crystals, readily soluble in water. From solutions of this salt on electrolysis, the thallium separated in leaflets and not in coherent form.

G. S.

**The Photo-electric Effect.** OWEN W. RICHARDSON and KARL T. COMPTON (*Phil. Mag.*, 1912, [vi], 24, 575—594).—The photo-electric properties of platinum, copper, bismuth, tin, zinc, aluminium, magnesium, and sodium have been investigated by means of an arrangement of apparatus in which the ultra-violet rays were allowed to fall on a small strip of the metal placed at the centre of a bulb of 7.5 cm. diameter, the inner surface of which was silvered. With this arrangement, the applied electric field is approximately radial, and electron reflexion is almost entirely eliminated without the use of a screen and an auxiliary field. At the same time, it enables the distribution of total kinetic energy to be measured, instead of merely the distribution of the velocity component normal to the emitting electrode.

For each metal, measurements were made with light of various wave-lengths, and the electrometer readings, obtained in the application of different electrical fields, were in all cases corrected for the contact difference of potential between the emitting and receiving electrodes.

The data obtained show that the maximum energy of the photo-electrons, expressed in volts, is a linear function of the frequency of the exciting light, and that the average energy, which is equal, within the limits of experimental error, to the most probable energy, also bears a linear relation to the frequency. The velocity distribution curves for the different wave-lengths indicate that this curve will degenerate into a straight line, coincident with the current axis, when the wave-length of the incident light is increased to a certain value. This represents the longest wave-length which will produce any photo-electric effect in the metal under investigation, and the electrons emitted by this light are emitted with zero velocity. This wave-length or the equivalent frequency represents therefore a constant which determines the photo-electric properties of the metal.

The values obtained for the maximum and mean energies of the electrons, and for the limiting wave-lengths of the photo-electrically active light are recorded for each of the metals investigated.

H. M. D.

**Magneto-optical Kerr Effect for Ferro-magnetic Compounds.** P. MARTIN (*Ann. Physik*, 1912, [iv], 39, 625—636).—The author has investigated the magneto-optical properties of alloys of manganese with tin, antimony, and bismuth having the composition corresponding with  $\text{Mn}_3\text{Sn}$ ,  $\text{MnSb}$ , and  $\text{MnBi}$  respectively. The dispersion curves for the region  $\lambda = 4350$  to  $\lambda = 6750$  are plotted from the experimental data. Corresponding curves have also been obtained for cementite, pyrrhotine, and a cerium iron alloy. The Kerr effect is not exhibited by manganese boride and amorphous iron sulphide ( $\text{FeS}$ ).

H. M. D.

**Fusibility Curves of Volatile Systems: Mechanism of the Formation of Esters.** GEORGES BAUME and P. PAMFIL (*Compt. rend.*, 1912, 155, 426—430. Compare *Abstr.*, 1911, i, 414).—By means of an apparatus previously described (*Abstr.*, 1909, ii, 545 ;

1911, ii, 696), the authors have studied the fusibility curve of mixtures of a known quantity of the compound  $\text{Et}\cdot\text{CO}_2\text{H}\cdot\text{HCl}$ , with increasing quantities of methyl alcohol, and find that there is a sharp maximum point corresponding with the compound  $\text{Et}\cdot\text{CO}_2\text{H}\cdot\text{HCl}$ , +  $\text{MeOH}$ . This constitutes the first stage in the formation of the ester. Starting with the compound  $\text{MeOH}\cdot\text{HCl}$ , and adding increasing quantities of propionic acid, the temperature readings are found to vary quite irregularly. Diagrams of the apparatus and the various fusibility curves are given. The results show the three temperature zones of indifference, addition, and substitution (compare Guye, Abstr., 1910, ii, 699). W. G.

**Form of the Fusion Curve (Solid-Liquid Equilibrium Curve) and its Critical End-points.** JOHANNES J. VAN LAAR (*Chem. Weekblad*, 1912, 9, 744—755).—A summary of previous papers by the author, and a criticism of Bridgman's results (*Proc. Amer. Acad. Sci.*, 1911, 47, No. 12; 1912, 47, No. 13). A. J. W.

**Cryoscopy in Paracetaldehyde.** WLADIMIR LUGININ and GEORGES DUPONT (*Bull. Soc. chim.*, 1912, [iv], 11, 904—909. Compare Abstr., 1911, ii, 369).—Paracetaldehyde is recommended as a solvent in cryoscopy on account of its rapidity of crystallisation, high cryoscopic constant, and fair stability.

The mean value of  $K$  is 70.5, but with increasing concentration the relation  $\Delta T/p$  varies, and then  $\Delta T = K_1 n/N + n$ , where  $K_1 = 100K/M_s = 53.2$ . The latter formula is in closer agreement with the results obtained than that proposed by Baud and Gay (Abstr., 1910, ii, 689). It is suggested that the formula  $M = p/N(K_1/\Delta T - 1)$  deduced from this is more suitable for general use in cryoscopy than that of Raoult.

Paracetaldehyde, like the hydrocarbons, gives anomalous results with hydroxy-compounds, except in very dilute solutions and with substances of comparatively high molecular weight; thus borneol gives normal values. T. A. H.

**Heat of Formation of Hydrogen Selenide.** LUIGI ROLLI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 278—283).—In view of the discordant values obtained for this quantity, the author has determined it anew. In a tube kept at constant temperature and containing hydrogen instead of air, a mixture of iodine and selenium is placed, and a current of pure dry hydrogen selenide is passed. In this way a gaseous mixture of  $\text{H}_2\text{Se}$ ,  $\text{HI}$ ,  $\text{I}_2$ , and  $\text{H}_2$  is obtained in equilibrium with solid iodine and selenium. The analysis of this mixture by appropriate methods gives the value of  $K$  for the equilibrium  $2\text{HI} + \text{Se} \rightleftharpoons \text{H}_2\text{Se} + \text{I}_2$ . When  $K$  is known, the heat change in this reaction can be calculated. It was found that  $\text{H}_2\text{Se} + \text{I}_2(\text{solid}) = 2\text{HI} + \text{Se}(\text{solid}) - 3953.65$  cal. Since the heat of formation of hydrogen iodide is known, that of hydrogen selenide can now be calculated; it is found to be  $-16025.6$  cal. This refers to amorphous selenium. For monoclinic selenium and the other modification, the values are consequently  $-17075$  cal. and  $-17455$  cal. respectively. R. V. S.

**Heat of Formation of Lead Iodide and Lead Chloride.** F. KOREF and H. BRAUNE (*Zeitsch. Elektrochem.*, 1912, 18, 818—821).—The determinations were made by a very accurate calorimetric method, a large Dewar flask being used as calorimetric vessel and the temperature measured with a platinum resistance thermometer. In the case of lead iodide, lead and iodine, on the one hand, and lead iodide on the other, were added to a solution of potassium iodide, and from the difference in the thermal effect the heat of formation of lead iodide was found to be 41,850 cal. For lead chloride the heats of solution of this salt and lead iodide respectively in sodium hydroxide were determined, and using the data of Thomsen for the difference of the heat changes which occur when iodide and chlorine change from the solid and gaseous forms respectively to the ionic condition, the value of 85,570 calories is obtained for the heat of formation of lead chloride.

This value is about 2215 cal. higher than the mean of the values of Berthelot and Thomsen, and is in good agreement with that calculated by Pollitzer (compare Abstr., 1911, ii, 180), and the criticisms by Cohen (compare Abstr., 1911, ii, 180) of Pollitzer's results are therefore not valid. G. S.

**Heat of Combustion of Ethylbenzene.** RICHARD H. JESSE, jun. (*J. Amer. Chem. Soc.*, 1912, 34, 1337—1341).—Richards and Jesse (Abstr., 1910, ii, 269) have determined the heat of combustion of several isomeric substances, including the three xylenes. In connexion with the xylenes, it was considered desirable to study the isomeric compound, ethylbenzene, and its heat of combustion has, therefore, been determined. The method of adiabatic calorimetry was used as in the earlier work.

If the heat of combustion of sucrose is taken as 16·545 kilojoules per gram (Fischer and Wrede, Abstr., 1904, ii, 469), the heat of combustion of ethylbenzene is 42·63 kilojoules per gram, or 4520 kilojoules per gram-mol. Regarding a large calorie as equivalent to 4·179 kilojoules, the heat of combustion is 1081·5 Cal. per gram-mol. If, on the other hand, the value of the Bureau of Standards for the heat of combustion of sugar (3943 cal.) is adopted, the heat of combustion of a gram-mol. of ethylbenzene is 1077·3 Cal. E. G.

**The Law of Molecular Attraction.** JAMES E. MILLS (*Phil. Mag.*, 1912, [vi], 24, 483—500. Compare Abstr., 1902, ii, 596; 1904, ii, 642).—On the assumption that molecular attraction varies inversely as the seventh power of the distance of separation of the molecules, Kleeman (compare Abstr., 1910, ii, 932) deduced the relationship  $\lambda/(d^2 - D^2) = \text{constant}$ , in which  $\lambda$  is the internal heat of vaporisation,  $d$  the density of the liquid substance, and  $D$  the density of the saturated vapour. As the author has shown previously (*loc. cit.*), the assumption of the inverse square law of attraction leads to the equation  $\lambda/(d^3 - D^3) = \text{constant}$ . By reference to the available experimental data for ethyl ether, *n*-pentane, isopentane, benzene, and carbon tetrachloride, it is now shown that the degree of constancy of  $\lambda/(d^3 - D^3)$  is much greater than that of  $\lambda/(d^2 - D^2)$  in the case of all five substances for temperatures varying from 0° to the respective critical temperatures. For

the remaining twenty-five non-associated substances investigated by Young, the divergences from the mean value of the constant are in all cases less than 2% if the data for 0° and for temperatures near the critical temperature are excluded. For eight of the twenty-five substances, the divergence is, throughout the entire range of temperature, less than 1%, and out of a total of 430 comparisons, there are only 17 cases in which the divergence exceeds 1.5%.

The later portion of the paper is devoted to a criticism of Kleeman's conclusions relating to the connexion between the internal heat of vaporisation and the change in density accompanying the transition from the liquid to the saturated vapour.

According to Tyrer (compare this vol., ii, 136), the increase in the specific heat of a fluid, which occurs when the density is increased, indicates that intra-molecular energy is liberated when isothermal expansion occurs, but this is probably not contradictory to the operation of the inverse square law of attraction. H. M. D.

**Alteration in Properties of Metals by Mechanical Treatment.** GUSTAV TAMMANN (*Zeitsch. Elektrochem.*, 1912, 18, 584—598).—A more detailed account of work already published (compare Abstr., 1912, ii, 21). G. S.

**Surface Tension of Protein Solutions.** FILIPPO BOTTAZZI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 221—230).—The author's measurements have been made with Traube's stalagmometer at 28°. Suspensions of casein of different origins have a lower surface tension than water. This indicates the presence of soluble impurities. When the suspension is converted into a solution by addition of sodium hydroxide, a great fall of surface tension occurs. From these experiments it appears that casein is not a suitable substance for this work, although it has been employed by other authors.

By prolonged dialysis of the blood-serum of the ox and of the dog, the author has obtained a protein, termed "mixed seroalbumin," of which dilute true solutions can be obtained, and these show a decreased surface tension due to the dissolved protein.

Seroglobulin, prepared by dialysing the blood-serum of the ox for many months, is insoluble in water, and its suspension in water does not lower the surface tension. When by the addition of sodium hydroxide a solution is obtained, this has a lower surface tension than water, and the surface tension decreases as the concentration of dissolved protein is increased. R. V. S.

**Viscosity of Casein Sols.** HARRIETTE CHICK and CHARLES J. MARTIN (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 102—105).—The influence of concentration and temperature on the viscosity of colloidal solutions of casein in sodium hydroxide has been investigated. The curve showing the connexion between the viscosity and concentration at 25° is strongly convex to the concentration axis, and this is attributed to the adsorption of water by the colloid. The density-concentration curve is slightly concave to the concentration axis, a result which appears to be due to the contraction which accompanies

the adsorption process. The ratio of the viscosity of a 9.39% solution to that of water at the same temperature falls very rapidly as the temperature rises and this is ascribed to the gradual dehydration of the colloidal particles. The effect is less marked in less concentrated solutions.

In the case of both acid and alkaline casein solutions, the viscosity increases with the quantity of acid or alkali present, which indicates that the casein salt particles have a greater adsorptive power for water than casein itself.

H. M. D.

**Diffusion of Alkali Salt Vapours in Flames and the Measurement of the Velocity of Flames.** ARTHUR BECKER (*Phil. Mag.*, 1912, [vi], 24, 707—708).—A claim to priority and a criticism of the values obtained for the coefficients of diffusion of alkali salt vapours in flames by Wilson (this vol., ii, 744). It is also pointed out that the average values obtained for the electric charges on the luminous particles are not in agreement with the results found by other observers.

H. M. D.

**Osmotic Properties of Solutions.** ALBERT REYCHLER (*Bull. Soc. chim. Belg.*, 1912, 26, 409—414).—A mathematical paper in which expressions for the vapour tension, elevation of b. p., depression of f. p., and the osmotic pressure of solutions are derived from consideration of the vapour tension.

H. W.

**Osmotic Pressure of Aqueous Solutions.** CAMILLE GILLET (*Bull. Soc. chim. Belg.*, 1912, 26, 415—418).—The author considers the osmotic pressure of aqueous solutions from the point of view that liquid water consists of an equilibrium mixture of molecules of hydrol and dihydrol, and that this equilibrium is disturbed by the dissolved substance (compare Abstr., 1909, ii, 388). He is led to the conclusion that the osmotic pressure is not proportional to the number of dissolved molecules, but depends on a number of factors of which the chief is the number of molecules of hydrol present on either side of the semipermeable membrane.

H. W.

**Mechanism of Osmosis.** ALF. GILLET (*Bull. Soc. chim. Belg.*, 1912, 26, 419—421).—The author is led to the conclusion that the osmotic pressure of a solution is only indirectly dependent on the state of the dissolved substance, and that the phenomena of osmosis can be adequately explained on the basis of the laws of Raoult and Schiller on the variation of vapour tension at constant temperature.

H. W.

**Theoretical and Experimental Researches on Solid Solutions.** GIUSEPPE BRUNI (*Mem. R. Accad. Lincei*, 1912, [v], 9, 40—116).—A résumé of the author's published work on this subject.

R. V. S.

**Experimental Researches on Solutions.** MICHELE CANTONE (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1912, [iii], 18, 262—270).—When a strip of filter paper is placed as a bridge between two vessels containing solutions of potassium ferrocyanide and copper sulphate,

respectively, a semipermeable membrane of copper ferrocyanide is produced in the form of a fine line in the filter paper where the two liquids meet. The membrane is persistent, and with it (and others similarly obtained) the properties of semipermeable membranes may be demonstrated. It is impermeable to the dissolved substances, which gradually accumulate on either side of it, forming crystalline deposits. A similar effect is also observed, however, even when the two liquids form no precipitate with one another, as, for instance, when an aqueous solution is placed in one vessel and water in the other; the line where the two liquids meet is a barrier which the solute cannot pass, and it gradually accumulates and crystallises there. In this way the dissolved salts of a natural water can be detected if distilled water is placed in the vessel at the other end of the filter paper. In explanation of the phenomenon, the author suggests an hypothesis analogous to that employed to explain the electromotive force of contact.

R. V. S.

**Optical Investigation of Crystallised Nitrogen, Argon, Methane, and Some of the Simpler Organic Compounds of Low Melting Points.** WALTER WAHL (*Proc. Roy. Soc.*, 1912, A, 87, 371—380).—The crystalline forms of various substances melting at low temperatures have been examined with the aid of a specially devised form of crystallisation vessel. This consisted of a quartz tube provided with a very narrow bulb, which was made by fitting together two small quartz glass plates and adding molten quartz glass to the edges. The tube containing the liquid substance was cooled in a suitable manner, and the layer of crystals examined by means of an ordinary polarisation microscope.

Nitrogen crystallises in the regular system, and its crystalline form is therefore in harmony with that of the other elements in the periodic group.

Argon and methane also crystallise in regular forms. Ethyl ether belongs to the rhombic system and separates in the form of long, well-developed, prismatic needles.

Ethyl alcohol crystallises with difficulty, but if the walls of the vessel are scratched, spherulitic groups of crystals are obtained, which belong to the rhombic, monoclinic, or triclinic system.

Acetone, methyl alcohol, and carbon disulphide form crystals belonging to the monoclinic or triclinic system. In the case of methyl alcohol, two polymorphic enantiotropic modifications have been observed.

H. M. D.

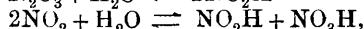
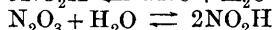
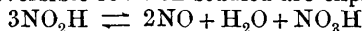
**Precipitation of Arsenious Sulphide Sol by Salts of the Rare Earths.** HERBERT FREUNDLICH and H. SCHUCHT (*Zeitsch. physikal. Chem.*, 1912, 80, 564—572).—The coagulating power of salts of the rare earths and certain complex cobalt compounds for colloidal solutions of arsenious sulphide has been measured by the method already described (compare Abstr., 1910, ii, 692). The efficiency of the salts of the rare earths and of indium and of trivalent complex cobalt compounds (cobaltiate compounds) is the same as that of aluminium salts in equivalent concentration, a result which supports

the view that the rare earths are tervalent. The change of purpureo-cobalt chloride (a bivalent cation) to roseo-cobalt chloride (tervalent cation) can be followed by measuring the alteration in coagulating power for colloidal arsenious sulphide. The arsenious sulphide precipitated from solution by xanthocobalt sulphate and purpureo-cobalt chloride slowly darkens on keeping, probably owing to the formation of cobalt sulphide; the reaction is accelerated by light.

The coagulation method probably cannot be made sensitive enough to determine the valency of radioactive decomposition products, but the effect of salts of different valency on electro-osmosis (compare G. von Elissaff, this vol., ii, 419) may perhaps be suitable for this purpose.

G. S.

**Conditions of Formation of Nitrous and Nitric Acids from Oxides of Nitrogen and Water.** Application of the Law of Mass Action. EMIL BRINER and E. L. DURAND (*Compt. rend.*, 1912, 155, 582—585).—The authors have studied the systems  $\text{NO}-\text{NO}_3\text{H}$ ,  $\text{NO}_2-\text{H}_2\text{O}$ ,  $\text{N}_2\text{O}_3-\text{H}_2\text{O}$ , and  $\text{NO}_2-\text{NO}_3\text{H}$  within wide limits of pressure and concentration, the temperature remaining constant. The phenomena which occur in the systems are only equilibrium reactions of oxidation or reduction between the different oxygenated compounds of nitrogen. The blue colours which occur under varying conditions are due to  $\text{N}_2\text{O}_3$ , and the green colours to its mixture with more or less  $\text{NO}_2$ . The three reversible reaction studied are expressed by



and the authors give a brief discussion of these in relation to the law of mass action.

W. G.

**Molecular Statistics of Some Chemical Actions.** (Hon.) ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1912, A, 87, 302—309).—When a gas is absorbed or chemically acted on by a solid surface, the rate at which the change proceeds must depend on the number of collisions made by the gas molecules with the surface, and the question as to the number of such collisions which are required for the achievement of a successful result has been examined in the case of the action of ozone on silver and of active nitrogen on copper oxide. In the ozone experiments, a stream of air was made to pass through a discharge tube, in which the air becomes charged with ozone and nitric oxide. The presence of ozone in the air stream is recognised by the luminosity resulting from its interaction with the nitric oxide. By causing the gases to pass through a silver gauze partition, the ozone is destroyed and the glow ceases. The minimum area of silver surface which suffices to produce this result has been determined, and the data show that less than 1.6 collisions with the silver surface suffice to destroy a molecule of ozone. This result points to the conclusion that one collision with a silver surface is sufficient to destroy an ozone molecule.

Similar experiments with active nitrogen and copper oxide gave 780 as an upper limiting value for the number of collisions which occur before a molecule of active nitrogen is destroyed by a surface of oxidised copper. The data, obtained by Jones and Chapman (*Trans.*,

1910, 97, 2476) for the rate of decomposition of ozone in the absence of surface effects, have also been examined statistically, and the author calculates that at  $100^{\circ}$  two molecules of ozone must, on the average, collide  $6 \times 10^{11}$  times before the favourable type of collision occurs which results in chemical decomposition. H. M. D.

**Lecture Experiments on the Influence of Solvents on the Velocity of Reaction.** HANS VON HALBAN and ALEXANDER KIRSCH (*Ber.*, 1912, 45, 2418—2420).—The influence of different solvents on the decomposition of xanthic acid can be qualitatively illustrated as follows, the presence of any undecomposed acid being detected by cobalt nitrate, which forms therewith the dark green soluble cobaltic xanthate (Rosenheim and Davidsohn (*Abstr.*, 1904, i, 843). A solution of potassium xanthate, 0.8 gram in water at  $0^{\circ}$ , is treated with about 40 c.c. of xylene and the calculated amount of ice-cold dilute sulphuric acid. The mixture is shaken vigorously in a separating funnel, and the xylene solution is removed, dried with calcium chloride and then with phosphoric oxide, filtered, and diluted to 50 c.c. The solution can be kept for a day. One c.c. is treated with 10 c.c. of a solvent, and then, after a definite interval of time, which is different for each solvent, 10 c.c. of a solution of 0.29 gram of hydrated cobalt nitrate in 100 c.c. of alcohol.

In the cases of ethyl, amyl and benzyl alcohols, and acetone, the cobalt nitrate does not produce a coloration after a few minutes; with nitromethane and with dry glacial acetic acid, colorations are produced faintly after thirty minutes and one hour respectively. With nitrobenzene, an intense coloration is observed after half an hour, whilst in the cases of chloroform, benzene, toluene, petroleum, carbon disulphide, and ether, the mixture of xanthic acid solution and solvent can be boiled throughout the lecture without any marked decomposition of the xanthic acid.

The spontaneous decomposition of xanthic acid (Zeise, *Pogg Ann.*, 1835, 35, 500) is an example of autocatalysis brought about by the alcohol liberated. When the acid is mixed with a large quantity of phosphoric oxide, it may be kept at the ordinary temperature for a day, or at  $50^{\circ}$  for several hours, without appreciable decomposition.

C. S.

**Hydrolytic Decomposition of Acetylated Hydroxy-acids.** II. RICHARD ANSCHÜTZ and OSKAR MOTSCHMANN (*Annalen*, 1912, 392, 100—126. Compare Rath, *Abstr.*, 1908, ii, 94).—The rates of the hydrolysis of the acetyl derivatives of the following hydroxy-acids have been determined under the conditions employed by Rath (*loc. cit.*):  $\alpha$ - and  $\beta$ -hydroxybutyric acids,  $\alpha$ -hydroxyisobutyric acid,  $\beta$ -phenyl-lactic acid,  $\beta$ -phenylhydracrylic acid, *o*-, *m*- and *p*-cresotic acids, and *m*- and *p*-hydroxybenzoic acids. In all cases the hydrolysis is a unimolecular reaction. The velocity constant diminishes towards the end of the hydrolysis, indicating that the acetylated hydroxy-acids are more extensively electrolytically dissociated than are the hydroxy-acids themselves.

The most important results of the research are as follows: There is not in all cases a parallelism between the dissociation constants of

hydroxy-acids and the velocity constants of the corresponding acetyl derivatives. In homologous series of acetylated  $\alpha$ -hydroxy-acids, the rate of hydrolysis diminishes as the molecular weight increases. The acetyl derivatives of normal  $\alpha$ -hydroxy-acids hydrolyse more rapidly than those of the *iso*- $\alpha$ -hydroxy-acids. Acetylated  $\beta$ -hydroxy-acids hydrolyse more slowly than their  $\alpha$ -isomerides, *o*-acetylresotic acid hydrolyses more slowly than the *meta*- and *para*-isomerides, and all three more slowly than *o*-acetoxybenzoic acid. The last is hydrolysed more rapidly than *m*- or *p*-acetoxybenzoic acid.

The following new compounds are described:  *$\alpha$ -acetoxybutyric acid*, m. p.  $43^{\circ}$ , from the acid and acetyl chloride in the cold;  *$\beta$ -acetoxybutyric acid*, b. p.  $93-94^{\circ}/0.5$  mm., from the acid and boiling acetyl chloride;  *$\alpha$ -acetoxyisobutyric acid*, m. p.  $61^{\circ}$ , from the acid and acetic anhydride on the water-bath;  *$\alpha$ -acetoxy- $\beta$ -phenylpropionic acid*, m. p.  $72^{\circ}$ , from the acid and boiling acetyl chloride. G. S.

**New Neutral Salt Reaction.** M. FORT (*J. Soc. Dyers*, 1912, 28, 314—316).—It is known that neutral salts increase the effect of weak acids on indicators, and the author now shows that there is a similar enhancing effect of neutral salts on the activity of weak bases as measured by indicators.

Kraus previously showed (*Farb. Zeitung*, 1911, 333) sodium sulphate solution when hot has an alkaline reaction on litmus, whilst sodium chloride shows no such reaction. Hot solutions of potassium sulphate and of sodium nitrate behave like sodium sulphate, whereas potassium chloride and nitrate, like sodium chloride, give no indication of alkalinity under similar conditions. In these experiments, alizarin was used as indicator. It is suggested that the salts which are alkaline on heating have undergone hydrolysis.

Aniline has only a slight action on alizarin at the boiling point of water, but an immediate deepening of colour takes place when sodium sulphate or chloride is added. Other bases show a similar behaviour, and it is suggested that the weak base liberates a trace of alkali hydroxide from the neutral alkali salt. When sufficient ammonia is present in a boiling aqueous solution to give a faint colour with phenolphthalein, an immediate deepening in colour takes place on the addition of a neutral alkali salt.

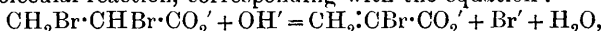
The importance of such reactions for the dyeing industry is indicated. G. S.

**Catalysis. XII. Mechanism of Organic Reactions.** SALOMON F. ACREE (*Amer. Chem. J.*, 1912, 48, 352—380. Compare Abstr., 1907, i, 566; ii, 855; 1909, ii, 652).—The paper contains a discussion of the author's theories of catalysis based on the assumption that in all reactions it is necessary to consider the possibility of direct transformation of both ions and non-ionised substances. Fresh evidence is adduced from the results of investigations which will be published shortly, and it is also shown that the author's views are supported by the work of Stieglitz, Goldschmidt, and Tubandt.

E. G.

**Catalysis by Cations. II.** BROR HOLMBERG (*Zeitsch. physikal. Chem.*, 1912, 80, 573—596. Compare this vol., ii, 443).—The investigation has now been extended to  $\alpha\beta$ -dibromopropionic acid,  $\alpha\beta$ -dibromobutyric acid,  $\gamma$ -valerolactone, and  $\alpha$ -bromobutyric acid.

The decomposition of  $\alpha\beta$ -dibromopropionic acid in alkaline solution is a bimolecular reaction, corresponding with the equation :



and the velocity coefficient is proportional to the eighth root of the cation concentration. Under equivalent conditions at 25° the catalysis coefficients with the different bases are in the following ratio : Na=12·14, K=11·68, Ca=17·92, Ba=16·68. The effect of a mixture containing Na' and K' ions is the sum of the separate effects, but Na' and Ba'' ions have together a smaller influence than the sum of the separate effects. The results obtained with  $\alpha\beta$ -dibromobutyric acid correspond with those obtained for  $\alpha\beta$ -dibromopropionic acid. The catalysis coefficients at 25° for different bases are in the following ratio : Na=0·206, K=0·218, Ca=0·319, Ba=0·302.

The results of the hydrolytic decomposition of  $\gamma$ -valerolactone by sodium, potassium, calcium, and barium hydroxides confirm the conclusions of Henry (Abstr., 1892, ii, 1303) that the rate is independent of the nature of the base, so that there is in this case no cation catalysis.

The results obtained with  $\alpha$ -bromobutyric acid agree in all respects with those of Senter (Trans., 1907, 91, 460 ; Abstr., 1910, ii, 276).

G. S.

**Organic Acids as Catalysts.** HENRY C. BIDDLE (*Ber.*, 1912, 45, 2832—2837).—A development of the results already published (this vol., i, 296). It is shown that organic acids act as catalysts and convert cinchonine and quinine into cinchotoxine and quinotoxine respectively, and that of the inorganic acids examined, phosphoric acid alone exhibits a similar action and that only to a slight extent. In this type of catalysis the velocity of the reaction is greater the lower the dissociation constant of the acid used, and is proportional to the molecular concentration of the acid.

T. A. H.

**Theory of the Solid State of Monatomic Elements.** EDUARD GRÜNEISEN (*Ann. Physik*, 1912, [iv], 39, 257—306).—A theory of the solid state of monatomic isotropic substances is developed, in which the assumption is made that the attraction and repulsion between the atoms is due to the operation of forces which vary inversely as some power of the distance between the atoms. In general, the conclusions to which this theory leads, are in satisfactory agreement with the experimental data for many of the elements, especially at low temperatures.

The assumption that the sphere of action of the attractive forces is limited to the atoms which are nearest to the particular atom considered does not harmonise with the facts so well as the hypothesis that the sphere of action extends beyond this limit.

H. M. D.

**Observations on the Natural System of the Elements.** RUDOLF LAEMMEL (*Ann. Physik*, 1912, [iv], 39, 485—488).—In a

previous paper (Abstr., 1907, ii, 530) the view was put forward that all the elements have the same atomic heat at comparable temperatures. This equality is now supposed to hold for all the properties of the elements, provided comparable conditions of temperature and pressure are chosen. If not exactly equal, the observed differences may be expected to show a connexion with the atomic weight.

Since both chemical and physical properties are influenced by temperature and pressure, the natural relations between the elements can only be brought to light in a satisfactory manner if the properties are determined under comparable conditions. H. M. D.

**Sodium Lamps for Polarisation Measurements.** ERNST BECKMANN (*Ber.*, 1912, 45, 2523—2529).—A full description of various burners which can be used for obtaining sodium flames. A 2—4% solution of sodium hydroxide or sodium carbonate is electrolysed between two nickel electrodes, the electrolyser being so arranged that the spray of electrolytic gas is carried by the air current of the burner into the flame. The intensity of the flame can be increased by feeding oxygen round the flame, so as to form an oxygen zone for the gas to burn in.

It is not necessary for the electrolytic spray to be carried up by the air current; it is sufficient for it to be distributed into the outer zone of the flame, and appropriate arrangements are described for doing this.

The greatest intensity is obtained with a hydrogen flame. With such flames the colour nuance is somewhat altered, but it may be corrected for in the usual way by a filter of potassium chromate solution.

The advantages of the lamps described are that the air of the laboratory does not become appreciably contaminated, and that it is possible, owing to the intense light produced, to measure the rotation of coloured or turbid liquids. T. S. P.

**Dephlegmator.** RUDOLPH KRECH (*Chem. Zeit.*, 1912, 36, 1152).—The dephlegmator is constructed of aluminium, copper, or silver, and is maintained at a constant temperature by the vapour of a suitable liquid, which circulates on the inside and outside on the principle of a double surface condenser. The vapour to be fractionated, after having passed through a Young fractionating column of eight divisions, enters the lower part of the dephlegmator, and passes through a wide spiral tube, an expansion chamber, a narrower spiral tube wound in the reverse direction, a second expansion chamber, and a fine spiral again reversed in direction. The final section is a wider spiral tube, lined with a spiral of fine wire in order to increase the metallic surface. A mixture, b. p. 10—150°, containing 40% of two liquids boiling within a few degrees of one another, is separated in one operation into fractions, 90% of which distil within 0.2°.

C. H. D.

**New Apparatus.** D. MARINO (*Ann. Lab. Gabelle*, 1912, 6, 651—658).—The new apparatus for fractional distillation is based on

the same principle as that of Hahn (Abstr., 1910, ii, 183), being so constructed that the vapour of the boiling mixture, as it ascends the column, passes through tubes and bulbs, on the other sides of the walls of which there is a liquid of boiling point so chosen that only the more volatile constituent of the mixed vapour can pass on. With the apparatus it is possible to separate quantitatively methyl alcohol from a mixture of it with water and ethyl alcohol.

The extractor for solids in the warm differs from the usual Soxhlet form in two respects: (1) a perforated disc is placed over the orifice of the tube of the syphon in the container, so that the action of the syphon is more regular; (2) the container with its attached syphon is sealed into a wider tube, which serves as a steam-jacket, so that the extraction proceeds almost at the boiling point.

The extractor for liquids by solvents lighter than themselves consists of three concentric tubes. The outside tube contains, at the bottom, the liquid to be extracted, and at the top is connected with the condenser. The innermost tube carries the vapour of the solvent from the boiling vessel; it is sealed through the bottom of the outer tube already mentioned, passes half way up the middle tube, is there bent at right angles, and its orifice is sealed into the side of the middle tube. The middle tube reaches almost to the top of the outer one, and terminates in a wide mouth just under the end of the condenser; its lower end is pierced with a number of small holes, and is situated below the level of the liquid to be extracted.

The bunsen burner gives by one automatic regulator large and small oxidising flames, and large and small reducing flames.

The apparatus for the preparation of gases consists of a very wide tube bent once at right angles. The long vertical arm has a bulb at its upper extremity, and another large bulb (which has a tubulure closed with a tap and stopper) is sealed on to the upper side of the horizontal arm at its upper extremity in such a way that the vertical axis of the bulb passes through the tubulure and the small hole which connects the bulb with the tube. When in use, this bulb is filled with marble or iron sulphide, etc., and the acid is poured into the vertical arm.

R. V. S.

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### Inorganic Chemistry.

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Hydrogen Peroxide. II. KARL BORNEMANN (*Zeitsch. anorg. Chem.*, 1912, **78**, 33—40. Compare Abstr., 1903, ii, 281).—More recent experiments give values for the reduction potential of hydrogen peroxide of  $-0.66 \pm 0.03$  volt, and for the oxidation potential of  $-1.80 \pm 0.03$  volt, calculated for 1 mol. per litre.

A reply is also made to the criticisms of Richarz (Abstr., 1904, ii, 114).  
C. H. D.

**Reductions and Reactions in Reversed Flames. I. Reduction of Chlorides in the Chlorine-Hydrogen Flame.** FRIEDRICH MEYER (*Ber.*, 1912, 45, 2548—2554).—The principle made use of is that the outer zone of a reversed flame, in contradistinction to the strongly oxidising zone of a normal flame, will possess strongly reducing properties, so that any substance which is made to pass through the flame, from the inside to the outside, will be reduced and will remain reduced in the atmosphere consisting of the reducing agent which forms one of the components of the flame. In order to exclude all subsidiary reactions, it is necessary that the combustion product of the flame should be identical with one of the products formed by the reduction of the substance under investigation. Thus, for the reduction of chlorides, it will be necessary to use a chlorine-hydrogen flame.

An apparatus is described by means of which chlorine is burned in an atmosphere of hydrogen. The vapour of the chloride to be reduced is carried with the chlorine into the flame, which burns in a glass vessel cooled externally by water, so that the products of reaction are immediately cooled. The jet at which the flame burns is made of quartz.

With such an apparatus, stannic chloride is readily reduced to stannous chloride, arsenic trichloride to arsenic, and titanium tetrachloride to titanium trichloride. T. S. P.

**Physical Constants of Sulphur and their Connexion.** HUGO R. KRUYT (*Zeitsch. Elektrochem.*, 1912, 18, 581—583).—Part of the results described in the paper have already been published (compare *Abstr.*, 1911, ii, 879). There is evidence that  $S_{\mu}$  is only very slightly soluble in solid monoclinic sulphur, but is soluble to a considerable extent in solid rhombic sulphur. The conclusion is drawn that the transition point of sulphur will be very slightly raised by the presence of  $S_{\mu}$ , and preliminary investigations appear to confirm this deduction. An equilibrium diagram of sulphur in the light of recent investigations is given. G. S.

**Modified Ostwald's Hydrogen Sulphide Apparatus.** R. HASE (*Chem. Zeit.*, 1912, 36, 1127), A. M. SKLEPINSKI (*ibid.*), NICOLAUS TECLU (*ibid.*).—A correspondence relating to a piece of apparatus described recently by Sklepinski (this vol., ii, 932). Hase states that he has, for the last fifteen years, used a very similar piece of apparatus devised by Teclu. In drawing attention to the fact that the apparatus was described by him as a modification of Ostwald's apparatus, Sklepinski says Teclu's apparatus was not then known to him. Teclu points out that his apparatus possesses an advantage over that of Sklepinski, in that the acid, etc., can be removed without interfering with the evolution of the hydrogen sulphide, and that the principle of the apparatus was devised by Döbereiner. W. P. S.

**Complexity of Tellurium.** WILLIAM R. FLINT (*J. Amer. Chem. Soc.*, 1912, 34, 1325—1328).—Harcourt and Baker (*Trans.*, 1911, 99, 1311) have suggested that the low atomic weights found by the author for the metal present in certain fractions obtained in his

experiments (Abstr., 1910, ii, 845) may have been due to the presence of tellurium trioxide, and have stated that they obtained an orange-coloured precipitate which proved to be tellurium trioxide.

The orange-coloured, crystalline precipitate obtained by the author in his earlier work (*loc. cit.*) has therefore been re-investigated, and it is shown that the low atomic weights could not have been due to the presence of tellurium trioxide.

The fractionation of crude material with purification of the final fraction is not effective in securing any separation. It is considered that if tellurium is really a complex substance, the best method for attempting to resolve it into its constituents is the hydrolytic method already described (Browning and Flint, Abstr., 1909, ii, 996; Flint, *loc. cit.*).  
E. G.

**The Catalytic Preparation of Ammonia from its Elements by the Employment of Pure Iron as the Contact Substance.** BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 247852. Compare Abstr., 1907, ii, 454; 1908, ii, 362, 819).—When pure iron is used as the catalytic agent in the preparation of ammonia from its elements, the reaction can be satisfactorily carried out at temperatures of about 600°.  
F. M. G. M.

**Absorption of Helium and Other Gases under the Electric Discharge.** (Hon.) ROBERT J. STRUTT (*Proc. Roy. Soc.*, 1912, A, 87, 381—384).—According to Berthelot, absorption of helium occurs when the vapour of benzene or carbon disulphide is decomposed by the silent electric discharge. The experiments have been repeated in the case of carbon disulphide with negative results. In similar circumstances, nitrogen was found to be steadily absorbed by the products of decomposition of the carbon disulphide.

When phosphorus is introduced into a discharge tube containing nitrogen or hydrogen, the gases are quickly absorbed. By the introduction of successive quantities of gas, it was found that 200 c.c. of nitrogen and 84 c.c. of hydrogen are absorbed per gram of phosphorus. The gases are not evolved when the tube is heated, and this suggests that chemical combination takes place. In the same conditions, helium is absorbed by phosphorus to the extent of 0.16 c.c. per gram, but the gas is nearly all evolved again on heating. In this case, the gas is therefore not chemically combined.  
H. M. D.

**Stability of Argon and Helium in Solid and Liquid Metals.** ADOLF SIEVERTS and E. BERGNER (*Ber.*, 1912, 45, 2576—2583).—Argon and helium do not show a measurable solubility in either solid or liquid copper, silver, gold, nickel, iron, palladium, aluminium, magnesium, uranium, or tantalum. At 1100° powdered quartz glass (6.7 grams) absorbs 0.1 c.c. of helium or of hydrogen, a fact which is in accordance with the diffusion of these gases through quartz at this temperature.

The connexion between the temperature and the amount of helium evolved from cleveite was investigated, and it was found that the best results are obtained by direct heating of the mineral at 1000—1200°

in a porcelain tube. At high temperatures porcelain is much less permeable to helium than quartz glass.

It is probable that uranium dissolves hydrogen, 100 grams of the metal absorbing 1.6 mg. of hydrogen at 1100° and 760 mm.

T. S. P.

#### Action of Some Elements on Fused Potassium Hydroxide.

II. MAX LE BLANC and O. WEYL (*Ber.*, 1912, 45, 2300—2315).—The arrangement previously described (*Abstr.*, 1910, ii, 123) has been improved by substituting an electric oven for the gas oven used to heat the fusions.

Potassium hydroxide can be obtained in the anhydrous condition by heating at 400°; even at 660° there is no appreciable dissociation into  $K_2O$  and  $H_2O$ , but vaporisation takes place to some extent. The gold crucible was attacked to some extent, although not chemically; a nickel crucible is attacked with the formation of nickel hydroxide.

Contrary to the usually accepted statement, potassium does not act on potassium hydroxide at temperatures up to 555°. By the action of potassium on sodium hydroxide and of sodium on potassium hydroxide at 550—660°, it is probable that the equilibrium  $Na + KOH \rightleftharpoons K + NaOH$  is set up; superposed on this is the reaction  $Na + NaOH = H + Na_2O$  and vaporisation of the potassium.

At temperatures between 550° and 660°, gold, aluminium, and manganese have no, or at all events an extremely small, action on potassium hydroxide in an atmosphere of nitrogen. Iron, cobalt, and nickel are appreciably attacked, without, however, it being possible to prove the formation of water, hydrogen, or potassium. The reaction with chromium, molybdenum, and tungsten is also very slight, but the formation of potassium and hydrogen can be proved. Carbon and magnesium are readily attacked, potassium and hydrogen being formed, whilst with silicon the reaction proceeds violently at 400°, hydrogen alone being formed.

The reactions taking place with magnesium can be formulated as follows:  $Mg + 2KOH = Mg(OH)_2 + 2K$ ;  $Mg(OH)_2 = MgO + H_2O$ ;  $H_2O + K = KOH + H$ . Similar equations can be written to represent the action on chromium, molybdenum, tungsten, and carbon.

T. S. P.

**Metal Organosols.** CONRAD AMBERGER (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 97—100).—If lanolin, impregnated with an aqueous solution of the salt of a heavy metal, is triturated with a solution of alkali hydroxide, double decomposition takes place, and the oxides or hydroxides of the heavy metals are obtained in colloidal form. If the oxides are readily reduced, this treatment gives rise to the colloidal metals. After removal of water and the electrolytes present, the residual product is found to dissolve quite readily in all organic solvents in which lanolin is soluble. In this way metal organosols can be easily prepared, and by evaporation of the volatile solvent, solid colloidal products containing a high percentage of metal are obtained.

The protective action exerted by the lanolin is exhibited in a still

greater degree by the lanolin alcohols (cholesterol, ischolesterol) and by the use of the unsaponifiable wool-fat residue, organosols containing a higher percentage of metal can be prepared.

Details are given of the preparation of silver organosols by this method, one of the products obtained containing as much as 74.3% of silver.

H. M. D.

**The Affinity between Iodine and Silver.** ULRICH FISCHER (*Zeitsch. anorg. Chem.*, 1912, 78, 41—67).—A detailed account of experiments, the results of which have been already published (this vol., ii, 536).

C. H. D.

**Solubility of Silver Oxide in Litharge.** ERNST J. KOHLMAYER (*Chem. Zeit.*, 1912, 36, 1079—1082).—The author has determined the heating and cooling curves of mixtures of lead oxide and silver oxide in the molecular proportions of 2 : 1 and 10 : 1. The amount of silver remaining after the cupellation of the mixtures has also been determined, and analyses made of various portions of the fusion after the mixtures have been used for taking the heating and cooling curves in a platinum crucible.

The results show that fused lead oxide dissolves 3—6% of silver, which is present as an oxide of, at present, unknown composition. The melting point of the lead oxide is thereby lowered by 45°. This solubility of silver in lead oxide accounts for the low results obtained in the dry assay of silver.

In some experiments a mixture of lead oxide with silver oxide, containing 0.863% of silver, was fused at 900° in a cupel, and it was found that as much as 28.7—36% of silver was absorbed by the cupel.

T. S. P.

**Hammer-hardening and Annealing of Zinc.** G. TIMOFÉEF (*Compt. rend.*, 1912, 155, 430—432).—Eight microphotographs are given, showing the influence of hammer-hardening and annealing, under different conditions, on the micrographic structure of zinc. The rate of crystallisation increases rapidly with the temperature, and, for the same duration of heating, the size of the crystals obtained is much greater at higher temperatures.

W. G.

**Crystallisation by Annealing of Hammer-hardened Metals.** FÉLIX ROBIN (*Compt. rend.*, 1912, 155, 585—587).—An examination of the size of the crystals formed during annealing in relation to the temperature of annealing in the cases of tin, lead, zinc, aluminium, copper, and iron. The size of the crystals does not increase regularly with the temperature. In general, the crystals, voluminous at a temperature near the melting point, at first diminish rapidly in size with the temperature, and then more slowly to the beginning of annealing, although sometimes they commence to increase again and attain a maximum at the annealing temperature. Impurities generally reduce the size of the crystals without modifying the temperature at which annealing begins.

W. G.

**Crystalline Forms and Genetic Conditions of the Sulphides of Zinc, Cadmium, and Mercury.** EUGENE T. ALLEN and J. L. CRENSHAW. *Microscopic Study*, by H. E. MERWIN (*Amer. J. Sci.*, 1912, [iv], 34, 341—396).—Sphalerite (zinc-blende), from Sonora, Mexico, containing 0.15% Fe, has  $D_4^{25}$  4.090 and  $n_{Na}$  2.3688. Heated to 1020° it becomes transformed into the hexagonal wurtzite with  $D_4^{25}$  4.087 and  $\omega_{Na}$  2.356,  $\epsilon_{Na}$  2.378. The reverse change, wurtzite to sphalerite, takes place more slowly, and at 800—900° is complete only after sixty-six hours. The two forms,  $\beta$ -ZnS (sphalerite) and  $\alpha$ -ZnS (wurtzite), are thus enantiotropic. In sphalerites containing more iron, the density and inversion temperature are lower, whilst the refractive index is higher, these characters varying progressively with the amount of iron. Sphalerite, from Breitenbrunn, Saxony, with 17.06% Fe, has  $D_4^{25}$  3.935,  $n_{Na}$  2.47, and inversion temperature 880°. Crystals of wurtzite were obtained by sublimation at 1200—1300°; and of sphalerite from molten sodium chloride at 800°, or molten potassium polysulphide at 350°. From alkaline aqueous solutions between 200° and 400° only sphalerite was formed, but from acid solutions both sphalerite and wurtzite were deposited. The higher the temperature for a given acid concentration the greater is the percentage of sphalerite (the stable form) crystallised, and the higher the acid concentration for a given temperature the greater is the percentage of wurtzite (the unstable form) crystallised.

Only one cadmium sulphide was obtained. Crystals, 20 mm. in length, were prepared by the action of hydrogen sulphide on cadmium vapour. These are identical with the mineral greenockite, and have  $D_4^{25}$  4.820,  $\epsilon_{Na}$  2.529,  $\omega_{Na}$  2.506. The various hues of different preparations of cadmium sulphide depend on whether the substance is crystalline or amorphous, and on the size and nature of the surface of the grains.

Mercuric sulphide exists in three different crystalline forms: (1) cinnabar,  $\sigma$ -HgS,  $D_4^{25}$  8.176, which is readily prepared by digesting any other form of mercuric sulphide with a solution of alkali sulphide; (2) metacinnabarite (black and cubic),  $\alpha'$ -HgS,  $D_{25}^{25}$  7.60, is precipitated from dilute acid solutions of mercuric salts by sodium thiosulphate; and (3) a new form,  $\beta$ -HgS,  $D_{25}^{25}$  7.20, obtained as a fine crystalline powder from more concentrated neutral solutions of mercuric salts with sodium thiosulphate. This has the same red colour as cinnabar, and is likewise hexagonal, but the refractive indices are much lower. Cinnabar is the stable form of mercuric sulphide at all temperatures up to its sublimation point, about 580°. None of the sulphides of the zinc-cadmium-mercury group melts at atmospheric pressure.

The stable forms sphalerite, cinnabar, and iron-pyrites (this vol., ii, 354) are always obtained by crystallisation from alkaline solutions (solutions of alkali sulphides), whilst the unstable forms wurtzite, metacinnabarite, and marcasite are obtained from acid solutions only. The stable forms may also be crystallised from acid solutions under certain conditions of temperature and acid concentrations. These points are discussed in relation to the occurrence and genesis of these minerals in ore-deposits.

L. J. S.

**Alloys of Lead, Tin, and Antimony.** WILLIAM CAMPBELL (*Metallurgie*, 1912, 9, 422—425).—A microscopical investigation of these ternary alloys fixes the two ternary transformation points at 245° and Pb 80%, Sb 10%, and Sn 10%, and at 190° and Pb 40·0%, Sb 2·5%, and Sn 57·5% respectively (compare Loebe, Abstr., 1911, ii, 204). The structure often shows constituents inconsistent with equilibrium, owing to the slowness of reaction between solid constituents.  
C H. D.

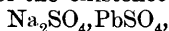
**The Solubility of Metallic Oxides and Sulphides in Fused Sodium Chloride.** H. HOUBEN (*Metallurgie*, 1912, 9, 592—600).—Tin, zinc, lead, and copper oxides, and zinc, lead, and copper sulphides are appreciably soluble in fused sodium chloride, but solution takes place very slowly, and even at 1200° the solubility has not been found to reach 1%.  
C. H. D.

**Anhydrous Sulphates.** GENNARO CALCAGNI and D. MAROTTA (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 240—246, 284—286).—The first paper deals with the thermal analysis of the systems  $\text{Li}_2\text{SO}_4$ — $\text{PbSO}_4$  and  $\text{Na}_2\text{SO}_4$ — $\text{PbSO}_4$ .

Contradictory statements have appeared as to the m. p. of lead sulphate. The authors find that it lies at 1000—1010° (decomp.). There is a transformation point at 850°, and at 950° the substance sinters.

Lithium sulphate and lead sulphate do not form any compound; there is an eutectic corresponding with 53%  $\text{Li}_2\text{SO}_4$  and 638°.

In the system  $\text{Na}_2\text{SO}_4$ — $\text{PbSO}_4$  mixed crystals are formed as far as 65%  $\text{Na}_2\text{SO}_4$ ; the eutectic corresponds with 35%  $\text{Na}_2\text{SO}_4$  and 735°. No evidence was obtained of the existence of a compound,



which is indicated in Le Chatelier's diagram of this system (*Ann. des Mines*, 1897, [ix], 11, 209).

The second paper deals with the system  $\text{K}_2\text{SO}_4$ — $\text{PbSO}_4$ , in which there is formation of mixed crystals, the gap extending from 22% to 63% of  $\text{K}_2\text{SO}_4$ . The eutectic corresponds with 40%  $\text{K}_2\text{SO}_4$  and 796°. There is evidence of the formation of the compound  $\text{K}_2\text{SO}_4, \text{PbSO}_4$  at about 620°.  
R. V. S.

**Thermal Investigation of the Phosphates of Lead.** The Constitutional Formulæ of the Phosphates and their Derivatives in the Form of Complex Salts, especially those of Thomas Slag. VIKTOR ADOLF KROLL (*Zeitsch. anorg. Chem.*, 1912, 78, 95—133. Compare this vol., ii, 755).—Mixtures of glassy phosphoric oxide and lead oxide are fused in a platinum crucible, and cooling curves are taken by means of an unprotected thermocouple. The lag is considerable, and undercooling takes place to a marked extent in the case of compounds and eutectics. The mixtures have not been examined optically.

The complete freezing-point curve has been determined. The most acid mixtures are glassy, but the softening-point is sufficiently distinct for the construction of a curve, which has a break corresponding with

the ultraphosphate. Crystallisation begins at the composition at which the pyrophosphate first appears. From this point onwards the curve has five distinct maxima, corresponding respectively with the pyrophosphate,  $2\text{PbO}, \text{P}_2\text{O}_5$ ; a new compound, the anorthophosphate,  $5\text{PbO}, 2\text{P}_2\text{O}_5$ ; the orthophosphate,  $3\text{PbO}, \text{P}_2\text{O}_5$ ; the tetraphosphate,  $4\text{PbO}, \text{P}_2\text{O}_5$ ; and an octaphosphate,  $8\text{PbO}, \text{P}_2\text{O}_5$ . The mixtures frequently expand very largely after solidification, and other indications show that equilibrium is not readily attained, other compounds probably being formed at lower temperatures. The bearing of these results on the nature of the basic calcium phosphates in Thomas slag is discussed, especially in regard to the tetraphosphate, which is sometimes obtained in a crystalline form. Constitutional formulæ are assigned to many of the basic phosphates and the apatite group, on the assumption of a group  $(\text{P}_2\text{O}_5)_3$ .

C. H. D.

**The Alloys of Thallium and Tellurium.** MASUMI CHIKASHIGÉ (*Zeitsch. anorg. Chem.*, 1912, 78, 68—74).—Thallium and tellurium may be fused together in Jena glass tubes in hydrogen. The freezing-point curve has a single maximum at  $428^\circ$ , corresponding with the compound  $\text{Te}_2\text{Tl}_3$ , whilst a break on the curve at  $305^\circ$  and 40.5% Te corresponds with a second compound  $\text{TeTl}$ . The eutectic point lies at  $200^\circ$  and 58.5% Te. The alloys separate into two liquid layers between the limits 1.5 and 24% Te at  $393^\circ$ . Solid solutions are only formed by the compound  $\text{Te}_2\text{Tl}_3$  with 5.5% of thallium. This compound is very brittle, whilst the compound  $\text{TeTl}$ , which forms long needles, is much less so.

C. H. D.

**Melting Point of Cupric Oxide.** ROLAND E. SLADE and FREDERICK D. FARROW (*Zeitsch. Elektrochem.*, 1912, 18, 817—818).—Wöhler (compared Abstr., 1907, ii, 33) has found that cupric oxide, heated in a current of oxygen at atmospheric pressure, melts at  $1085^\circ$ . The authors show that under these conditions partial decomposition of the cupric oxide takes place with formation of cuprous oxide, and the liquid contains more than 50% of the latter oxide. The liquid solidifies completely about  $1064^\circ$ , and this was taken by Wöhler as the melting point of cupric oxide. When cupric oxide is heated to  $1148^\circ$  under an oxygen pressure of 2.5 atmospheres, partial decomposition occurs, but no fusion takes place.

G. S.

**The Liquidus Curves and Constitutional Diagram of the Ternary System Aluminium-Copper-Zinc.** HENRY C. H. CARPENTER and C. A. EDWARDS (*Intern. Zeitsch. Metallographie*, 1912, 2, 209—242).—The liquidus surface of this ternary system has been determined for all alloys containing more than 40% of copper, and the constitution of those containing 16% or less of zinc. Ternary compounds and a ternary eutectic are not formed. There is one univariant line on the surface, connecting the  $\alpha\beta$ -transformation points in the copper-aluminium and copper-zinc series respectively. The two  $\alpha$ -constituents are perfectly miscible. The eutectoid line representing the transformation  $\beta \rightarrow \alpha + \gamma$  is a continuous one, extending from  $570^\circ$  on the aluminium side to  $470^\circ$  on the zinc side.

The thermal change is much greater in those alloys which are rich in aluminium. The microscopic structure of the ternary alloys accords well with the thermal indications. C. H. D.

**Passivity of Iron under Boiler Conditions.** HORACE G. BYERS and FLOYD T. VORIS (*J. Amer. Chem. Soc.*, 1912, **34**, 1368—1379).—Cushman (*Off. Public Roads, U.S. Dept. Agric.*, Bull. **30**, 29) has suggested that the pitting of boilers could be prevented by the introduction of small quantities of substances which inhibit rusting. In view of the work of Dunstan and Hill (*Trans.*, 1911, **99**, 1835) and others, a study has been made of the effect of potassium dichromate.

It has been found that iron as an anode is rendered passive by dichromate solutions of concentration as low as 0.125%, and is kept passive, even when the anode current is very small, at all temperatures from the ordinary temperature up to 160°. When moderate quantities of sodium chloride are present, the concentration of the dichromate necessary to maintain the passive condition is, at the ordinary temperature, about 40 times as great as that of the sodium chloride; at 93°, 25 times as great, and at 125—150°, 40 times as great. In presence of sodium sulphate of moderate concentrations, an equal concentration of dichromate is sufficient to ensure passivity at all temperatures up to 150°. Carbonates and hydrogen carbonates do not seem to have any destructive effect on the passivity induced by the dichromate.

From these results, it seems probable that the addition of a quantity of potassium dichromate, forty times as great as that of the chlorides present, calculated as NaCl, in addition to that needed to precipitate the scale-forming substances, would be of much value as a boiler preservative. The extent to which the results obtained were due to the effect of the anodic current, however, is not known, and experiments are therefore being made to ascertain the length of time during which iron will remain free from rust in such an inhibitive solution in the absence of the electric current. E. G.

**The System Iron-Carbon.** ANDREAS SMITS (*Zeitsch. Elektrochem.*, 1912, **18**, 816—817. Compare this vol., ii, 769; Ruff, *ibid.*, ii, 353).—The view of the author that the form of the iron-carbon equilibrium diagram indicates the existence under certain conditions of a number of iron carbides, has now been confirmed by the experimental work of Wittorf (this vol., ii, 259). In some respects Wittorf's theoretical treatment of the subject is inaccurate, and the matter will be fully considered in a later communication. G. S.

**The Intercrystalline Fracture of Iron and Steel.** J. C. W. HUMFREY (*Iron Steel Inst. Carnegie Mem.*, 1912, **4**, 80—107).—Electrolytic and other pure forms of iron become extremely brittle when annealed above 670° in an atmosphere containing a small quantity of oxygen or carbon dioxide, fracture taking place between the crystals instead of through them. If the annealing is conducted under a very low pressure, the  $\gamma$  and  $\alpha$  crystalline boundaries become visible, the fracture occurring along the former. The brittleness does not occur if oxidising gases are present in sufficient quantity to form

a continuous layer of oxide, and it increases with the time of annealing. The softness of the metal is restored by quenching from  $1000^{\circ}$ , or by heating in hydrogen at  $1000^{\circ}$  for a sufficient time, but not by annealing. These facts are explained by the formation of a lower oxide which forms a solid solution with  $\gamma$ -iron, but is insoluble in  $\alpha$ -iron, and is therefore thrown out of solution during slow cooling, forming thin intercrystalline layers. Quenching from above the transformation point retains this constituent in solid solution, whilst heating in hydrogen reduces it to the metallic state. C. H. D.

**The Constitution of the Sulphide Enclosures in Iron and Steel.** G. RÖHL (*Iron Steel Inst. Carnegie Mem.*, 1912, 4, 28—79).—The mixtures are prepared from electrolytic iron, annealed in a vacuum, ferrous sulphide, prepared by heating pure pyrites in a porcelain tube in nitrogen, and manganous sulphide freed from oxygen by mixing with sulphur and heating in hydrogen. The ingredients are melted together in fireclay tubes in a carbon-resistance furnace. Ferrous and manganous sulphides are best distinguished by etching lightly with picric acid, and then heating the dry specimen until the ferrite becomes yellow. The ferrous sulphide then appears dark blue, and manganous sulphide pale grey.

Manganous sulphide melts at  $1620^{\circ}$ , and does not attack porcelain when free from oxygen. The eutectic point of its mixtures with ferrous sulphide lies at  $1182^{\circ}$  and 7% MnS. A compound,  $3\text{FeS}, 2\text{MnS}$ , m. p.  $1362^{\circ}$ , exists, and forms solid solutions in all proportions with manganous sulphide. Manganous sulphide appears to be immiscible with iron in the molten state. C. H. D.

**The Action of Oxygen on Heated Iron under Pressure.** JAROSLAV MILBAUER (*Chem. Zeit.*, 1912, 36, 1170—1171).—Iron in the form of sheet or tube is not oxidised by dry oxygen at  $500^{\circ}$  under 12 atmospheres pressure, but remains bright. Even at  $550^{\circ}$  only a thin film of oxide is produced. C. H. D.

**The System Nickel-Cobalt.** RUDOLF RUER and KIOSUKE KANEKO (*Metallurgie*, 1912, 9, 419—422).—A new investigation of this system by thermal and magnetic methods confirms, in general, the conclusions of Guertler and Tammann (*Abstr.*, 1905, ii, 92). The interval between the two magnetic transformation curves is very small, not exceeding  $4^{\circ}$ . All the alloys of the series have a uniform polygonal structure, those towards the cobalt end of the series, including pure cobalt, showing repeated twinning, which is absent from the alloys rich in nickel.

Nickel readily dissolves nickel oxide, the freezing point being lowered, and a well defined eutectic structure produced.

C. H. D.

**Gold Organosol.** CONRAD AMBERGER (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 100—101).—Details are given of the preparation of colloidal gold by the method described in the previous paper (this vol., ii, 1053). Complete reduction of the initially precipitated oxide is effected by the

addition of hydrazine hydrate. The product, containing lanolin as protective colloid, dissolves in ethyl ether, light petroleum, fats, and liquid paraffin, giving colloidal solutions of a deep blue colour; it is very readily soluble in chloroform, giving reddish-violet solutions. By precipitation of the colloidal solution in light petroleum by the addition of alcohol, a pasty product containing 84% of gold is obtained. When dried, the preparations which contain a large percentage of the metal consist of granular masses of a golden-brown colour. These dissolve readily in chloroform, fats, and liquid paraffin, but only to a small extent in light petroleum and ethyl ether.

H. M. D.

**Reduction of Auric Chloride by an Ethereal Solution of Phosphorus.** ANT. GALECKI (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 105—110).—An examination has been made of the changes in colour and electrical conductivity which accompany the formation of colloidal gold when aqueous solutions of auric chloride are reduced by means of an ethereal solution of phosphorus. The purple-red colour assumed by the solutions at the ordinary temperature does not correspond with complete reduction, for if the solutions are boiled, the electrical conductivity increases until a definite maximum value is reached. The final maximum, which is attained by a given solution of the gold salt, is found to be considerably less if potassium carbonate is added to the gold solution before reduction. This is probably due to neutralisation of the acids which are liberated in the reaction. In consequence of this, the reduction at the ordinary temperature proceeds more completely when potassium carbonate is added in small quantity to the original solution.

H. M. D.

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### Mineralogical Chemistry.

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**Arsa Coal.** EDUARD DONATH and A. INDRA (*Chem. Zeit.*, 1912, 36, 1118—1120).—This coal, found in Carpano, Istria, has been classified by some authors as a lignite and by others as a true coal. On the basis of the following results, the authors regard it as a true coal. It has the following percentage composition :

Moisture.	C.	H.	O.	N.	S.	Ash.	Calorific value, calories.
1.83	65.6	4.58	17.14	1.24	9.01	11.44	6618

It absorbs very little moisture when exposed to air saturated with water vapour, "cakes" when heated, gives a pale-coloured extract with potassium hydroxide solution, yields a tar containing phenol, aromatic hydrocarbons and a little paraffin on destructive distillation, gives a red solution showing a green fluorescence on extraction with benzene, is scarcely attacked by dilute nitric acid at 100°, is not dissolved by a mixture of sulphuric acid and potassium dichromate, and behaves like true coal towards (1) melted alkali hydroxides and (2) a mixture of sulphuric and nitric acids.

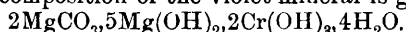
The coal is peculiar in containing 7.90% of its sulphur in the form of organic compounds, and the tar produced on destructive distillation has a strong odour of "ichthyol," the tarry product obtained by the destructive distillation of Seefeld shales. T. A. H.

**Marcasite from Castelnovo di Porto.** G. SIROVICH (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 352—354).—The marcasite has the following composition:

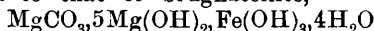
Fe.	S.	As.	SiO <sub>2</sub> .	Total.
46.20	53.25	0.32	0.24	100.01

It occurs in crusts and also in stalactites in the neighbourhood of ferruginous springs and natural hydrogen sulphide, and is thus still being formed by the method of Allen, Crenshaw, and Johnstone (this vol., ii, 354) which those authors suggested was responsible for the natural production of this mineral. R. V. S.

**A New Chromiferous Magnesium Hydroxy-carbonate.** LAURA HEZNER (*Centr. Min.*, 1912, 569—571).—In a bright green serpentine (anal. I) from Dundas, Tasmania, are lilac-coloured, lenticular masses, which are composed largely (83.51%) of a scaly micaceous mineral intermixed with some serpentine and chromite. Deducting from anal. II. the silica as serpentine and the ferrous oxide as chromite, the composition of the violet mineral is given as



This is analogous to that of brugnattellite,



(Abstr., 1909, ii, 247), and the mineral may be described as a *chrom-brugnattellite*:

	SiO <sub>2</sub> .	CO <sub>2</sub> .	Cr <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	H <sub>2</sub> O ( < 120° ).	H <sub>2</sub> O ( > 120° ).	Total.	Sp. gr.
I.	38.70	—	3.60	2.54	40.75	0.81	14.01	100.41	2.53
II.	3.87	10.45	20.44	1.10	37.12	0.95	26.31	100.24	2.16

L. J. S.

**Formation of Apatite.** RICHARD NACKEN (*Centr. Min.*, 1912, 545—559).—Fluor-spar (m. p. 1392°) when fused with an excess of calcium phosphate gives needles of fluor-apatite ( $3\text{Ca}_3\text{P}_2\text{O}_8, \text{CaF}_2$ , m. p. about 1650°); there is a eutectic with 64%  $\text{CaF}_2$  at 1205°. Fusions containing calcium chloride (m. p. 772°) and calcium phosphate give chlor-apatite ( $3\text{Ca}_3\text{P}_2\text{O}_8, \text{CaCl}_2$ , m. p. 1530°), and also the compound  $\text{Ca}_3\text{P}_2\text{O}_8, \text{CaCl}_2$ ; the latter is stable only below 1040°. Calcium fluoride and chloride together do not form mixed crystals, but a eutectic with 16%  $\text{CaF}_2$  at 650°. Fluor-apatite and chlor-apatite form a continuous series of mixed crystals. The crystallisation of the ternary system  $\text{CaCl}_2\text{--Ca}_3\text{P}_2\text{O}_8\text{--CaF}_2$  is discussed. L. J. S.

**Constitution of the Volcano of the Island of Reunion.** ALFRED LACROIX (*Compt. rend.*, 1912, 155, 538—544).—In addition to the basaltic lavas of which this island is largely composed, there are ancient intrusive rocks of which the following are selected as types:

Series *A*.—Dunites, harrisites, felspathic picrites, and olivine-gabbros. Series *B*.—Microgabbros and gabbros. Series *C*.—Essexitic gabbro, ophitic basalt, trachyandesite with olivine (resembling mugearite), akerite, phonolitic trachyte, and quartz-syenite with ægirite and katoforite. Analyses by Boiteau are given of the rocks of each of these types. The wide range in composition is illustrated by the following analyses of the extreme members and one from the series *B*; I, dunite; II, microgabbro; III, quartz-syenite with ægirite and katoforite:

	SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	CaO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	TiO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub> .	Loss on ig- nition.	Total.
I.	39·85	0·65	—	12·95	45·09	0·99	0·19	0·09	0·10	0·09	—	100·00
II.	43·28	13·58	5·43	8·03	7·63	13·19	2·04	0·66	3·81	0·41	1·82	99·86
III.	64·01	13·96	7·31	0·20	0·21	1·02	5·30	5·10	1·66	0·08	1·38	100·23

These different types have been produced by differentiation from the same magma. They represent both the sub-alkaline and the alkaline groups which have been regarded as typical of the igneous rocks of different regions of the world (the Pacific and the Atlantic facies).

L. J. S.

## Physiological Chemistry

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**A Respiration Apparatus for Animals of Medium Size.** FRANZ TANGL (*Biochem. Zeitsch.*, 1912, 44, 234—251).—The apparatus, which is illustrated by several figures, is intended for animals of the size of sheep or pigs. In principle, it is a Pettenkoffer-Voit apparatus, with two alternative methods for estimating the respiratory products and oxygen consumption. The one of these methods is, in its essentials, an Attwater-Benedict apparatus, by means of which the total amount of water and carbon dioxide formed during the whole course of the experiment is estimated. The other alternative method is a modification of the Tigerstedt-Sondén apparatus, by means of which an aliquot part of the air from the chamber is drawn off into receivers and analysed from time to time. Both methods can be used at once, the latter determining the variations of respiration at different intervals of the experiment. The methods of ventilating the cage and of introducing foodstuffs is also described, and also the process of estimating the hydrogen and combustible gases (methane) formed by the animal during the experiment. For the last-named purpose, a portion of the expired air is, after deprivation of its carbon dioxide and water vapour, passed over platinised kaolin, and the carbon dioxide and water vapour formed in this process is estimated in the usual manner.  
S. B. S.

**The Action of Phloridzin on Gaseous Metabolism and on the Work of the Kidneys.** ALEXANDER BELÁK (*Biochem. Zeitsch.*, 1912, 44, 213—234).—The experimental method was the same as that

generally adopted in Tangl's laboratory of determining the respiratory quotient of the animal (dog) before and after the removal of an organ under varying conditions. It was found that in "non-toxic" doses, phloridzin increases the oxygen consumption of the organism, partly by increasing the work of the kidneys, and partly by increasing the work of other organs of the body. Phloridzin can also act toxically. If this is the case, the oxygen consumption diminishes, and the blood-pressure sinks.

S. B. S.

**The Gaseous Metabolism of the Heart and Lungs.** C. LOVATT EVANS (*J. Physiol.*, 1912, 45, 213—234).—In the dog, the carbon dioxide output of the heart-lung varies from 3 to 5 c.c. per gram of heart per hour, and the oxygen intake 3.5 to 6 c.c. (or 0.058 to 0.1 c.c. per minute); the values in the cat are somewhat lower. The respiratory quotient for the heart averages 0.9, but it varies greatly, and under conditions of augmented oxygen usage may be very low (0.6 or less). A rise of temperature from 32° to 39° increases the gaseous exchanges, which is almost proportional to the increase in the number of heart beats. The efficiency of the beat as a machine is low (from 2 to 10%); this is owing to the peculiar mechanical conditions of the heart beat. The original paper must be consulted for the forms of apparatus employed. In the isolated lung the total metabolism is small, and has to be corrected for metabolism in the blood itself.

W. D. H.

**The Capacity of the Air Passages under Varying Physiological Conditions.** C. G. DOUGLAS and JOHN S. HALDANE (*J. Physiol.*, 1912, 45, 235—238).—During the hyperpnoea of muscular work there is a great increase in the effective dead space in breathing, due to dilatation of the bronchial passages.

W. D. H.

**Lactic Acid Formation in Blood. II.** BRIGITTE KRASKE (*Biochem. Zeitsch.*, 1912, 45, 81—87. Compare Fries, Abstr., 1911, ii, 994).—The author confirms the results of Fries, who showed that human blood contains appreciable quantities of lactic acid, which increase on incubating the mixture for various times up to two hours. She also shows that there is a corresponding diminution in the amount of sugar, which in four out of the five cases investigated is almost identical in amount with that of the lactic acid formed. The sugar would therefore appear to be the substance from which the lactic acid is formed.

S. B. S.

**Lactic Acid Formation in Blood. III.** KURA KONDO (*Biochem. Zeitsch.*, 1912, 44, 88—93).—As in human blood, so in dog's blood, there is an increase of lactic acid and diminution of sugar when the blood is incubated up to periods of two hours. The diminution of sugar is more than sufficient to account for the increase in lactic acid. The lactic acid, isolated as a zinc salt, was estimated by von Fürth and Charnass's method, but the author shows that when the acids in the fresh blood and the incubated blood are estimated gravimetrically,

a correct amount for the increase is obtained, as the same amount of impurities is present in the zinc salt got from the two samples.

S. B. S.

**Lactic Acid Formation in Blood. IV.** KARL VON NOORDEN, jun. [with ELFER and PIANTONI] (*Biochem. Zeitsch.*, 1912, 45, 96—107).—According to Lépine, the destruction of sugar is confined to the corpuscles of the blood, the serum taking no part in the action. It is shown now by Elfer and Piantoni, an abstract of whose work is given by the author, that only the corpuscles on incubating show an increase of lactic acid on incubation, the serum showing practically no increase. These results conform to results of the previous communications of Kraske and of Kondo, that the lactic acid is formed from the sugar of the blood. This conception is further confirmed by the author, who shows, in numerous experiments, that the amount of lactic acid formed can, on incubation, be considerably increased by the addition of dextrose. It is shown that the increase of lactic acid on incubation can be determined accurately by the gravimetric method (weighing as zinc salt), and by the volumetric method of von Fürth and Charnass. Pure *d*-lactic acid could be isolated in the form of its zinc salt.

S. B. S.

**The Hydroxyl Ion Concentration of the Blood in Hyperthermia Produced by Heat Piqûre.** G. QUAGLIARIELLO (*Biochem. Zeitsch.*, 1912, 44, 162—164).—In rabbits, hyperthermia caused by heat piqûre of the brain produces no change in the reaction of the blood.

S. B. S.

**The So-called "Lipolysis" [in Blood].** L. BERCZELLER (*Biochem. Zeitsch.*, 1912, 44, 193—200).—See this vol., ii, 1109.

**The Division of the Blood Sugar between the Corpuscles and Plasma.** RUDOLF HÖBER [with FELIX SPERLING] (*Biochem. Zeitsch.*, 1912, 45, 207—220).—Estimations were made on the blood of dogs and rabbits of the sugar in the corpuscles and plasma, both in normal cases and in animals rendered hyperglycæmic, either by extirpation of the pancreas, injection of adrenaline or production of alimentary glycosuria. It was found that in changing the total sugar content of the blood, no parallelism could be detected between the changed amounts in the plasma and in the corpuscles. This would have been expected if the corpuscles had been, in a physical sense, permeable to sugar, provided that the sugar had not been destroyed when inside the corpuscles. Experiment, however, indicates that such chemical changes cannot alone account for this want of parallelism. The conclusion is drawn that the corpuscles themselves possess a mechanism for regulating their sugar supply, and in accordance with the experiments of the author and of those of Frank and Bretschneider in the case of adrenaline-glycæmia, the excess of sugar remains entirely in the plasma. The same is probably also true for other cases of hyperglycæmia.

S. B. S.

**Coagulation of Blood.** EMIL ZAK (*Arch. expt. Path. Pharm.*, 1912, 70, 27—54).—A diminution of the lipoids of the plasma (oxalate plasma of horse) leads to a delay in its coagulation. Phosphatides from other organs (brain) act even more strongly than those naturally present in the blood in aiding coagulability. Fermentative splitting of the plasma lipoids leads to the occurrence of an uncoagulable state. Certain alkaloids which unite with lecithin are also inhibitory to coagulation. Such results agree with the views of Alexander Schmidt on zymoplastic substances, and render the assumption of thrombokinas (Morawitz) unnecessary.

W. D. H.

**Hæmolysis by Formaldehyde.** PHILIPP EISENBERG (*Biochem. Zeitsch.*, 1912, 45, 303—327).—Formaldehyde solutions of 8% and higher concentrations lyse and precipitate blood-corpuscles, whereas solutions of 4% or less leave them apparently unchanged, but fix them, the time of fixing depending on the concentration. The corpuscles treated with weak formaldehyde are rendered, however, osmotically hypersensitive, and lyse on dilution with isotonic salt solution. There appears to be a substance inhibitory to the hæmolysis in the treated corpuscles, the action of which is weakened on dilution. This is either formaldehyde itself, or some product of its action on the corpuscles; for formaldehyde can inhibit the hæmolysis of the corpuscles which have been treated with the aldehyde itself, the dilution serving for this purpose being half the concentration with which they have been treated.

An action similar to that of formaldehyde is produced by a combination of saturated salt solutions and formic acid. The formaldehyde action is strengthened by a higher concentration of neutral salts, and the hæmolysis of the treated corpuscles is inhibited. The hæmolytic action of alcohol, phenol, saponin, chloral hydrate, and sodium glycocholate is increased by formaldehyde. Acetone inhibits the hæmolytic action of the stronger formaldehyde solutions, but accelerates that of the weaker ones; hæmolysis by acetone is strongly inhibited by formaldehyde. Hæmolysis by potassium cyanide and permanganate, and ammonia is inhibited by higher formaldehyde concentrations, but accelerated by lower ones. Hæmolysis by potassium hydroxide, calcium bromide, and potassium arsenite is inhibited by formaldehyde. Hæmolysis by urea is strengthened. Hæmolysis by strong formaldehyde solutions is inhibited by urea, whereas that produced by weaker solutions is strengthened. Serum does not inhibit formaldehyde hæmolysis.

S. B. S.

**The Cholesterase of Blood-corpuscles.** SEWERYN CYTRONBERG (*Biochem. Zeitsch.*, 1912, 45, 281—283).—In opposition to results recently obtained by Schultz (this vol., ii, 852), the author finds that horse-blood contains a ferment capable of hydrolysing the cholesterol esters contained in the blood, as there is an increase of this substance, which was precipitated by digitonin, after incubation of the blood. In the plasma alone, no cholesterase could be detected. The experiments also demonstrate the presence both of cholesterol and its esters in the blood-corpuscles.

S. B. S.

**The Union of Thymol in Red-blood Corpuscles.** RYUTA USUI (*Zeitsch. physiol. Chem.*, 1912, 81, 175—182).—The greatest amount of thymol is united to the stromata of the red-blood corpuscles; these constituents contain about half of the thymol taken up, although their nitrogen content is only one-eighth of the total in the cells. This relationship is not materially altered by removing the lipoids by boiling with alcohol and ether; as what then remains is almost completely nucleic acid and histone, it is probable that these form a compound with the thymol. W. D. H.

**The Changes of Hydrogen Ion Concentration Produced by the Action of Pepsin, and the Acid-combining Capacity of Some Hydrolysis Products of Egg-albumin.** HUGO ROHONYI (*Biochem. Zeitsch.*, 1912, 44, 165—179).—In an egg-albumin solution in hydrochloric acid, the  $H^+$  concentration diminishes considerably during peptic digestion, but the  $Cl^-$  concentration remains practically unchanged. The diminution of the  $H^+$  concentration is explained by the greater combining capacity of the products of peptic scission for  $H^+$  ions than that of the original protein. The same is true for products of tryptic digestion. This does not explain the fact that the  $Cl^-$  concentration remains unchanged during digestion, and the combining capacity for  $Cl^-$  ions also increases during digestion. The diminution of conductivity during digestion is smaller than can be accounted for by the decrease of the  $H^+$  concentration. S. B. S.

**The Adaptative Capacity of the Alimentary Tract to Ferment Formation.** ARMIN VON TSCHERMAK (*Biochem. Zeitsch.*, 1912, 45, 452—461).—The experiments were carried out on rabbits with the object of ascertaining whether the animals if fed on carbohydrates, which were not customary constituents of their foods, acquire the capacity of producing ferments in their alimentary tract which could hydrolyse such substances. The carbohydrates were lichenin and inulin, and as their source, Iceland moss and Jerusalem artichoke bulbs were employed, these products being added to the ordinary foodstuffs over prolonged periods. Extracts were then made of the pancreas and mucous membrane of the small intestine, which was incubated with the carbohydrates. The digest was then treated with yeast, and the amount of carbon dioxide evolved was measured. Evolution of this gas indicated the production of dextrose as a result of enzyme action. The author draws the conclusion that, in the majority of cases investigated, the animals acquire the capacity of forming a licheninase and inulase in their alimentary tract. S. B. S.

**The Digestion of Inulin.** HENRY BIÉRRY (*Biochem. Zeitsch.*, 1912, 44, 402—414).—No inulase has been found in the higher animals. The gastric juice of such animals, however, is capable of hydrolysing inulin by virtue of the hydrochloric acid which they contain. The gastric juice of the snail (*Helix pomatia*) contains a true inulase, which is destroyed on heating. S. B. S.

**The Stomach Lipase.** HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1912, 45, 284—302).—The author has found that the method of investigating lipase content, by a stalagmometric measurement, using triolein emulsions, as recommended by Izar, is unsatisfactory. He has employed, instead, stalagmometric measurements of a saturated tributyrin solution. It was found that the inhibitory action of sodium fluoride is greater on the pancreas lipase than on the stomach lipase. The optimal action of the former is with the hydrogen ion concentration  $1.0 \times 10^{-8}$ , and with the latter  $2.0 \times 10^{-6}$ . The two ferments appear, therefore, to be different, and the facts offer support for the supposition of the existence of a distinct gastric lipase. S. B. S.

**The Effects of Section of the Spinal Cord on Temperature and Metabolism.** ERNEST L. KENNAWAY and MARCUS S. PEMBREY (*J. Physiol.*, 1912, 45, 82—105).—When the posterior portion of an animal's body is paralysed owing to division of the spinal cord, that part responds to changes in external temperature like a cold-blooded animal. The effect on the respiratory exchange is the resultant between what occurs in the paralysed half of the body and the anterior half which still remains normal. The latter portion in its attempt to maintain normal conditions draws upon the paralysed muscles, which waste for the increased supply of combustible material needed. W. D. H.

**The Influence of Ammonium Salts and Acetates on the Nitrogenous Metabolism of Carnivora.** ERNST PESCHECK (*Biochem. Zeitsch.*, 1912, 45, 244—280).—In view of the experiments of Grafe, Abderhalden, and others on the apparent capacity of ammonium salts to maintain animals in nitrogenous equilibrium in the absence of other sources of nitrogen in the food, the effect of various ammonium and other salts on the nitrogenous metabolism has been investigated by the author. Dogs were placed on a basal diet with insufficient protein to maintain equilibrium, and then on the same diet with addition of salts, and finally for a period on the original basal diet. The effect of the salts on the degradation of body protein could thereby be ascertained. It was found that ammonium lactate had no effect. Ammonium acetate, on the other hand, caused a diminution of the nitrogen output, which could not be increased by the addition to the diet of raw fibre. Sodium acetate also causes diminution of the nitrogen output, and at the same time a marked diuresis. A mixture of the acetates of sodium, potassium, calcium, and magnesium was without effect. Calcium acetate alone had a deleterious action on the nitrogenous output. The results generally indicate that salts, as such, can influence the nitrogen balance, and that the maintainance of nitrogenous equilibrium by ammonium salts does not indicate that the latter can replace proteins in a diet.

S. B. S.

**The Calcium, Magnesium, Phosphorus, and Nitrogen Metabolism of the Growing Pig.** STEPHAN WEISER (*Biochem. Zeitsch.*, 1912, 44, 279—289).—There is a continuous deficit in calcium and

phosphorus in a growing pig when fed on an exclusive maize diet, which continues even after the addition of meat and fat. There is at the same time a retention of magnesium. The addition of calcium carbonate, not only stops this deficit, but causes a marked retention of calcium and phosphorus; there is a corresponding diminution in the magnesium retention. The amount of calcium carbonate which can produce this marked calcium retention is 10—11 grams per kilo. of living body-weight of the animal. These facts indicate the importance of addition of calcium carbonate to the ordinary maize and barley diet of young pigs. S. B. S.

The Minimal Energy Needs of the Pig. (Metabolism of Matter and Energy during Starvation.) FRANZ TANGL (*Biochem. Zeitsch.*, 1912, 44, 252—278).—It was found, by the ordinary methods of metabolism experiments, that the smallest energy needs of a fattened pig were at a temperature of 20—23°. These do not diminish in the fattened animal when the temperature sinks down to 16°, whereas, in growing animals, on account of the chemical heat regulation, the energy needs sink on lowering the temperature. There is little difference between the minimal energy needs of the fattened and the unfattened growing animal. For the former they were calculated as 19.6 Calories per kilo. and 1060 Calories per square metre of body surface. S. B. S.

The Nutrition and Metabolism of Marine Animals in Relation to (a) Dissolved, (b) Particulate Organic Matter of Sea-water. BENJAMIN MOORE, EDWARD S. EDIE, EDWARD WHITELEY, and W. J. DAKIN (*Biochem. J.*, 1912, 6, 255—296).—It has been suggested that marine organisms can utilise as foodstuff either the plankton or the dissolved organic matter ordinarily distributed in the water. The latter theory has been put forward more especially by Pütter. The authors show that both theories are theoretically unlikely. They criticise Pütter's experimental methods, pointing out his errors of technique, and have themselves made several estimations of the organic matter in the various samples of the whole sea-water, and of the organic matter filtered off from the same by the finest tow-nets and by Chamberland filters. They find that in all cases the quantity of organic matter is very small, quite insufficient for the purposes of nutrition. They have, furthermore, estimated the energy needs of various marine organisms by estimating the carbon dioxide output and oxygen intake in sea-water. So far from finding a diminution of organic matter in the water under these conditions, they find an increase, suggesting that part of the organic matter is actually to be ascribed to the excreta by the organisms. They draw the conclusion from the latter experiments that the organic matter in sea-water is much too small to satisfy even the minimal energy needs of the marine organisms.

In the marine animals employed for experiments, the respiratory quotients were greater than 1. To explain this fact it is suggested that the body contains some oxygen storage in the tissues.

S. B. S.

**The Work of the Pancreas, and its Influence on the Combustion of Carbohydrates.** FRITZ VERZÁR (*Biochem. Zeitsch.*, 1912, 44, 201—212).—After extirpation of the pancreas, the oxygen consumption and carbon dioxide output sink and then rise again. Owing to the general disturbance of the whole organism, it is not possible to calculate the work of the pancreas. If the work is calculated on the effect produced in the first hour after extirpation, it would appear, however, that the pancreas uses up 8% of the oxygen. After extirpation, the respiratory quotient sinks gradually, reaching a constant value some hours after the operation. This seems to indicate that some substance disappears which keeps the respiratory quotient high, that is, regulates the combustion of the carbohydrates. If dextrose is injected intravenously a short time after the extirpation of the pancreas, there is a rise of the respiratory quotient, a fact which seems to indicate that sugar can be burnt without the pancreas. Starch injected intravenously is not, however, burnt, as, apparently, it is not first hydrolysed in the blood. S. B. S.

**The Uptake and Value of Calcium and Phosphoric Acid in the Intestine.** F. ZUCKMAYER (*Pflüger's Archiv*, 1912, 148, 225—256).—In isolated loops of intestine (rabbit and dog), the calcium and phosphoric acid are much better absorbed when administered in the form of a colloidal preparation called "tricalcol" than when inorganic phosphates mixed with protein are given. The preparation is recommended for therapeutic purposes. W. D. H.

**Absorption of Monoglycerides of the Higher Fatty Acids.** ALFRED ARGYRIS and OTTO FRANK (*Zeitsch. Biol.*, 1912, 59, 143—164).—From experiments on dogs fed on monoglycerides, the conclusion is drawn that these are completely broken down in the process of digestion, and appear in the chyle as triglycerides. W. D. H.

**The Ferments Capable of Hydrolysing Sucrose.** HENRY BRÉRY (*Biochem. Zeitsch.*, 1912, 44, 415—425).—A sucrase is located in the cells of the mucous membrane of the small intestine of higher animals (dogs and rabbits), which can be filtered through a Berkefeld filter. It loses its activity on dialysis, but this activity is restored by the addition of chlorides, especially sodium chloride. The presence of an electronegative ion appears to be indispensable for its action. A sucrase is not found either in the pancreas or the liver. It can be extracted from the intestinal mucous membrane of the ripe foetus. It is not found in the clear secreted intestinal juice. S. B. S.

**An Explanation of Chauveau's Experimental Results, which Indicate the Diminished Value of Fats as Compared with Carbohydrates as Source of Energy in Muscular Work.** NATHAN ZUNTZ (*Biochem. Zeitsch.*, 1912, 44, 290—291).—The author claims priority for the explanation of Chauveau's experiments recently offered by Fridericia (this vol., ii, 853). S. B. S.

**Fat Metabolism.** ERNST FREUDENBERG (*Biochem. Zeitsch.*, 1912, 45, 467—487).—The liver of rabbits, during aseptic autolysis, can

hydrolyse neutral fats quantitatively when they exist in the proportion of 2%. In other organs, the lipoclastic action is less marked. It exists in the organs in the following (diminishing) order: spleen, muscles, lungs, kidneys, lymph glands. In the fatty tissues and blood, the lipoclastic action is very small. The content of fat in a fasting dog shows no diminution as compared with that in the fed animal. After withdrawal of blood, the fat rapidly increases in the blood to its normal proportions. From this fact the conclusion is drawn that the organism possesses some special mechanism for regulating the fat supply in the blood. S. B. S.

**Ovomucoid and Sugar in the White of the Bird's Egg.** CARL TH. MÖRNER (*Zeitsch. physiol. Chem.*, 1912, 80, 430—473).—A detailed account of the properties of ovomucoid and its amount in the white of the eggs of various birds. There appear to be two varieties of egg-white, which can be distinguished by the author's "perch extract reaction" as positive and negative; this is due to differences in the ovomucoid. Similar quantitative details are given in reference to sugar. W. D. H.

**Gaseous Metabolism of the Liver. I.** JOSEPH BARCROFT and LEWIS E. SHORE (*J. Physiol.*, 1912, 45, 296—306).—The methods of collecting blood and determining the rate of flow through the liver are modifications of those previously employed in similar experiments on other organs. In the present research, cats were employed, and the hepatic artery was found to be the dominating source of oxygen supply to the liver especially in fed animals. The amount of oxygen used does not appear to be governed by the blood supply if above a certain limit, either in liver or intestines. The amount of oxygen used in the liver at rest (that is, animals fed thirty-six hours previously) varies from 0.005 to 0.018 c.c. per gram per minute, and for the viscera drained by the portal vein taken together the figures are 0.008 to 0.013 c.c. The resting value for the liver is thus lower than that of the salivary glands and pancreas, and the highest figures are about equal to that found in the kidney. Increase in the gaseous metabolism occurs when the organs are more active (that is, eighteen hours after feeding), the figures for oxygen used being 0.024 to 0.050 c.c. for the liver, and 0.011 to 0.018 c.c. for the viscera of the portal area. These figures are also less than those found in other active secreting organs, but the work is to be continued in animals where the liver is rendered still more active. W. D. H.

**Lactic Acid Formation in the Artificially Perfused Liver.** I. GUSTAV EMBDEN and FRIEDRICH KRAUS (*Biochem. Zeitsch.*, 1912, 45, 1—17).—The lactic acid was estimated in the blood before and after perfusion, in the form of its zinc salt, the proteins being precipitated by hydrochloric acid and mercuric chloride, and the zinc salt prepared from the ethereal extract of the protein-free liquid after separation of phosphoric acid, which is found in the ethereal extract as lead salt, this acid being employed to acidify the liquid before extraction with ether. No lactic acid is formed when a glycogen-free liver of a

dog (which had been starved and poisoned with strychnine to free the liver from glycogen) is perfused with ox-blood. On the other hand, when a liver rich in glycogen (of a well-fed animal which had received large quantities of sugar) is treated in the same way, there is a considerable amount of lactic acid formed. If, to the perfusing blood, dextrose or *dl*-alanine is added, lactic acid is formed. The experiments indicate that both proteins and carbohydrates can serve as a source of lactic acid. In the case of *dl*-alanine, pyruvic acid is formed as an intermediary product. S. B. S.

**The Behaviour of Glycerol During Artificial Perfusion Through the Liver.** ERNST SCHMITZ (*Biochem. Zeitsch.*, 1912, 45, 18—29).—The glycerol content of blood, etc., was estimated by the following method (of which full details are given). The proteins were precipitated by mercuric chloride and hydrochloric acid, and the filtrate was freed from mercury in the usual way, and evaporated after neutralisation at low temperatures. The inorganic salts were precipitated by alcohol, and the alcoholic filtrate evaporated to a small bulk and treated with a mixture of alcohol and ether. The filtrate was evaporated, and the residue again treated with the alcohol-ether mixture. In the filtrate from this precipitation, the glycerol was estimated, after evaporating off all alcohol by the Zeisel-Fanto method. It was found that the glycerol content of ox-blood varied only between 0.0017 and 0.0024%, whereas that of pig's blood varied between 0.0029 and 0.0048%. This amount decreased after perfusion through a dog's liver, when the latter was glycogen-free. No decrease was observed if the latter were rich in glycogen, although there was no increase outside the range of experimental error. If glycerol is added to the perfused blood, it disappears to a large extent during perfusion, and the liver appears therefore to be able to destroy glycerol. S. B. S.

**Lactic Acid Formation in the Artificially Perfused Liver.** II. SIEGFRIED OPPENHEIMER (*Biochem. Zeitsch.*, 1912, 45, 30—43).—The technique was similar to that in Embden and Kraus's experiments. In some cases, however, the zinc lactate was not estimated gravimetrically, as it was found to be impure, but was treated by the method of von Fürth and Charnass with permanganate, whereby lactic acid was converted into acetaldehyde, which was estimated volumetrically by Ripper's method. By perfusing dog's liver, either glycogen-rich or glycogen-free, with blood to which lævulose was added, lactic acid was formed in far larger quantities than when the corresponding amount of dextrose was used. Glycerol also, under similar conditions, gives rise to lactic acid, but not either arabinose or inosite. S. B. S.

**Lactic Acid Formation in Expressed Muscle Juice.** I. GUSTAV EMBDEN, FR. KALBERLAH and H. ENGEL (*Biochem. Zeitsch.*, 1912, 45, 45—62).—Numerous experiments were carried out with the expressed juice of dog's muscle, and the lactic acid was estimated both gravimetrically as zinc salt and by the method of von Fürth and Charnass. The acid was estimated in the expressed juice of the well-cooled muscles, collected as nearly as possible under sterile conditions,

and the acid was estimated in this immediately and after incubation (with addition of small quantities of sodium carbonate to neutralise the acid), the periods of incubation lasting up to two hours. The initial quantity of lactic acid was found to increase during incubation, rapidly reaching its maximum. The authors discuss in some detail the origin of this acid, and draw the conclusion that it exists in the muscles in the form of some precursor which they call *lactacidogen*.

S. B. S.

**Lactic Acid Formation in Expressed Muscle Juice. II.** KURA KONDO (*Biochem. Zeitsch.*, 1912, 45, 63—80).—In continuation of the previous research (preceding abstract), it is now shown that the separation of lactic acid from lactacidogen is very rapid, and is practically complete in thirty minutes at 40°. Addition of acid inhibits the separation, whereas the addition of sodium carbonate accelerates it, there being a special concentration at which the optimal effect is exerted for each juice. If alkali is not added, then the lactic acid set free entirely inhibits after a certain time any further formation of acid.

S. B. S.

**The Ferments Capable of Hydrolysing Stachyose and Manninotriose.** HENRY BIERRY (*Biochem. Zeitsch.*, 1912, 44, 146—471).—As is the case with raffinose and gentianose, no ferment has been discovered in the higher animals capable of causing the hydrolysis of stachyose and manninotriose, although a certain amount of degradation can take place when these polyoses are treated with the acid gastric juice. Certain invertebrates (snails, crustacea) produce enzymes which can hydrolyse stachyose and manninotriose. The former undergoes hydrolysis in three stages. In the first stage, lævulose, and the triose, manninotriose, are produced. In the second stage, galactose is set free from the manninotriose, and a biose is produced, which, in the third stage, itself undergoes scission. The ferments producing these reactions are active even at 15°, but the action is more energetic at 38°, and stronger still at 56°. The author succeeded in isolating lævulose and manninotriose when stachyose is treated with ferments, the former by means of its calcium compound, and the latter by means of alcohol, and also in the form of its urea derivative. The first action of all the ferments acting on the polyoses investigated is to cause the scission of lævulose. Attention is called to the similarities and differences in the action of these ferments acting on polyoses and invertin, all of which are claimed to belong to a class for which the name *laevulopolyases* is suggested. It is shown that the action on the simpler sugars is more rapid than that on the more complex. From their action the conclusion is also drawn that in raffinose the dextrose residue is united both to the lævulose and galactose residues.

S. B. S.

**The Ferments Capable of Hydrolysing Raffinose and Gentianose.** HENRY BIÉRRY (*Biochem. Zeitsch.*, 1912, 44, 426—445).—No ferments capable of hydrolysing these polyoses have been discovered by the author amongst the higher animals, even in the tissues

containing an invertin. On the other hand, the gastric juice of *Helix*, and the digestive juices of other lower organisms, amongst which are the marine crustacea *Carcinus moenas* and *Maja squinado*, contain a gentianase, although in the last-named cases the action is slow. The best sources of gentianase are the digestive juices of *Helix*, *Astacus fluviatilis*, and *Astacus leptodactylis*. The digestion proceeds in two phases, the first consisting of a scission of l  vulose. The biose thus set free, the hydrolysis of which constitutes the second phase, only undergoes scission slowly. The changes were investigated chiefly by tracing the alterations in the reducing power and the optical rotations of the solutions. S. B. S.

**The Chemical Mechanism of the Formation of Lactic Acid from Dextrose in the Animal Body.** GUSTAV EMBEDEN, KARL BALDES, and ERNST SCHMITZ (*Biochem. Zeitsch.*, 1912, 45, 108—133).—As intermediary products in the conversion of dextrose into lactic acid, both glyceraldehyde and dihydroxyacetone have been suggested (compare Oppenheimer, this vol., i, 1071). The authors have, consequently, investigated the formation of lactic acid in the animal body from these supposed intermediary products, using for this purpose the methods of incubation of these substances with blood corpuscles, and perfusion through the liver of blood to which they have been added. It was found in the incubation experiments with blood that glyceraldehyde forms lactic acid much more readily than dextrose, whereas dihydroxyacetone (with the exception of one experiment) is a much more feeble lactic acid former than the sugar. Similar results were obtained when blood containing glyceraldehyde and dihydroxyacetone were perfused through the liver of a fasting dog. There was, however, a notable difference for whereas in the incubation experiments a mixture of *dl*-lactic acid and *l*-lactic acid, which is not the usual form of lactic acid formed in the animal body, was isolated, in the perfusion experiments almost all the lactic acid was in the optically inactive form, with indications of the presence of the *l*-acid. These results are in marked contrast to the fact, that dextrose yields the natural *d*-acid both on perfusion and on simple incubation. The theory respecting this difference is discussed in some detail by the authors. In their experiments the *dl*-glyceraldehyde was used, and reasons are given for supposing that in the formation of the aldehyde from sugar, only one optically active form is produced. To account for the formation of an excess of *l*-lactic acid rather than that of the natural *d*-form, it is assumed that the latter is either more readily destroyed or used for synthetical purposes by the organism than the *l*-form to which the organism is not so readily accustomed, and analogous results with the perfusion experiments with the various isomerides of leucine are quoted in support of this hypothesis. In the case of the experiments with dihydroxyacetone, much smaller quantities of lactic acid were obtained, and the amounts were not sufficient for very accurate determination of the properties. It appeared, however, that in the perfusion experiments the natural *d*-lactic acid was obtained, whereas in the incubation experiments the optically inactive acid was formed. From the fact that glyceraldehyde yields lactic acid so much more readily than

dihydroxyacetone, the conclusion is drawn that the former is the more readily formed intermediary product than the latter in the degradation of sugar in the animal organism. This is probably not the case in yeast fermentation, when, in accordance with the results of Buchner and his co-workers, dihydroxyacetone is the more probable intermediary product. This substance has a symmetrical structure, and should yield, as in fact it does in the cell-free sugar fermentation by yeast, a racemic acid. S. B. S.

**The Formation of Substances of Aldehydic Character on Perfusion of the Liver, and the Synthesis of Acetoacetic Acid from Ethyl Alcohol.** NIRO MASUDA (*Biochem. Zeitsch.*, 1912, 45, 140—156).—It is shown that by treatment of a solution containing both acetone and acetaldehyde with moist silver hydroxide, the latter substance only is destroyed, and on this fact the author has evolved a process for estimating the amounts of aldehydic substances present in fluids containing acetone. By the application of this method to products obtained by blood-perfusion through the liver, it was found, that in the perfusion of glycogen-poor dog's liver with ox-blood, no substances of aldehyde nature could be detected. The same is the case when the acetoacetic acid forming isovaleric acid or acetoacetic acid itself are added to the perfused blood. On the other hand, when *d*-saccharic acid is added, a volatile substance which, like acetone, reacts with iodine is formed, which is destroyed by silver hydroxide. The nature of this substance has not yet been determined. Substances of aldehyde-like character are also formed in very appreciable quantities on perfusion with ethyl alcohol, and also acetoacetic acid. It is assumed that the alcohol is oxidised in the liver to acetaldehyde, which by the aldol condensation yields acetoacetic acid. S. B. S.

**The Conversion of Acetaldehyde into Ethyl Alcohol in the Animal Organism.** GUSTAV EMBDEN and KARL BALDES (*Biochem. Zeitsch.*, 1912, 45, 156—166).—In view of the results of the preceding communication of Masuda, that acetaldehyde is probably an intermediary product in acetoacetic acid formation, it was of interest to ascertain whether acetaldehyde can give rise to ethyl alcohol in the tissues, and whether this alcohol is normally present. In view of the recent investigations of Battelli and Stern, and of Parnass, who showed that aldehyde, by the Cannizzaro reaction, can give rise to acetic acid and ethyl alcohol, by virtue of the presence of a ferment (aldehyde-mutase) in the liver, the supposition of the formation of ethyl alcohol from aldehyde was not improbable. The alcohol was estimated in a mixture of minced liver tissue and aldehyde immediately after mixture, and after keeping at 40° for thirty to forty minutes. The authors describe in detail the method of destroying the aldehyde contained in the distillate obtained from the various experiments after separation of the proteins by hydrochloric acid and mercuric chloride. This is done by repeated distillation over silver hydroxide in a special apparatus which is figured in the text. The alcohol is finally estimated by Zeisel-Fanto's method in a Stritha apparatus. It was found, not only in experiments in which aldehyde was incubated with liver tissue (from dogs), but also in perfusion experiments, that

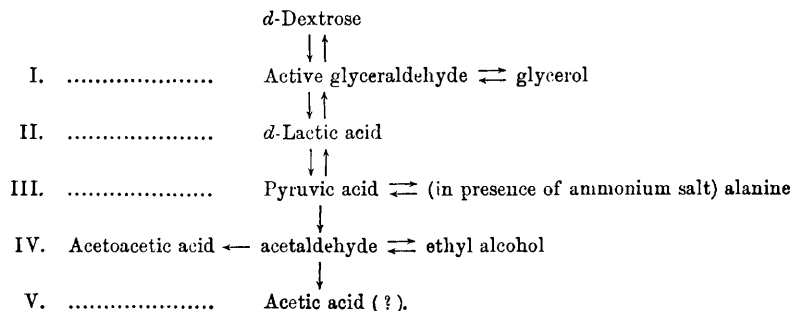
acetaldehyde gives rise to ethyl alcohol. The tissues, apart from the aldehyde treatment, appear to contain ethyl alcohol. It is not, however, determined yet whether this is a true product of intermediary metabolism, or whether it is derived from the narcotic used, or is a product of bacterial action resolved from the alimentary tract.

S. B. S.

**The Formation of Acetoacetic Acid from Certain Dicarboxylic Acids with Four Carbon Atoms.** KOSHI OHTA (*Biochem. Zeitsch.*, 1912, 45, 167—173).—In view of the results of J. Wirth, who showed that acetoacetic acid could be formed from saccharic acid by perfusion in ox-blood through dog's liver, it was of interest to investigate whether acetone substances could be produced from other dicarboxylic acids, some of which are possible intermediary degradation products of saccharic acid. It was found that if *d*-tartaric acid or malic acid is added in sufficient quantities to the ox-blood, there is markedly more acetoacetic acid produced than in the perfusion experiments where no such addition had taken place. The results with succinic acid were somewhat doubtful. The mechanism of the degradation of these acids is discussed by the author, who suggests the possibility of the formation of acetaldehyde as an intermediary product, and he shows, in fact, that a substance reacting with iodine is produced which is destroyed when the liquid containing the acetone produced in the experiments is treated with silver hydroxide by Masuda's method (this vol., ii, 1074).

S. B. S.

**The Degradation of Pyruvic Acid in the Animal Body.** GUSTAV EMBDEN and MAX OPPENHEIMER (*Biochem. Zeitsch.*, 1912, 45, 186—206).—In view of the chemical relationship of pyruvic acid to lactic acid on the one hand, and to alanine on the other, it was of interest to ascertain whether this substance on perfusion through the liver gives rise to acetone substances. The experiments were carried out with the usual technique, and it was found that in the majority of cases there was an increased formation of such products as compared with the amounts obtained in blank experiments. The authors summarise the results of the investigations on the degradation of dextrose, as obtained chiefly by Embden and his pupils, which can be schematically represented as follows :



S. B. S.

**The Behaviour of Malic Acid in the Animal Body.** KOHSHI OHTA (*Biochem. Zeitsch.*, 1912, 44, 481—490).—It was found that a part of *l*-malic acid when administered in sufficient doses to rabbits and dogs was excreted unchanged in the urine. In large quantities, the acid, orally administered, is toxic. In the case of rabbits of 2—3 kilos. weight, malic acid in quantities of 10—20 grams given by the mouth were entirely destroyed. When the quantities reached 25—30 grams, about 5% was excreted in the urine unchanged. On subcutaneous injection, when quantities of only 10 grams were given, 6% was excreted unchanged. On subcutaneous injection of 10—20 grams in dogs of 7 kilos. body-weight, 1—1.5% was excreted in urine, which quantity rose to 4% when the dose was increased to 30 grams. In the latter case, the acid was isolated from the urine as such, being precipitated therefrom as barium salt, and purified by conversion into its lead salt and recrystallisation from acetone. In other cases, the amount excreted was approximately estimated by determining the optical rotatory power after addition of uranyl acetate and acetic acid to the urine, it having been shown by Walden that the addition of uranyl salts enormously increases the rotatory power of malic acid, a fact which was taken advantage of by Goder for devising a method for the quantitative estimation of this acid. S. B. S.

**Mobilisation of Sugar in the Surviving Liver.** ERNST MASING (*Arch. exp. Path. Pharm.*, 1912, 69, 431—457).—Experiments on rabbits' livers show that adrenaline, lessened oxygen supply, hydrocyanic acid, and cooling are all agencies that increase the sugar output in that organ. During life they cause glycosuria. The rapid formation of sugar in the liver post-mortem, and the glycosuric effect of stimulation of the splanchnic nerves (Macleod) may be due to lessened oxygen supply, in the latter case produced by arterial constriction. Sugar possibly partly originates from other substances than glycogen. W. D. H.

**The Catalytic Action of Lead on the Formation and Destruction of Uric Acid.** LUIGI PRETI (*Biochem. Zeitsch.*, 1912, 45, 488—499).—Small quantities of lead nitrate or acetate further the formation of uric acid during the aseptic autolysis of calves' liver. In larger quantities this action is inhibited. The destructive action of extracts of calves' liver on uric acid is not, however, appreciably influenced by lead salts. The general action of lead salts on uric acid metabolism is exerted therefore on the xanthinodase, and not on the uricolytic ferment. S. B. S.

**The Chemical Mechanism of the Formation of Glycerol in the Animal Body.** GUSTAV EMBDEN, ERNST SCHMITZ, and K. BALDES (*Biochem. Zeitsch.*, 1912, 45, 174—185).—In view of the fact that glyceraldehyde is probably an intermediary product of the degradation of dextrose to lactic acid, it was of interest to ascertain whether it can be converted into glycerol in the body, and so indicate a possible origin of this substance from sugar in the animal organism. The authors show that this conversion of glyceraldehyde can take place both when it is

incubated with the mashed liver, or when artificially perfused through this organ. The technique is the same as in the earlier experiments of Embden and his pupils, and the glycerol was estimated by a slight modification of that described by Schmitz (this vol., ii, 1071). The chief modification consisted in the treatment of the protein-free liquids with either silver hydroxide or mercuric oxide in the cold to destroy the unchanged aldehyde. The exact process is given in detail.

S. B. S.

**Reductase of Liver and Kidney.** DAVID F. HARRIS and HENRY J. M. CREIGHTON (*Proc. Roy. Soc.*, 1912, B, 85, 486—494).—Mammalian liver contains a catalytic enzyme; the decomposition of hydrogen peroxide is effected by this enzyme, and is not due to proteins or other organic matter present. A reducing endo-enzyme is also present; it reduces nitrates to nitrites and ferric chloride to ferrous chloride.

Whilst the presence of proteins in press juice is not responsible for the reduction of Prussian-blue for instance, the proteins form with the pigment a colourless compound. The change is rapid at 100°, but very slow at the ordinary temperature. The fading of pigments due to combination with proteins should be distinguished from true vital reduction; the so-called reduction effected by colloids (Heffer, *Med. Naturwiss. Arch.*, 1, 81) is perhaps of the nature of the fading of pigments.

N. H. J. M.

**Contraction of Striated Muscle.** WILLIAM N. BERG (*Biochem. Bull.*, 1912, 1, 535—537).—A criticism of Zuntz's theory of muscular contraction.

W. D. H.

**Muscle Chemistry. I. The Total Amino-nitrogen Titratable with Formaldehyde in the Smooth, Striped, and Cardiac Muscle of Mammals.** GIUSEPPE BUGLIA and A. COSTANTINO (*Zeitsch. physiol. Chem.*, 1912, 81, 109—110).—Full analytical details are given on the subject mentioned in the title. No differences between the various kinds of muscle mentioned were found.

W. D. H.

**Muscle Chemistry. II. The Nitrogen of Certain Extractives and Purine Bases in the Smooth, Striped, and Cardiac Muscle of Mammals.** GIUSEPPE BUGLIA and A. COSTANTINO (*Zeitsch. physiol. Chem.*, 1912, 81, 120—129).—The following table gives the chief results obtained:

	Total nitrogen, % in muscle.	Creatinine nitrogen after inversion in % of total N.	Purine nitrogen in % of total N.	Carnosine nitrogen in % of total N.
Smooth muscle.....	2.90	1.24	1.68	1.24
Striped „ .....	3.40	3.44	2.00	3.08
Heart „ .....	2.77	2.85	3.06	1.60

W. D. H.

**Muscle Chemistry. III. The Free Amino-nitrogen Titratable with Formaldehyde in the Smooth, Striped, and Cardiac Muscle of Mammals.** GIUSEPPE BUGLIA and A. COSTANTINO (*Zeitsch. physiol. Chem.*, 1912, 81, 130—142).—The amount of free amino-nitrogen is greatest in striped muscle, and least in cardiac muscle. This difference is due to free diamino-acids, the amounts of mono-amino-acids being about the same in all varieties. The relationship of these facts to function is not yet clear.

W. D. H.

**Chemistry of the Embryo. I. The Total Amino-nitrogen Titratable with Formaldehyde in Mammalian Embryonic Muscle.** GIUSEPPE BUGLIA and A. COSTANTINO (*Zeitsch. physiol. Chem.*, 1912, 81, 143—154).—The total amino-nitrogen in embryonic muscle is smaller than in the adult. In the embryonic period also the amount of mono-amino-acids is greater than that of diamino-acids. In the adult, the opposite is the case. The total nitrogen of embryonic muscle is less than in the full-grown tissues.

W. D. H.

**Chemistry of the Embryo. II. The Free Amino-nitrogen Titratable with Formaldehyde in the Musculature of the Ox-Embryo.** GIUSEPPE BUGLIA and A. COSTANTINO (*Zeitsch. physiol. Chem.*, 1912, 81, 155—162).—The free amino-nitrogen in embryonic muscle is higher than in the adult.

W. D. H.

**Muscle Chemistry. IV. The Sulphur of the Smooth, Striped, and Cardiac Muscle, also of Muscle Proteins in Mammals.** A. COSTANTINO (*Zeitsch. physiol. Chem.*, 1912, 81, 163—174).—The total sulphur in striped and cardiac muscle is the same, and in smooth muscle is a little higher. The amount of sulphur in the different muscle proteins is the same in all; but the amount which blackens lead shows slight variations, to which no importance is attached, owing to the limited number of observations made.

W. D. H.

**The Nature and Action of the Thromboplastic (Zymoplastic) Substance of the Tissues.** WILLIAM H. HOWELL (*Amer. J. Physiol.*, 1912, 31, 1—21).—The experiments were performed with "peptone plasma," and a method is described for preparing a stock material, which can be used for testing the thromboplastic action of tissue extracts. Tissue extracts hasten coagulation of blood-plasma, not because they contain an activating substance, but because the substance they contain neutralises anti-thrombin. The substance in question appears thermolabile, because when extracts are heated, the protein in them, coagulating at 60°, carries down with it the active material. Evidence is adduced that this active material is a phosphatide of a nature akin to kephalin. It is precipitated from aqueous solutions by the addition of neutral salts, or salts of the alkaline earths.

W. D. H.

**The Lipolytic Action of the Extracts of Various Organs.** L. BERCZELLER (*Biochem. Zeitsch.*, 1912, 44, 185—192).—In the subcutaneous fatty tissue, no ferment could be found causing the

hydrolysis of fats into fatty acids. With the exception of blood, muscle, and heart muscle, all organs were capable of producing fat scission. The hydrolysis by blood and muscle was so small, that it scarcely exceeded the limits of experimental error. The lipolytic capacity of the same organs of different animals shows considerable variations; this capacity varies even with different individuals of the same species. If the enzyme content in one organ is great, it is also relatively great in other organs and vice versa. This rule does not apply, however, to the pancreas.

S. B. S.

**Cholesterol and Accompanying Substances in the Dépôt Fat of Carcinoma in Man.** LEONHARD WACKER (*Zeitsch. physiol. Chem.*, 1912, 80, 383—408).—Cholesterol and accompanying unsaponifiable substances increase in the dépôt fat in human carcinoma, but this is not specific for that disease, for it occurs also in chronic infectious disease such as tuberculosis, sepsis, and in diabetes. The increase occurs first in the mesenteric fat, and later in the subcutaneous region. The failure of cholesterol in the suprarenals in carcinoma, and the occurrence of lipoidæmia in diabetic coma show that the phenomenon is not altogether due to cell degeneration.

W. D. H.

**The Origin of Creatine in the Body.** KATSUJI INOUE (*Zeitsch. physiol. Chem.*, 1912, 81, 71—79).—Guanidine has been regarded by several observers as an intermediate product in the formation of creatine. This might originate from the arginine of proteins, or from the guanine of nucleic acid. The present experiments on autolysis and perfusion show that the former possibility does occur, and thus a certain amount of creatine is accounted for. The amount so originating is, however, small.

W. D. H.

**The Significance of the Hydrogen Ion in Milk Clotting.** O. ALLEMANN (*Biochem. Zeitsch.*, 1912, 45, 346—358).—If different acids are added to milk, the clotting time by rennet does not depend on the degree of acidity, as determined by titration, but on the hydrogen ion concentration. The experiments were carried out also in the presence of phosphate mixtures, and mixtures of acetic acid and sodium acetate. Increase of acidity diminishes the clotting time up to the concentration of hydrogen ions of  $1.3 \times 10^{-5}$ , the point at which the acid alone is sufficient to produce a clot. Measurements were made of the coagulation points with the whole milk, skimmed milk, and caseinogenate solutions, which show certain differences.

S. B. S.

**Diuresis.** WILHELM GINSBERG (*Arch. expt. Path. Pharm.*, 1912, 69, 381—392).—As food and certain narcotics influence urinary secretion, it is necessary to investigate the action of diuretics when an animal is fasting and not anæsthetised. The present experiments made on dogs with a permanent bladder fistula deal with the influence of food and water on the renal secretion. Water diuresis is reduced by giving atropine, and increased by pilocarpine.

W. D. H.

**Diuresis.** DOUGLAS COW (*Arch. exp. Path. Pharm.*, 1912, 69, 393—411).—Aqueous extracts of juniper and *Ononis* are stronger diuretics than those of *Equisetum* and *Petroselinum* if given by the mouth. Subcutaneously administered their effect is small. The same difference between enteral and parenteral administration is noted when water is given; the amount of water in the tissues already is another factor of importance. There is a substance possibly of enzymatic nature which is developed during the absorption of water from the alimentary tract which stimulates the activity of the kidney. Atropine acts mainly, if not entirely, on the smooth muscle of the urinary tract; the action of pilocarpine is in the main on the same tissue, but the fall of blood pressure it produces also leads to fall in urinary secretion.

W. D. H.

**Enzymes as Possible Factors in the Development of Œdema.** IV. FRANK R. ELDER and WILLIAM J. GIES (*Biochem. Bull.*, 1912, 1, 540—545. Compare this vol., ii, 856).—Proteases increase the absorption of water by protein particles in acid or alkaline media containing more sodium chloride than occurs in protoplasm. This supports the authors' belief that such enzymes may favour the development of œdema.

W. D. H.

**The Action of Thorium-X on Intravenous Injection in the Rabbit.** A. TSIWIDIS (*Pflüger's Archiv*, 1912, 148, 264—272).—The injection produces a fall of arterial pressure and a slow heart. The details of the alterations in the heart-beat were studied by electrocardiogram records.

W. D. H.

**Excretion of Alkaloid into the Stomach into which Salts have been Introduced.** HANS LANGER (*Biochem. Zeitsch.*, 1912, 45, 239—243).—It was observed that when moderately toxic doses of heroine were introduced subcutaneously into rabbits, there were no convulsions produced when salts had been introduced into the stomach. Similar phenomena were observed in the case of codeine and morphine, but not in the case of strychnine. The alkaloids when the toxicity is diminished after introduction of salts are excreted into the stomach, and the explanation of the phenomena is, that the salts facilitate this excretion. The explanation was directly confirmed by estimating the amount of intravenously introduced morphine excreted in the stomach in the presence and absence of salts. In the former case it was considerably larger than in the latter.

S. B. S.

**Secretion and Tolerance of Heroine.** HANS LANGER (*Biochem. Zeitsch.*, 1912, 45, 221—238).—The greater part of the heroine (diacetylmorphine) is separated unchanged in the urine. A small part is excreted in the fæces in the form of an alkaloid which has not yet been characterised. Animals, in acquiring tolerance, acquire the capacity of destroying the alkaloid, so that none can be detected finally in the urine and fæces. Dogs acquire a tolerance only as regards the narcotic action, but not towards the action which produces convulsions. The tolerance can therefore be acquired only to sublethal doses, and is of a functional character. The lethal dose both to

dogs and rabbits is about 0.15 gram per kilo. of body-weight. The convulsive action is the cause of death, and not the action on the breathing centre, for if the former is antagonised by ether narcosis, the lethal dose is increased to 0.32 gram per kilo. of body-weight.

S. B. S.

**The Antagonistic Action in the Animal Organism of Nucleic Acid and the Nucleic Acid-splitting Ferments.** M. TSCHERNORUZI (*Biochem. Zeitsch.*, 1912, 44, 353—391).—Preliminary experiments on rabbits showed that injection of sodium nucleate (from yeast) caused a marked hyperleucocytosis, but no marked action on the hæmoglobin content or number of erythrocytes. The nucleolytic functions of the organs were also discussed. The toxic dose was 1.5 to 2 grams per kilo. of body-weight. The chief experiments were carried out on dogs in the following way. Five animals from the same litter were employed, one being used as a control, and the others were immunised over a prolonged period, the sodium nucleate being administered orally, intravenously, subcutaneously, and intraperitoneally in different animals. The effect of these treatments on the general well-being, the blood, the nitrogenous metabolism, and the nucleolytic activity of the organs was investigated. There was no marked effect on the weight observed. The hæmoglobin content in all animals was about the same, although the treated animals had a larger number of erythrocytes. There was an increase in the number of leucocytes. The treatment caused in all cases a rise of temperature. The intraperitoneal injections caused toxic symptoms when the dose approached 1 gram per kilo. of body-weight. If sodium nucleate is administered orally to treated animals, the purine bases secreted were less in quantity than that administered. There was a marked increase, however, in both the nitrogen and phosphorus excreted, and the general results indicated, not only increased tissue metabolism, but also an increase in the oxidative processes. The nuclease content of the organs and blood was investigated both by purely chemical methods (estimation of phosphoric acid or purine bases set free on incubation with the organs) and by the optical method of Pighini. The dried organs were chiefly employed. Blood was removed from time to time during the course of immunisation, and in the case of intravenous injection, the negative phase was observed, that is, there was at first a decrease of nuclease content followed by an increase. At conclusion of the immunisation, the animals were killed, and the nuclease content of the organs was estimated. As compared with the control animal, there was a general marked increase of nucleoclastic power of the organs, especially in the bone-marrow. In the brain and lungs, the increase was either absent or small, but in other organs it was large, if not as large as in the bone-marrow and the thymus. The maximum increases were found in the animal in which sodium nucleate had been administered orally, and the smallest in the animal which had received the nucleate subcutaneously. Attention is called to the similarity of the action of nucleate administration and the action of various infections, and suggestions as to the therapeutic use of sodium nucleate were made.

S. B. S.

**The Action of Monoatomic Alcohols on Trout and their Brood.** GUSTAV OTTO (*Zeitsch. Biol.*, 1912, 59, 165—170).—The present experiments on trout confirm those previously performed on other fish and tadpoles, and support the Meyer-Overton theory of narcosis.  
W. D. H.

**The Chemical Action of Blood Poisons which Produce Anæmia.** R. MAIDORN (*Biochem. Zeitsch.*, 1912, 45, 328—345).—Cases of pernicious anæmia and other clinical conditions are discussed, where destruction of blood-corpuscles takes place. In these cases it is suggested that hæmolytic substances may be produced by abnormal processes in the liver. *p*-Tolylenediamine does not produce hæmolysis *in vitro*, although in cases of chronic poisoning in animals, destruction of blood-corpuscles takes place. In this case, according to Joannovics and Pict, a hæmolytic substance is produced by the action of the drug in the liver. The author amplifies these experiments, investigating the hæmolytic action of the lipoids obtained from the liver (the preparation of which he describes) in normal cases and in cases of poisoned animals. He finds that in cases of acute poisoning by phosphorus or tolylenediamine there is an increase in the hæmolytic power of these substances which is not influenced by the extirpation of the spleen. In sub-acute and chronic cases the hæmolysis values are normal. In chronic tolylenediamine poisoning the hæmolytic value sinks after extirpation of the spleen, whereas it is higher in phosphorus poisoning. The probable explanation of these facts is that after extirpation of the spleen, in consequence of inanition, less hæmolytically active depôt fat is transported; in phosphorus poisoning the increased hæmolytic action may be ascribed to a greater degradation of the organ in consequence of greater inanition. The active hæmolytic substances are due to fat-degeneration. The lipoid substances in the liver with fat-infiltration have but little hæmolytic power.  
S. B. S.

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### Chemistry of Vegetable Physiology and Agriculture.

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Influences Acting on the Alcoholic Fermentation in the Cell and in the Expressed Cell Juice. ALFRED DORNER (*Zeitsch. physiol. Chem.*, 1912, 81, 99—108).—It is generally stated that toluene, which stops the alcoholic fermentation due to yeast cells, does not inhibit that produced by the cell juice. The difference is only one of degree; antiseptics (such as various urethanes and alcohols) stop fermentation more easily when applied to the cells themselves.

W. D. H.

Zopf's "Fibrinkörper" and Their Relation to the Metachromatic Corpuscles. E. FOEX (*Compt. rend.*, 1912, 155, 661—662).—A further study of Zopf's "Fibrinkörper," which the

author has found in a large number of the *Erysiphaceae*, a description of their properties being given. Volutin precedes the "Fibrinkörper," and seems to play some active part in their formation, the mechanism of which is not known. W. G.

**The Passage of Salts Through Protoplasm. II. A Method for Estimating the Isoelectric Point of Protoplasm, which Depends on the Influence of the Hydrogen and Hydroxyl Ions on the Passage of Dyes.** JOSEF ENDLER (*Biochem. Zeitsch.*, 1912, 45, 359—411).—The experiments were carried out with various plant cells and dyes (methylene-blue, neutral-red, etc.). The entrance and exit of the dye is furthered by the presence of hydroxyl ions up to a certain concentration, above which there is an inhibition of the passage. There is a difference in the action of potassium and ammonium hydroxides. Hydrogen ions inhibit the entrance of dyes. Hydroxyl ions compensate the inhibitory action of neutral salts on the storage of dyes. In solutions of acids up to the strength of  $N/12,800$ , neutral salts effect the exit of the dyes in the way already described by the author (this vol., ii, 863). At the concentration  $N/6,400$  they inhibit the exit, and it is then necessary to add more salt to cause the dyes to leave the cell. At this concentration there is a reversal of the relative action of the anions, whereas the reversal of the cation action is only distinctly marked when the acid reaches the concentration  $N/3,200$ . From these observations, the conclusion is drawn that the isoelectric point of the *elodea* plasma is between  $H = 1.56 \times 10^{-4}$  and  $0.78 \times 10^{-4}N$ . The isoelectric point of dead cells is somewhat lower. In this case the tannin also leaves the cells. As regards the reversibility, the anions act in the following order: nitrate > chloride > sulphate > citrate > tartrate. Acid dyes do not, as a rule, enter the cell, but if they do their entrance is accelerated by acids and impeded by alkalis. Amphoteric electrolytes enter more rapidly under the influence of both acids and alkalis. Sugars, when they reach a certain concentration (lævulose  $0.8N$ , lactose  $0.6N$ , and dextrose  $0.4N$ ), inhibit the entrance, but this inhibitory action is neutralised by alkalis. Asparagine and urea also exert an inhibitory action. Alcohol has no effect on the action of dyes when fat drops are in the cell. Colloids influence the action in so far as their adsorptive capacity can alter the concentration of the dyes outside the cell. S. B. S.

**The Action of Narcotics on Plasma Movements.** HELENE NOTHMANN-ZUCKERKANDL (*Biochem. Zeitsch.*, 1912, 45, 412—451).—From experiments on *Vallisneria*, the following conclusions were drawn. The toxic action of the monohydric alcohols approximates to Traube's law. The inhibitory action on the plasma movements is not, however, determined by the surface tension of the solutions. Increase of temperature up to  $38^{\circ}$  increases the action. A combination of alcohols with the sulphates of manganese and zinc acts more feebly than alcohol alone, with the exception of isoamyl and heptyl alcohols. The action of these salts on other narcotics and on hydrochloric acid and fatty acids was also investigated. In the latter case the salts accelerate this action, a fact which is probably due

to alterations in the permeability of the cell membrane. They do not act in this way in the presence of higher alcohols and chloroform, probably because these substances, by being adsorbed, displace the salts. Alcohol and potassium cyanide mutually accelerate the action of one another. The action of ethylurethane is strengthened by potassium cyanide, which has either no action, or at most only a very slight one, on the action of chloral hydrate and chloroform. Deprivation of oxygen only when the temperature reaches 30° and higher diminishes the resistance of the cells to alcohols and other substances.

S. B. S.

**Behaviour of Plants Towards Lithium Salts. II.** CIRO RAVENNA and A. MAUGINI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 292—298. Compare Ravenna and Zamorani, *Abstr.*, 1910, ii, 235).—The names of the following plants are arranged according to the degree to which they tolerate lithium sulphate, the least resistant being first: tomato, mustard, hemp, sunflower, flax, vetch and maize. Except in the case of the tomato the salt is not so toxic as is usually supposed. From experiments on tobacco, it appears capable of replacing potassium salts to some extent, for plants treated with a culture solution in which most of the potassium was replaced by lithium grew much larger than others not so treated. R. V. S.

**Action of Some Aromatic Substances in the Cyanogenesis of Plants.** CIRO RAVENNA and G. BOSINELLI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 286—292).—The authors have inoculated *Sorghum vulgare* with various aromatic substances with a view to determining whether the production of hydrogen cyanide is affected (compare Ciamician and Ravenna, *Abstr.*, 1911, ii, 761). The substance administered was introduced into the stem of the plant, the wound being then sealed with paraffin wax. The following compounds were employed: sodium benzoate, sodium salicylate, potassium phthalate, catechol, resorcinol, quinol, and pyrogallol. In all cases the amount of hydrogen cyanide in the plant was diminished. R. V. S.

**Presence of Hydrogen Cyanide in Plants. III.** CIRO RAVENNA and G. BOSINELLI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 355—358. Compare Ravenna and Babini, this vol., ii, 798).—The authors have continued the study of this question in view of the fact that, in the experiments formerly recorded (*loc. cit.*), hydrogen cyanide could be detected in some of the distillates by sodium picrate papers, although not by the Prussian-blue reaction. The new experiments were carried out with cherry laurel, *Phaseolus lunatus*, and almond (sweet and bitter, in germination), and instead of boiling dilute alkali, concentrated salt solutions boiling at 110° were treated with a little alkali and employed. In this way the plant enzymes are more rapidly destroyed, and it is found that the amount of hydrogen cyanide obtained is in all cases even less than in former experiments. In the case of *Phaseolus lunatus*, four out of six experiments, and in the case of the almonds all the experiments, yielded no hydrogen cyanide.

R. V. S.

**Presence of Hydrogen Cyanide in *Trifolium repens*.** MARCEL MIRANDE (*Compt. rend.*, 1912, 155, 651—653).—*Trifolium repens* contains a cyanogenetic substance and an enzyme, which is capable of splitting it, liberating hydrogen cyanide. The amount of hydrogen cyanide obtained varies with the different organs of the plant, and is also very variable with the nature of the soil, the period of vegetation, and from sample to sample grown in the same neighbourhood.  
W. G.

**Plant Chemistry.** P. Q. KEEGAN (*Chem. News*, 1912, 106, 181—182).—Analyses of wild plants showed that of the plants examined, tufted vetch and the great valerian contained the highest percentages of calcium in the ash ( $\text{CaO} = 40.6$  and  $37.5\%$  respectively). Tufted vetch produces large amounts of oxalic acid, whilst the acid of valerian is mainly malic acid.

The ash of oak leaves contains  $\text{CaO} = 44\%$ , whilst autumn leaves of ash, which contain little tannin and much acid, contain  $45.8\%$  of lime in the ash.

Caffetannin was found in small quantities in the leaves of foxglove, ash, and watercress. In the first two it is accompanied by a tannoid, perhaps identical with the one which occurs in ragwort, marigold, and tansy.  
N. H. J. M.

**Behaviour of Pentosans and Methylpentosans in Seeds of *Glycine hispida* and *Phaseolus vulgaris* during Germination.** K. MIYAKE (*J. Coll. Agric. Imp. Univ. Sapporo*, 1912, 4, 327—335).—The pentosans and methylpentosans present in the cotyledons are not utilised during germination unless the nutritive substances of the seedlings are exhausted. In that case the pentosans and methylpentosans may be utilised as food, and it was found that relatively more of the methylpentosans was used up than of pentosans.

N. H. J. M.

**Presence of Quebrachite in the Leaves of *Grevillea robusta*.** ÉMILE BOURQUELOT and (Mlle.) A. FICHTENHOLZ (*Compt. rend.*, 1912, 155, 615—617; *J. Pharm. Chim.*, 1912, [vii], 6, 346—349).—Quebrachite (compare Tanret, *Abstr.*, 1890, 226) was isolated from the fresh leaves of *Grevillea robusta* to the extent of 4 grams per kilo. by extraction with alcohol, the arbutin being removed from the extract by means of ethyl acetate. The chemical and physical properties of quebrachite are given.  
W. G.

**Application of the Bio-chemical Method to *Hepatica triloba*.** Presence of a Glucoside Hydrolysed by Emulsin. A. DELATRE (*J. Pharm. Chim.*, 1912, [vii], 6, 292—298).—Preliminary tests by Bourquelot's method (*Abstr.*, 1902, ii, 55) showed that this plant (*Anemone hepatica*, Linn.) contained the two enzymes invertase and emulsin, as well as sucrose and a glucoside hydrolysed by emulsin. Two fractions of the glucoside were obtained from an alcoholic extract of the plant. These crystallised in needles, had  $[\alpha]_D - 127.71^\circ$  and  $-147.637^\circ$  respectively, and were hydrolysed by emulsin producing reducing sugars.  
T. A. H.

**Influence of Temperature on the Absorption of Water by Seeds of *Hordeum vulgare* in Relation to the Temperature-coefficient of Chemical Change.** ADRIAN J. BROWN and FREDERICK P. WORLEY (*Proc. Roy. Soc.*, 1912, B, 85, 546—553).—The results of experiments on the absorption of water by barley seeds at different temperatures showed that at 3·8°, 21·1°, and 34·6° the rates of absorption are in the proportion of 1:3·40:8·30. When the logarithms of the velocities are plotted against the temperature, the course of the lines shows conclusively that the rate of absorption is an exponential function of the temperature. The relation between temperature and the rate of absorption of water or the vapour pressure of water is approximately expressed by the equation:  $v = ae^{k\theta}$ , in which  $v$  is either the velocity of absorption or vapour pressure, and  $\theta$  the temperature,  $a$  being a constant. The value of  $k$  in the present case, derived from mean ratios of velocities, is 0·069. The conclusion is drawn that only the simple molecules existing in the water are directly assimilated, or are transmitted by the differential septum.

Further experiments in which barley seeds were steeped in "weight normal" solutions of ethyl acetate gave similar results, except that the velocity of absorption is increased, owing, perhaps, in a large measure, to the simplifying action of the solute on the molecular structure of the water. If this be the case, it seems probable that small amounts of ethyl acetate increase the partial pressure of the vapour of water.

N. H. J. M.

**Alkaloid Contained in the Leaves of Mate.** A. CAPPELLI (*Ann. Lab. Gabelle*, 1912, 6, 419—424).—The author has investigated the alkaloids obtainable from this source, and has hitherto been able to isolate only caffeine, although the statement has recently been made that the leaf yields only traces of caffeine, matteine being the alkaloid present in greatest amount.

R. V. S.

**Carbohydrates and Nitrogenous Substances of Vine Leaves.** N. T. DELEANO (*Zeitsch. physiol. Chem.*, 1912, 80, 79—94).—Grape vine leaves detached from the plant during the day and quickly dried were found to contain dextrose, lævulose, inositol, glutamine, and choline. The following substances were proved to be absent: sucrose, amino-acids, alloxuric bases, histidine, arginine, and betaine.

E. F. A.

**Composition of the Ash of the Sap, Leaves, and Young Stems of the Wild Grape Vine (*Vitis cordifolia*).** OLIVER M. SHEDD and JOSEPH H. KASTLE (*J. Amer. Chem. Soc.*, 1912, 34, 1415—1424).—In view of the lack of knowledge with regard to the relations between the mineral constituents of the sap and those of the growing parts of a plant, a comparative study has been made of the composition of the ash of the sap, leaves, and young stems of the wild grape vine (*Vitis cordifolia*).

The results show that the concentration of the mineral constituents is much greater in the stem and leaf than in the sap, and that the total amount of ash given by the leaf is more than twice as great as

that yielded by the stem. The following is a comparison of the amounts of the constituents of the fresh materials, those of the sap being taken as unity in each case; the figures are given in the order sap, stem, leaf. Organic matter, 1, 72, 82; total ash, 1, 9, 20;  $\text{SiO}_2$ , 1, 8, 274;  $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ , 1, 1, 35;  $\text{CaO}$ , 1, 5, 33;  $\text{MgO}$ , 1, 8, 30;  $\text{Na}_2\text{O}$ , 1, 10, 20;  $\text{K}_2\text{O}$ , 1, 8, 7;  $\text{P}_2\text{O}_5$ , 1, 22, 39;  $\text{SO}_3$ , 1, 4, 12. It is evident from this comparison that there is a marked accumulation of the mineral constituents of the sap in the growing leaf, and this indicates that there is a close correlation between these constituents and the chemical changes taking place in the leaf.

E. G.

**Oil of the Seeds of *Strychnos nux vomica*.** ALFRED HEIDUSCHKA and R. WALLENREUTER (*Arch. Pharm.*, 1912, 250, 398—402).—An oil obtained from the seeds of *Strychnos nux vomica* (saponification number 124.4, Reichert-Meissl number 3.7, Hehner number 81, acid number 18.5, iodine number [by Hübl's process] 64.5 after three hours, and 67.6 after eighteen hours) has been hydrolysed and the unsaponifiable portion isolated by Heiduschka and Gloth's method (*Abstr.*, 1909, i, 381). The unsaponifiable portion, amounting to about 20%, has iodine number 45.4 after three hours and 60.2 after eighteen hours. The chloroform is coloured brown and the sulphuric acid yellow when the substance is examined by Salkowski's method, whilst in the Liebermann-Burchard reaction a reddish-brown coloration and green fluorescence, and subsequently a dirty green coloration, are produced.

Three crystalline substances have been obtained from the unsaponifiable portion. The one, which is obtained in very small amount, is isolated by extracting the substance with 80% alcohol; it has m. p. 165°, and gives colour reactions almost identical with those of phytosterol. The other two crystalline substances are obtained by fractional crystallisation of the unsaponifiable portion from acetic anhydride. The more soluble substance,  $\text{C}_{40}\text{H}_{70}\text{O}_2$ , m. p. 121°, colourless leaflets, has iodine number 57.2 after twenty hours, and yields by hydrolysis a substance,  $\text{C}_{38}\text{H}_{68}\text{O}$ , m. p. 99°, iodine number 79.7 after twenty hours. The less soluble substance,  $\text{C}_{32}\text{H}_{54}\text{O}_2$ , m. p. 221°, almost white leaflets, yields a substance, m. p. 186°, by hydrolysis. These two substances do not give colour reactions similar to those of phytosterol.

C. S.

**The Causes of the Current of Injury.** JACQUES LOEB and REINHARD BEUTNER (*Biochem. Zeitsch.*, 1912, 44, 303—317).—By connecting the undamaged surface of an apple in contact with a salt solution with an acid solution of the same strength, an *E.M.F.* is set up of the same order of strength as that observed in the current of injury. The position in the acid is negative towards the other position. Isohydric acids have the same strength of action. The expressed juice of an apple acts as a salt solution. On exerting a pressure on the undamaged surface of the apple, juice is expressed under the skin, and by connecting the damaged surface with an undamaged part of the surface, an *E.M.F.* is set up of the same order of magnitude and size

as if the connexion were made with no skin existing over the damaged part. The skin itself shows no change in electromotor properties. The authors draw the conclusion that in the undamaged apple, the under layer of the skin, and the neighbouring cells, there is a solution containing acid, or a substance with the same electromotor properties as an acid, which is replaced by the expressed juice on pressure. By the replacement of this normal juice, the relative electro-negativity is destroyed. This conception is confirmed by measurements of *E.M.F.* by connexions with different depths of the apple. The current of injury does not appear, therefore, to be a concentration current, but is determined by chemical reactions.

S. B. S.

**Plant Chlorosis Provoked by Calcium Carbonate.** PIÉRE MAZÉ, RUOT, and LEMOIGNE (*Compt. rend.*, 1912, 155, 435—437. Compare Mazé, Abstr., 1911, ii, 1126).—A study of the chlorosis in plants, adapted to acid soils, when grown on calcareous soils. Maize plants do not become chlorotic when grown in a medium strongly charged with calcium salts even when calcium carbonate is present. The white lupin and *Viscia Narbonnensis* both become chlorotic in a few days, even in the presence of ferrous sulphate, in solutions containing calcium carbonate, although they develop green leaves in solutions containing calcium chloride or nitrate, but no carbonate. In the case of the second plant, by putting a few drops of ferric nitrate solution on decolorised leaves, the chlorophyll reappears after three days. The calcium carbonate causes the chlorosis by rendering the iron completely insoluble, the maize plant overcoming this difficulty by its roots excreting malic acid which promotes solution of the iron.

W. G.

**Acidity of Soils.** ACH. GRÉGOIRE [with J. HENDRICK, EM. CARIANA, and E. GERMAIN] (*Bull. Soc. chim. Belg.*, 1912, 26, 336—342, 362—375, 386—409).—The authors discuss the function of lime in the soil and the factors which tend towards its removal. The methods of determining the "active" lime in soils are examined. After critically reviewing the methods of estimating the acidity of soils, the following procedure is proposed. Ten grams of the finely powdered earth are covered with 15 c.c. of a solution containing 55.3 grams of potassium iodide, 14.3 grams of potassium iodate, and 99.2 grams of sodium thiosulphate per litre. After remaining during twenty-four hours at the ordinary temperature, the solution is diluted and filtered, after which it is acidified, and the excess of sodium thiosulphate determined by means of standard iodine. This reagent appears to be well adapted for the titration of very weak organic acids even when the latter are sparingly soluble in water. It has, however, very little action on silicic acid or analcime, and only indicates two-thirds of the acid hydrogen in orthophosphoric acid. Further, a part of the acidity indicated may be due to the solution of salts of aluminium and iron, and hydrolyses of these latter.

For the determination of organic carbon in soils, the authors recommend the combustion of the earth in a stream of oxygen, absorption of carbon dioxide by barium hydroxide, filtration of the

barium carbonate, and gasometric measurement of the carbon dioxide evolved when the latter is treated with an acid. Full details of the necessary precautions and corrections are given.

A considerable number of soils has been investigated with regard to action towards litmus, lime dissolved by 10% ammonium chloride solution during ten hours' heating on the water-bath, carbonic acid, organic carbon, and acidity, the latter being determined by the iodometric method. If the soils are classified according to their reaction towards litmus, the mean results show that with increasing alkalinity of the soil, the proportion of soluble lime and of carbonic acid increases, whilst that of organic carbon decreases. The total acidity and the degree of acidification of the organic matter vary regularly with the reaction towards litmus, and, further, the total acidity diminishes with increase in the amount of soluble lime. These results are only obtained by considering the mean values given by a number of soils. Individual soils frequently show considerable discrepancies. H. W.

**Behaviour of Nitrates in Soils.** VOGEL (*Lundw. Versuchs-Stat.*, 1912, 78, 265—301).—Under some conditions, nitrates present in soils may be decomposed with production of different oxides of nitrogen; probably free nitrogen and ammonia are sometimes liberated. The most favourable conditions for the chemical destruction of nitrates is when the nitrates are distributed in a thin layer of soil containing about 15—20% of water.

The decomposition of nitrates, which may reach its maximum in three or four days, was found to occur in all kinds of soils, whether light or heavy, and cannot be due to the presence of humus.

N. H. J. M.

**Solubility of the Manganese of Soils.** P. DE SORNAY (*Bull. Assoc. Chim. Sucr. Dist.*, 1912, 30, 96—100).—Analyses of a number of Mauritius soils show that they contained from 0.027% to 0.409% of manganese. Dilute mineral acids and aspartic acid dissolved amounts of manganese which could be determined, whilst aqueous extracts of the soils were, in most cases, found to contain traces of manganese. Ashes of a number of plants were invariably found to contain manganese, sometimes in considerable quantity. The assumption that manganese, when present in soils, is in a form which is unavailable to plants is, therefore, incorrect. In experiments on the effect of manganese salts on plants grown in soils, the manganese originally present must be taken into account.

N. H. J. M.

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### Analytical Chemistry.

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New Forms of Gas Analysis Apparatus. G. A. BURRELL  
(*J. Ind. Eng. Chem.*, 1912, 4, 297—302).—A description with sketches  
of forms of apparatus which are employed in the U.S. Bureau of Mines  
for the analysis of gases. F. M. G. M.

[The Measurement of Gases.] GEORGE F. JAUBERT (*Rev. gén. chim. pure appl.*, 1912, 15, 228—231).—A sketch, with description of an apparatus which consists of a graduated measuring cylinder connected at the base with a levelling bulb; the top of the cylinder is drawn out and connected by a rubber tube to a corked flask, the side of which contains a pocket in which acid is placed. A carbonate (or other material evolving the gas to be measured) is placed in the flask, the cylinder filled with water, the pressure adjusted, and a reading taken. The acid is then shaken on to the carbonate, and the volume of carbon dioxide evolved measured by the lowering of the surface of the water in the cylinder. F. M. G. M.

*iso*Picramic Acid and its Use as an Indicator. RAPHAEL MELDOLA and ARTHUR JAMES HALE (*Chem. World*, 1912, 1, 327—329).—An alcoholic solution of *isopicramic acid* (2:6-dinitro-4-amino-phenol) may be used as an indicator in certain acidimetric titrations. The colour change is from pink in dilute alkaline solution to pale yellow in neutral solution. From results of experiments which are recorded, it is seen that the indicator, although useless in the case of weak acids, such as oxalic and acetic acids, is slightly superior to methyl-orange for the titration of alkalis and carbonates with mineral acids, and of equal sensitiveness to litmus in the case of alkalis. The method of preparing the substance is given. W. P. S.

An Inorganic Indicator for Use in the Volumetric Estimation of Alkalis and Carbonates. C. REICHARD (*Pharm. Zentr.-h.*, 1912, 53, 1033—1037).—The indicator consists of bismuth oxyiodide, and is prepared as follows: 0.1 gram of bismuth subnitrate is dissolved in 1 c.c. of 25% hydrochloric acid and 5 c.c. of water; 0.5 gram of potassium iodide is now added, and the mixture is diluted gradually with water to a volume of about 400 c.c. After the lapse of three days, a clear yellowish-green supernatant liquid is obtained above a yellow deposit. When this liquid is treated with the smallest excess of alkali, it becomes colourless, the addition of a trace of acid causing the yellow colour to reappear. Carbon dioxide does not cause the colour change. W. P. S.

An Improved Extraction Apparatus. WALTER C. BLASDALE (*J. Ind. Eng. Chem.*, 1912, 4, 302. Compare Hopkins, *Abstr.*, 1899, ii, 645).—The apparatus consists of five different heating plates, and condensers with a supporting rack; the plates are heated by an electric current, the energy of which is converted into heat by passing through resistance wire instead of incandescent lamps. Sketches with exact details of the construction and working are given in the original. F. M. G. M.

New Form of Extraction Thimble. P. A. BOECK (*J. Ind. Eng. Chem.*, 1912, 4, 303—304).—"Alundum," which is practically pure fused alumina and is prepared from bauxite, when mixed with a suitable ceramic binding material, furnishes extraction thimbles which

are porous to gases and liquids. They can be used for filtration, and are of special use in analyses of caoutchouc, fats, soaps, etc.

F. M. G. M.

**Detection of Chlorides in the Presence of Thiocyanates.** H. CORMIMBOEUF (*Ann. Chim. anal.*, 1912, 17, 329—330).—Chlorides may be detected in a solution containing both chlorides and thiocyanates by precipitating the latter with copper sulphate. In the presence of ferrous sulphate and sodium acetate, separating the cuprous thiocyanate by filtration, acidifying the filtrate with nitric acid, and adding silver nitrate.

W. P. S.

**Some Methods of Estimating Iodides.** WOLFGANG SCHIRMER (*Arch. Pharm.*, 1912, 250, 448—451).—The iodine in alkali iodides can be estimated as follows. The iodide (0.4 gram dissolved in not more than 20 c.c. of water) and 5 grams of official ferric chloride solution are kept for one hour. The solution is then diluted with 100—120 c.c. of water, 10 c.c. of official 25% phosphoric acid are added, and the liberated iodine, after being dissolved completely by the addition of 0.5 gram of potassium iodide, is titrated by *N*/10-sodium thiosulphate.

In another process, 0.5 gram of the iodide dissolved in about 50 c.c. of water is treated with 10 c.c. of dilute sulphuric acid and 10 c.c. of 1% sodium nitrite; after one to two minutes, 1 gram of carbamide is added, the mixture is vigorously shaken for five minutes, 0.5 gram of potassium iodide is added to dissolve the iodine, which is then titrated with *N*/10-sodium thiosulphate.

A third process is as follows: 20 c.c. of about 1% iodic acid or potassium iodate are acidified with 5 c.c. of dilute sulphuric acid, and then diluted with about 50 c.c. of water. A solution of about 0.4 gram of the iodide in 5—10 c.c. of water is added; after one to two minutes, the solution is neutralised by the addition of 5 grams of borax. After an interval of five minutes, 1 gram of potassium iodide is added, and the iodine is titrated by *N*/10-sodium thiosulphate.

C. S.

**Estimation of Iodides by Direct Titration.** JOHN W. TURRENTINE (*J. Ind. Eng. Chem.*, 1912, 4, 435—436).—A description of the method of estimation of iodine in the presence of bromine and chlorine described by Bray and MacKay (*Abstr.*, 1910, ii, 996), and adapted by the author for the rapid estimation of iodine in kelps. F. M. G. M.

**Estimation of Oxygen and Occluded Gases in Copper, and a Correction to the Electrolytic Assay in the Complete Analysis of Copper.** GEORGE L. HEATH (*J. Ind. Eng. Chem.*, 1912, 4, 402—404. Compare *Abstr.*, 1900, ii, 756).—The author reviews and points out discrepancies in the methods previously advocated by himself (*J. Amer. Chem. Soc.*, 1905, 27, 308) and others for the estimation of oxygen and occluded gases in copper; he considers that the loss in weight on heating copper filings at a red heat in a current of hydrogen is not entirely due to oxygen from cuprous oxide and

sulphurous acid, but includes the gases derived by the metal from the fuel and the refining furnace.

Within the limits of an ordinary analysis, red-hot copper has practically no affinity for carbon dioxide, and the loss of weight by subsequently heating in hydrogen does not express the true oxygen of the cuprous oxide present in the cast-metal, for the metal retains, after long exposure to a current of hydrogen, nearly twice as much hydrogen in an occluded state or solid solution as was present in the absorbed gas of the cast-metal; the original occluded hydrogen gas was driven out by the preliminary heating in carbon dioxide, and the hydrogen retained after heating in a current of hydrogen should be finally expelled from the reduced copper by exposing the hot metal to a stream of carbon dioxide during twenty minutes before cooling and weighing in air.

The preparation and purification of the carbon dioxide (compare Abstr., 1908, ii, 688), hydrogen, and copper sample for ignition are described together with suggested improvements in the methods of ignition for estimating absorbed gas, total oxygen, and sulphur in copper.

The exact electrolytic assay of refined copper as previously described by the author gives results sufficiently accurate for the valuation of the metal, but as pointed out by Ferguson (*J. Ind. Eng. Chem.*, 1911, 3, 372) the deposition on the cathode is not absolutely complete when a test of 1 c.c. of the electrolyte remains colourless with hydrogen sulphide, but about 0.005—0.008% of copper is left in the solution.

F. M. G. M.

**Estimation of Ozone.** EMERICH CZAKÓ (*J. Gasbeleuchtung*, 1912, 55, 768—772).—A sketch with description of the form of burette which the author employs for estimating ozone in mixed gases by the liberation of iodine from potassium iodide and subsequent titration with sodium thiosulphate (compare Lechner, Abstr., 1911, ii, 822).

F. M. G. M.

**Application of Electrolytic Conduction to the Analysis of Mixtures of Sulphuric and Nitric Acids.** H. CORVAZIER (*Mon. Sci.*, 1912, [v], 2, I, 322—323).—The conductivity studies of Dutoit which have been applied to the analysis of wines can be employed for the estimation of mixtures of sulphuric and nitric acids by means of the variation in conductivity of a solution of barium nitrate during the addition of sodium carbonate.

The mixed acids are accurately neutralised with barium hydroxide, whereby the sulphuric acid is eliminated and barium nitrate formed, which solution is then titrated with standard sodium carbonate.

During the addition of sodium carbonate with formation of barium carbonate, the conductivity changes little, as the number of ions in the solution does not change, although their concentration does to a slight extent, and the difference between the conductivity of barium nitrate and sodium carbonate is but slight; when, however, all the barium carbonate is precipitated and sodium carbonate is still added, the number of ions increases, the conductivity rises rapidly, and by plotting

a curve the exact point where the barium was all precipitated is accurately indicated, and from this the amount of nitric acid in the mixture deduced. The number of c.c. of sodium carbonate used form the abscissæ and the increase in conductivity the ordinates of the curves.

F. M. G. M.

**Iodimetric Titration of Sulphites in Presence of Alcohol and Sugars.** JULIAN L. BAKER and FRANK E. DAY (*Analyst*, 1912, 37, 439—442).—An investigation as to the accuracy of the titration of sulphites by means of iodine. The final conclusions arrived at are:

1. Sulphur dioxide is readily oxidised by dissolved oxygen in dilute acid solutions. 2. The action is much promoted by the occurrence in the solution of a reaction between alkali and acid. This affects the results obtained by Farnsteiner's method. 3. Commercial alcohols and alcoholic liquids contain certain matters capable of combining with sulphites. These substances partly prevent the oxidation of sulphites by iodine. 4. Dextrose, by virtue of its aldehydic structure, combines to a certain extent with sulphites, but sucrose does not.

L. DE K.

**The Detection of Nitric Acid in Sulphur Trioxide.** W. N. IWANOFF (*Chem. Zeit.*, 1912, 36, 1170).—The diphenylamine method of detecting nitric acid is not applicable when the sulphuric acid contains more than 20% of free trioxide, a coloration being then obtained, owing to the oxidising action of the trioxide; thus pure sulphuric acid remains colourless with diphenylamine up to 210°, but at higher temperatures, at which dissociation occurs, a coloration is produced. It is therefore necessary, in testing the commercial acid, to dilute with pure sulphuric acid until the concentration approaches that of the monohydrate.

C. H. D.

**A New Volumetric Estimation of Nitrites and Separation of Nitrous and Nitric Acids.** WALDEMAR M. FISCHER and N. STEINBACH (*Zeitsch. anorg. Chem.*, 1912, 78, 134—140).—There is no satisfactory method for the estimation of nitric acid in presence of nitrous acid. A method is provided by the rapid esterification of nitrous acid (Abstr., 1909, ii, 32) in which oxidation to nitric acid does not take place, as is proved by experiments with pure silver nitrite.

The solution is placed in a 300 c.c. flask, 5 c.c. of methyl alcohol are added, and a mixture of *N*/10-hydrochloric acid with a little methyl alcohol is allowed to flow in, whilst a current of air is drawn through the liquid. After 20 c.c. of acid have been run in, the stream of air is continued for five minutes, and the solution is then titrated with sodium hydroxide solution, free from carbonate and phenolphthalein. The reaction is:  $\text{NaNO}_2 + \text{HCl} + \text{CH}_3\cdot\text{OH} = \text{NaCl} + \text{CH}_3\cdot\text{O}\cdot\text{NO} + \text{H}_2\text{O}$ .

In the separation of nitric and nitrous acids, a mixture of sulphuric acid and methyl alcohol is placed in the flask, and the solution to be tested, mixed with methyl alcohol, is added drop by drop, air being passed through. The contents of the flask are then washed into

a Jena flask, 2.5—3 grams of Devarda's alloy are added, together with 20 grams of potassium hydroxide, and the ammonia formed is distilled into *N*/4-hydrochloric acid and titrated. C. H. D.

**Neutral Ammonium Citrate Solution.** A. J. PATTEN and CHARLES S. ROBINSON (*J. I. d. Eng. Chem.*, 1912, 4, 443—446).—The authors consider the "conductivity method" of obtaining a neutral ammonium citrate solution to be satisfactory, and describe their experiments which were being carried out at the time that Hall and Bell (*Abstr.*, 1911, ii, 657) and Hall (*J. Ind. Eng. Chem.*, 1911, 3, 559) published an account of the process, which the author considers satisfactory.

The official American method of preparing neutral ammonium citrate solutions is considered extremely untrustworthy, and the purified litmus method, although somewhat better, allows of a limit of error too great for accurate work. F. M. G. M.

**Estimation of Arsenic in Organic Compounds.** THEODOR ST. WARUNIS (*Chem. Zeit.*, 1912, 36, 1205—1206).—A résumé of the literature of this subject is given and a new method described.

In the case of arsenic compounds, which burn with difficulty, 0.2 to 0.4 gram in fine powder is mixed intimately with potassium nitrate, 10 grams, and sodium peroxide, 5 grams, and melted in a nickel dish, care being taken that all carbon particles are brought into the molten liquid and burnt. The product is dissolved in hot water, the solution made acid with hydrochloric acid, and the arsenic estimated as magnesium pyroarsenate in the usual way, or volumetrically by Brügelmann's uranium method.

In the case of volatile arsenic compounds the preliminary melting is done in a 35 cm. hard glass tube sealed at one end, containing a 2 cm. layer of sodium peroxide, next, the substance mixed with potassium nitrate and sodium peroxide, then 3 cm. of peroxide followed by a pad of asbestos; the rest of the tube is filled with dry sodium carbonate, which is heated first and the heating gradually extended to the other parts of the tube. When the reaction is completed, the arsenic is estimated as already described. T. A. H.

**Detection of Boric Acid in Butter.** G. CORNALBA (*Boll. chim. farm.*, 1912, 51, 433—435).—A small quantity of sodium carbonate is added to the butter (20 grams), which is then incinerated and heated until the ash is almost white. The residue is extracted with dilute hydrochloric acid, and after filtration the liquid is evaporated to dryness. The residue is taken up with a few drops of very dilute hydrochloric acid, and ten drops of turmeric tincture are added. On again evaporating to dryness, the presence of boric acid is indicated by the appearance of a cherry-red coloration. With practice, it is possible to judge approximately how much is present. The addition of 0.01% of boric acid to butter can be detected in this way. Boric acid may be found in butter to which no preservative has been added; it is derived probably from boric vaselin applied to the cow for medicinal purposes. R. V. S.

**Estimation of Carbon Dioxide in Soils.** LEON T. BOWSER (*J. Ind. Eng. Chem.*, 1912, 4, 265—266).—The volumetric estimation of carbon dioxide as recently described by the author (this vol., ii, 995) has been extended to the analysis of soils and other materials containing very small amounts of carbonate, and the following modifications are suggested under these conditions.

Soils containing 0.1% or less of carbon dioxide require for titration an acid of strength not exceeding *N*/50.

The degree of heat at first applied to the flask must be regulated, as at the moment before ebullition there is a sudden tendency to froth which must be carefully guarded against.

Several analysts have also noticed the fact (which needs explanation) that when 10 grams of soil are used for the analysis higher results are obtained than when larger amounts are employed. F. M. G. M.

**Estimation of Soluble Silica in Trass.** ANTON HAMBLOCH (*Chem. Zeit.*, 1912, 36, 1058—1059).—Freshly prepared 5% sodium hydroxide solution should be used for separating the silica from the sand, quartz, etc., in this mineral; the employment of potassium hydroxide is not recommended. The mineral should not be too finely powdered, and attention is drawn to the fact that other constituents, besides silica, may be dissolved by the alkali. W. P. S.

**Estimation of Total Potassium in Minerals.** CHARLES J. SCHOLLENBERGER (*J. Ind. Eng. Chem.*, 1912, 4, 436).—The author considers Lawrence Smith's method for estimating potassium in minerals to be tedious, and the modification by Pettit and Ystgard (*Proc. of Assoc. Official Agricultural Chemists*, 1906) to be unsatisfactory, and suggests the following procedure.

The operation is conducted according to Smith's procedure until the filtrate from washing out the alkalis from the fusion is obtained; this is evaporated to dryness with hydrochloric acid, taken up with 2 c.c. of hydrochloric acid, 25 c.c. hot water added, and the solution filtered. Chloroplatinic acid is added, and the mixture evaporated until of semi-solid consistency, treated with acidified alcohol (which dissolves calcium chloride), and collected in a special tubular filter (sketch given) with suction on a perforated platinum disk, which is covered with a layer of asbestos, a linen cloth disk, and glass wool. When thoroughly washed with acidified alcohol, the precipitate is dissolved with hot water into a tared platinum dish, and after evaporation dried and weighed.

F. M. G. M.

**Estimation of Potassium as Perchlorate in Potassium Manures.** ARTHUR STRIGEL and J. DODT (*Landw. Versuchs.-Stat.*, 1912, 78, 179—188).—The potassium salt (10 grams) is boiled for five minutes with water (about 300 c.c.) and hydrochloric acid (D 1.125, 2 c.c.), and the sulphuric acid precipitated, avoiding a large excess of barium chloride. The solution, when cold, is diluted to 500 c.c. and filtered. A portion of the filtrate (25 c.c. = 0.5 gram of substance) is then evaporated with 10 c.c. of 22% perchloric acid until quite syrupy. The residue is treated in the usual manner, and the

potassium perchlorate collected in a Gooch crucible and dried at 180°. N. H. J. M.

**Analysis of the Metals and of the Commonest Metallic Alloys by Electrolytic Methods.** R. BELASIO (*Ann. Lab. Gabelle*, 1912, 6, 245—303).—A detailed account of the methods employed in the Laboratori Chimici delle Gabelle in Rome for the estimation of certain metals and a large number of common alloys. R. V. S.

**Electrolytic Estimation of Zinc in the Presence of Ammoniacal Salts.** R. BELASIO (*Ann. Lab. Gabelle*, 1912, 6, 239—244).—The electrolytic estimation of zinc in presence of ammonium salts must take place in acid solution, and has been possible hitherto only when rotating electrodes are employed (compare Sand, *Trans.*, 1907, 91, 373). The author now finds that the estimation of zinc in the presence of ammonium salts can be effected with accuracy in the presence of free lactic acid, potassium and ammonium lactates and potassium sulphate, using stationary electrodes. The zinc solution (containing 0.1—0.3 gram in the form of sulphate) is acidified with lactic acid, made alkaline with potassium hydroxide, treated with a further 5 c.c. of lactic acid, made up to about 200 c.c., and treated with 3 grams of ammonium oxalate and 5 grams of potassium sulphate. The liquid is electrolysed for three to four hours with a current density 0.4—0.5 amp. at 3—3.5 volts, using a coppered Winkler electrode. After two or three hours it is well to increase the current density to 1 amp., and to add 2 c.c. of lactic acid. R. V. S.

**Rapid Electro-analysis under Diminished Pressure.** FRANZ. FISCHER and EMIL STECHER (*Zeitsch. Elektrochem.*, 1912, 18, 809—816).—The method already described (compare Abstr., 1911, ii, 1129) has been further tested in the estimation of single metals, and also in separations. Zinc, like copper, can only be rapidly estimated under diminished pressure when the temperature is high. The method is not particularly suitable for the estimation of lead as peroxide.

Good results were obtained in the estimation of copper in brass, the separation of copper and nickel, and the separation of silver and copper. In the latter case, neutral or acidified solutions of the sulphates were used, and Brunck's method of using an Edison accumulator was adopted (compare Abstr., 1911, ii, 1136). The advantage of the use of diminished pressure is shown by the fact that 0.1 gram of silver can be deposited in fifteen minutes (Brunck required about an hour to effect this), and the complete determination of silver and copper occupies only three-quarters to one hour. The arrangement for washing a deposit without interrupting the current is described. For full experimental details of the estimations the original paper must be consulted. G. S.

**Gravimetric Separation of Zinc and Nickel.** THOMAS COCKBURN, A. D. GARDINER, and JOHN W. BLACK (*Analyst*, 1912, 37, 443—446).—An investigation as to the accuracy of several methods proposed from time to time. Separation of the zinc as sulphide in

presence of formic acid (Waring's method) gives satisfactory results, but the precipitation of the nickel by dimethylglyoxime is still more delicate (Brunck, Abstr., 1907, ii, 989). L. DE K.

**Titration of Copper Salts with Titanium Trichloride.** LUDWIG MOSER (*Chem. Zeit.*, 1912, 36, 1126—1127).—Cupric solutions may be titrated directly with titanium trichloride in hydrochloric acid solution without the use of potassium thiocyanate and a ferrous salt as indicators; the end-point of the titration is shown when the greenish-yellow solution becomes colourless. The cupric solution is treated with from 20 to 30 c.c. of concentrated hydrochloric acid, boiled for about one minute, and titrated at once, or cooled in an atmosphere of carbon dioxide and then titrated (compare Trans., 1906, 89, 1491). W. P. S.

**Fusion of Certain Rare Earths with Sodium Carbonate, and the Separation of Tungsten from Iron, Glucinum, and Aluminium.** MAX WUNDER and A. SCHAPIRO (*Ann. Chim. anal.*, 1912, 17, 323—327).—When cerium oxide is fused with sodium carbonate for forty-five minutes, then treated with hot water, and a further quantity of the carbonate added, only a small quantity of the oxide (about 0.3%) goes into solution. Under similar treatment, lanthanum oxide yields 0.5% of soluble oxide, didymium oxide about 14%, erbium oxide 5 to 6%, and thorium oxide, 0.62%. Tungstic oxide was rendered completely soluble by fusion with sodium carbonate, and results of experiments are given showing that tungstic oxide may be separated in this manner from ferric oxide or glucinum oxide. Tungstic oxide may also be separated from aluminium oxide by fusion with sodium carbonate, and treating the resulting solution with an excess of ammonium nitrate (compare this vol., ii, 96, 687). W. P. S.

**Electrolytic Separation of Iron and Manganese. Analysis of Ferro-manganese.** R. BELASIO (*Ann. Lab. Gabelle*, 1912, 6, 207—216).—When a solution of iron and manganese in ammonium oxalate is electrolysed in the presence of hydrazine sulphate, iron is deposited quantitatively, whilst the hydrazine prevents the deposition of manganese dioxide at the anode. The process affords, therefore, a simple and convenient method of separation of the two metals.

The iron and manganese in the form of sulphates (up to 0.3 gram of each) are dissolved in warm water slightly acidified with sulphuric acid, and the solution is poured into a solution of 6 to 8 grams of ammonium oxalate in a little boiling water. The liquid is made up to about 200 c.c., and, when cold, 5 c.c. of a solution of hydrazine sulphate (1 gram in 50 c.c.) are added, and the solution is electrolysed with a current density of 0.7 ampere at 4 to 4.5 volts. The cathode is a Winkler electrode, and the anode a platinum spiral. During the electrolysis, which lasts two or three hours, the remainder of the hydrazine sulphate solution is added in the neighbourhood of the anode at the rate of 8 to 10 drops per minute from a tap-funnel terminating in a capillary tube. When a drop of the liquid gives a scarcely perceptible coloration with nitric acid, hydrochloric acid and

ammonium thiocyanate, the electrode is removed, washed, dried at 70–80°, and weighed. The liquid is evaporated to a volume of 70–80 c.c.; this also removes the ammonium carbonate it now contains. It is treated with 1.5 grams of chrome alum, 10 grams of ammonium acetate, filtered into a platinum dish, treated with 3 c.c. of 50% ammonia, and (the dish serving as the anode) electrolysed at 70–80° with a current density of 0.5–0.6 ampere at 2 to 3 volts. When the electrolysis is complete, the deposit of manganese dioxide is washed and heated to redness to convert it into  $Mn_3O_4$ , which is again washed with water, calcined, and weighed.

The method is suitable for the analysis of ferro-manganese, the metals being brought into the form of sulphates before electrolysis.

R. V. S.

**New Volumetric Estimation of Uranium.** VICTOR AUGER (*Compt. rend.*, 1912, 155, 647–649).—A volumetric method for the estimation of uranium in the presence of iron or titanium. In the absence of titanium the uranium is reduced by zinc in acid solution. If titanium is present, the reduction must be carried out by means of the exact amount of a titanous salt in the presence of a large excess of sodium tartrate. The containing vessel is then filled with carbon dioxide, and the reduced uranium is titrated back with a standard solution of a ferric salt, ammonium thiocyanate being used as indicator. In the presence of large quantities of iron, the results obtained are slightly too high.

W. G.

**The Valuation and Technical Extraction of Uranium Micas.** FRITZ GLASER (*Chem. Zeit.*, 1912, 36, 1166–1167).—In the separation of uranium from iron by means of ammonium carbonate, the iron is free from uranium, but the uranium always contains a little iron. This is removed by fusing the ignited precipitate with potassium hydrogen sulphate, dissolving in water, filtering, neutralising the filtrate, and precipitating the iron with an excess of ammonium sulphide.

In the extraction of autunite with acids, sulphates are always present, and in view of the fact that radium forms the most insoluble of all sulphates, the effect of other substances on its solubility has been studied. Experiments with autunite show that the solubility of radium sulphate is much increased by the presence of iron salts. Even if the hydrochloric acid used contains 10% of sulphuric acid, the greater part of the radium is then extracted. The quantity of autunite in the Portuguese rocks is, however, very small, and mechanical concentration is impracticable.

C. H. D.

**Analysis of White Metals for Bearings, Ornaments, and Type.** R. BELASIO (*Ann. Lab. Gabelle*, 1912, 6, 217–229).—The ordinary methods of analysing these alloys effect the separation of the tin and antimony from the lead and copper by means of sodium sulphide, and they have the disadvantage that some of the copper dissolves in the sodium sulphide when the latter contains traces of polysulphides. The author eliminates this error by recovering and

estimating the part of the copper so dissolved, taking advantage of the fact that, in the presence of potassium cyanide, the copper in question forms a complex ion and is not deposited when the antimony is obtained by electrolysis. After the removal of the antimony, the sodium sulphide solution contains the tin as well as the copper above-mentioned. The tin is converted into oxalate, and the traces of copper present are precipitated with hydrogen sulphide; the filtrate is then ready for the electrolytic estimation of the tin. Detailed schemes of analysis are given for anti-friction metals (containing a large amount of tin) and for type-metal, etc. (containing a large amount of lead). R. V. S.

**Electrolytic Estimation of the Tin in Metal Foil of Lead, Tin, and Antimony Externally Tinned.** R. BELASIO (*Ann. Lab. Gabelle*, 1912, 6, 231—237).—Owing to the high price of tin, "tin"-foil and other "tin" objects are often made of an alloy of lead, tin, and antimony, which is then tinned electrolytically. If such objects are treated at 40° with sodium hydroxide solution (10%) containing a few drops of hydrogen peroxide, the external tin is dissolved, whilst the tin of the alloy is attacked but slightly or not at all. The solution is neutralised, and treated with sodium sulphide. After filtering from traces of lead, the solution is decolorised with potassium cyanide, acidified with sulphuric acid, and boiled; the tin sulphide precipitated is dissolved in hydrochloric acid with addition of potassium chlorate, and the tin is estimated electrolytically as described below.

The author gives a description of his method for the electrolytic estimation of tin. The alloy is dissolved in Nissenson's mixture of nitric and tartaric acids; the lead is precipitated as sulphate, and the filtrate is rendered alkaline and boiled with sodium sulphide, which precipitates traces of lead, copper, etc. After filtration, the solution is decolorised with potassium cyanide, and at the boiling point it is treated with sulphuric acid until the reaction is acid. The precipitated sulphides of tin and antimony are dissolved in hydrochloric acid (with potassium chlorate), the solution is neutralised with ammonia, and boiled after the addition of oxalic acid. When the hydroxides have dissolved, ammonium oxalate is added, and the antimony is precipitated at 95—98° with hydrogen sulphide. After filtering and removing the hydrogen sulphide, the liquid is electrolysed with a current density of 0.4 amp. at 3—4 volts. The tin is deposited in ten to fifteen hours.

R. V. S.

**Detection of Antimony and of Tin in Metallic Alloys.** R. BELASIO (*Ann. Lab. Gabelle*, 1912, 6, 501—503).—The formation of an orange-red, sparingly soluble iodide of caesium and antimony, already employed by Behrens as a microchemical reagent for antimony, can be employed to detect this metal in alloys, and is especially convenient when much tin is present. A solution of 1 gram of potassium iodide and 1 gram of caesium chloride in 5 grams of distilled water is employed as a reagent. The alloy is dissolved in sulphuric acid, the liquid is diluted with an equal volume of water, and filtered. To a few drops of the filtrate a crystal of sodium sulphite is added, and, after warming, one or two drops of the above reagent are added.

In the presence of antimony, a permanent red precipitate is formed. After filtration, the rest of the liquid is boiled with antimony powder, which reduces stannic sulphate to stannous sulphate, so that a precipitate with mercuric chloride indicates the presence of tin.

R. V. S.

**Qualitative Detection of Zirconium.** WILHELM BILTZ and WERNER MECKLENBURG (*Zeitsch. angew. Chem.*, 1912, 25, 2110—2111\*).—A bead is prepared by fusing the substance to be tested for zirconium, which must be free from phosphoric acid, with sodium carbonate on a platinum spiral in the oxidising flame of the blowpipe. The mass is then dissolved in hydrochloric acid, boiled, and tested with disodium hydrogen phosphate. A more or less abundant gelatinous precipitate shows the presence of zirconium.

Iron, aluminium, the rare earths, thorium, glucinum, titanium, and silicic acid are inert; tin, however, should be absent, or else must be removed previously.

L. DE K.

**A New Method for the Estimation of Vanadium.** D. J. DEMOREST (*J. Ind. Eng. Chem.*, 1912, 4, 249—250).—The following method for the estimation of vanadium in steel depends on the selective oxidation of ferrous sulphate in the presence of vanadyl sulphate by means of manganese dioxide. The vanadyl sulphate is then estimated by adding excess of potassium permanganate and titrating back with sodium arsenite. This differential oxidising action apparently contradicts the results of J. R. Cain (this vol., ii, 390), but the discrepancy is explained (see following abstract).

The manganese dioxide should be sufficiently fine to pass through a 200-mesh sieve, and yet should settle in a beaker of water in thirty seconds.

The process is as follows: A 2-gram sample of the steel or iron is dissolved in a mixture of 30 c.c. of water with 12 c.c. of concentrated sulphuric acid by application of heat; 1 c.c. of nitric acid (D 1.42) is carefully added to oxidise the iron, and nitrous fumes removed by boiling. The solution is diluted with water (30 c.c.), and all carbon oxidised by boiling with a strong solution of potassium permanganate.

Ferrous sulphate is now added to reduce the  $\text{MnO}_2$ ,  $\text{HMnO}_4$ ,  $\text{H}_2\text{CrO}_4$ , and  $\text{H}_3\text{VO}_4$ , and any possible nitrous fumes removed by boiling; the volume of the solution is increased to 250 c.c., and potassium permanganate added until a pink coloration is obtained. The cooled solution is again reduced with an excess of ferrous sulphate, about 1 gram of manganese dioxide is added, and the solution vigorously shaken until ferrous iron is no longer present; the end should be taken when the test does not show blue immediately, as the vanadyl sulphate present reduces the ferri- to ferro-cyanide and exhibits a blue colour after a few seconds.

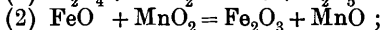
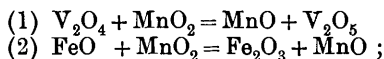
After separation of manganese dioxide (by filtration), the unoxidised vanadyl sulphate  $[\text{V}_2\text{O}_5(\text{SO}_4)_2]$  is treated with excess of standard potassium permanganate, and the excess subsequently titrated with

\* and *Anal. Fis. Quím.*, 1912, 10, 314—316.

standard sodium arsenite solution, when the end-point is very sharp. A blank experiment must be made on a vanadium-free steel, and the result deducted, which generally amounts to about 0.00075 gram of vanadium.

F. M. G. M.

**A New Method for the Estimation of Vanadium; an Explanation.** J. R. CAIN and D. J. DEMOREST (*J. Ind. Eng. Chem.*, 1912, 4, 256).—The discrepancy in the results obtained individually by the authors in this estimation (compare this vol., ii, 390 and preceding abstract) is found to be due to difference in size of the particles of manganese dioxide employed by these workers. They exchanged samples of manganese dioxide, and under these conditions corroborated each other's results; it was then noted that the dioxide which oxidised differentially was much coarser than that employed by J. R. Cain, which oxidised both the iron and vanadium. On grinding the coarse manganese dioxide very fine, it was found to oxidise both iron and vanadium, whilst a coarse portion which was isolated from J. R. Cain's sample was found to oxidise differentially. The discrepancy is thus evidently due to a difference in the velocities of the reactions:



with the finely powdered manganese dioxide both reactions went to completion, whereas in the other case (Demorest's) the reaction (1) was inappreciable, and reaction (2) completed during the period of treatment.

F. M. G. M.

**A Rapid Method for the Estimation of Vanadium in Steels, Ores, etc., based on its Quantitative Inclusion by the Phosphomolybdate Precipitate.** J. R. CAIN and J. C. HOSTETTER (*J. Ind. Eng. Chem.*, 1912, 4, 250—256).—When vanadium is carried down with an ammonium phosphomolybdate precipitate, the orange to brick-red substance so obtained shows markedly different properties from normal ammonium phosphomolybdate (compare Brearley and Ibbotson, *The Analysis of Steel Works Material*, 1902, 165), and precipitation being complete, it is possible by this means to separate iron from vanadium.

For steels containing vanadium, chromium, nickel, titanium, manganese, and molybdenum, the solution is prepared exactly as for a phosphorus determination, nearly neutralised with ammonium hydroxide, and treated with a solution of sodium phosphate containing at least ten times as much phosphorus as there is vanadium present; the precipitation is carried out by the ordinary method, and the precipitate, after being well washed with hydrogen ammonium sulphate, is dissolved in concentrated sulphuric acid (5—8 c.c. for every 10 mg. phosphorus present) with the addition of a few drops of nitric acid; the vanadium is then reduced, and subsequently titrated with potassium permanganate at 70—80°.

The following alternative methods of dealing with the mixed precipitate are also described in detail: (1) the reduction of vanadic acid by sulphur dioxide (Abstr., 1908, ii, 540); (2) colorimetric

estimation of vanadic acid (Gregory, *Proc.*, 1908, 232, and *Chem. News*, 1909, 100, 221).

A number of necessary precautions are described, and the author draws the conclusion that the precipitation is quantitative, that the vanadium can be subsequently separated from molybdic acid, or it can be reduced without simultaneously reducing the molybdic acid, and that the method is rapid and accurate.

F. M. G. M.

**The Rapid Estimation of Vanadium in Steel.** FRANK GARRATT (*J. Ind. Eng. Chem.*, 1912, 4, 256).—A modification of Johnson's method (*Chem. Analysis of Special Steels, etc.*, p. 8) for determining vanadium in steel in which the oxidation of the chromium and vanadium in hot dilute sulphuric acid with potassium permanganate (*loc. cit.*) is omitted.

The steel (2 grams) is dissolved in about 50 c.c. of dilute sulphuric acid, the iron and tungsten oxidised with nitric acid, and boiled until the precipitated tungstic acid is of a pure yellow colour. The solution is diluted, the tungstic acid separated, and a little ferrous sulphate solution added to the filtrate, which is immediately titrated with standard ferrous ammonium sulphate in the presence of potassium ferricyanide.

The author considers this method more suitable than those of Blair or J. R. Cain for employment in a technical laboratory.

F. M. G. M.

**Estimation of Small Quantities of Antimony in Lead-Antimony Alloys by means of the Quartz Mercury Thermometer.** K. FRIEDRICH (*Metallurgie*, 1912, 9, 446—449).—The estimation of small quantities of antimony, up to 6%, in lead is conveniently performed by determining the initial freezing point by means of a quartz mercury thermometer. The accuracy of the instrument is not injured by repeated use, the thermometer being introduced without previous heating into the lead at 350°. The error is less than 0.1% if the alloy is stirred. The accuracy falls off from 8% of antimony.

C. H. D.

**Action of Dimethylglyoxime on Platinum.** MAX WUNDER and V. THURINGER (*Ann. Chim. anal.*, 1912, 17, 328—329).—Although platinum salts yield a precipitate with dimethylglyoxime, the reaction is not quantitative, and, even when sodium acetate is added to reduce the action of the mineral acid present, the results obtained are untrustworthy.

W. P. S.

**Hübener's Method of Estimating Caoutchouc as its Bromide.** GERHARD HÜBENER (*Gummi Zeit.*, 1912, 26, 1281—1284).—A reply to the criticism of Hinrichsen and Kindscher (this vol., ii, 397); the author maintains his position and refers to the work of Budde (*Abstr.*, 1909, ii, 828) and Utz (this vol., ii, 1002).

F. M. G. M.

**Hübener's Method of Estimating Caoutchouc as its Bromide.** R. BECKER (*Gummi Zeit.*, 1912, 26, 1503. Compare *Abstr.*, 1911, ii, 445).—The author discusses the methods of estimat

ing caoutchouc as bromide which have been suggested by other workers (compare Abstr., 1911, ii, 545, 1036). F. M. G. M.

**Hübener's Method of Estimating Caoutchouc as its Bromide.** GERHARD HÜBENER (*Gummi Zeit.*, 1912, 26, 1711—1712).—Polemical (compare Korneck, Abstr., 1911, ii, 545, and Spence and Galletly, Abstr., 1911, ii, 1035). F. M. G. M.

**Methods of Testing Rubber Contents in Raw and Vulcanised Rubber.** W. A. DUCCA (*J. Ind. Eng. Chem.*, 1912, 4, 372—374).—A review of the most important results obtained by different workers regarding the direct determination of caoutchouc by means of the nitrosite (or nitrosate) and the tetrabromide methods.

The work of Harries is described, and the criticisms of Alexander and Gottlob on it discussed, the author considering (with the former) that the nitrosate method is of no value in estimating actual caoutchouc in either raw or vulcanised rubber, although it may prove an excellent method for determining the "vulcanisation coefficient," in which the nitrosate is only employed as a means to completely precipitate the sulphur of vulcanisation.

The tetrabromide method as originated by Budde, first as a gravimetric and subsequently modified to a volumetric process, is also discussed, together with a review of the criticisms of Fendler and Kuhn, Harries and Rimpel, Spence, Hinrichsen and Kindscher, Axelrod, and Hübener on the process, and the author considers that, although a satisfactory method is as yet unknown, much progress is being made towards elucidating this problem. F. M. G. M.

**The Estimation of Methyl Alcohol in Ethyl Alcohol and in Alcoholic Beverages.** ADOLFO BONO (*Chem. Zeit.*, 1912, 36, 1171).—The liquid to be tested is distilled, the vapours passing into a flask containing an acid solution of potassium dichromate. The escaping vapours are condensed. The first portion of the distillate contains only acetaldehyde. Formaldehyde is tested for in the following fractions by means of phenylhydrazine and sodium nitroprusside. The method is capable of detecting an admixture of 1—2% of methyl alcohol. C. H. D.

**Detection and Estimation of Methyl Alcohol in Alcoholic Liquids.** A. SCHLICHT (*Zeitsch. öffentl. Chem.*, 1912, 18, 337—340).—The method proposed is based on the fact that methyl alcohol is oxidised by chromic acid with the formation of carbon dioxide and water, whilst ethyl alcohol under similar conditions yields acetic acid. A quantity of the spirit to be tested, corresponding with about 0.5 c.c. of alcohol, is diluted with twenty times its volume of water, and then mixed with a solution consisting of 5 grams of potassium dichromate dissolved in 30 c.c. of dilute sulphuric acid, care being taken to keep the mixture cool. When methyl alcohol is present, carbon dioxide is evolved, and may be identified by absorbing it in barium hydroxide solution. The test will detect the presence of 0.5% of methyl alcohol in ethyl alcohol. The quantity of methyl

alcohol present may be estimated by collecting the carbon dioxide and measuring the amount of the latter; traces of acetic acid, which are evolved when the oxidising solution is warmed to expel the carbon dioxide, may be eliminated by passing the gases through a neutral or slightly acid soap solution. The amount of dichromate used in the oxidation also indicates the proportion of methyl alcohol to ethyl alcohol, 100 grams of methyl alcohol requiring 150 grams of oxygen, whilst 100 grams of ethyl alcohol require 69.6 grams of oxygen.

W. P. S.

**Estimation of Glycerol in Fats.** RICHARD WILLSTÄTTER and ANTONIO MADINAVEITIA (*Ber.*, 1912, 45, 2825—2828).—Of the various methods for the estimation of glycerol in fats, that devised by Zeisel and Fanto (*Abstr.*, 1902, ii, 111, 585) is the most satisfactory, but it involves the preliminary saponification of about 20 grams of fat and conversion of the resulting glycerol, by means of hydriodic acid, into isopropyl iodide, which is then estimated by the ordinary Zeisel process. The authors find that if a small quantity (0.15 to 0.35 gram) of fat is heated with 10 c.c of hydriodic acid (D 1.8), first at 100—115° until the reaction is apparently complete and then for one hour at 135—140°, the whole of the glycerol is obtained in the form of isopropyl iodide, which can be determined in the usual way by its action on alcoholic solution of silver nitrate.

Lewkowitsch's suggestion that the percentage of hydroxy-constituents in fats can be determined by direct acetylation of the fat with acetic anhydride (*Abstr.*, 1898, ii, 316) is untenable, since acetic anhydride attacks stearin and the glycerides of the ordinary fatty acids.

T. A. H.

**Estimation of Sucrose in the Presence of Other Sugars.** GIUSEPPI TESTONI (*Ann. Lab. Gabelle*, 1912, 6, 581—589).—The author confirms the trustworthiness of Jolles' method (*Abstr.*, 1911, ii, 74; compare Bardach and Silberstein, *ibid.*, ii, 663). The fermentation method with the Bulgarian bacillus can be made to give good results, but is less convenient.

R. V. S.

**Choice of Yeasts in the Bio-chemical Detection of Sugars and Glucosides.** ÉMILE BOURQUELOT and HENRI HÉRISSEY (*J. Pharm. Chim.*, 1912, [vii], 6, 246—253).—Rosenthaler has stated recently (this vol., i, 640) that Bourquelot's method for the detection of sugars and glucosides in plants is fallacious, since amygdalin is attacked by invertase, and consequently the initial change of rotation may be due to the decomposition of amygdalin as well as sucrose. This objection is ill-founded, since the enzyme which attacks amygdalin and produces mandelonitrile glucoside is not invertase, but amygdalase, and the latter is not present in "invertase" prepared by Bourquelot's method from "top-yeast," and the results of a number of new experiments are quoted in support of this. The second difficulty mentioned by Rosenthaler, that emulsin preparations are often laevorotatory, has not been experienced by the authors, but it is quite easy to allow for such initial rotation in making observations.

T. A. H.

**Short Notices.** CARL NEUBERG (*Biochem. Zeitsch.*, 1912, 43, 500—507).—*Polarimetric or Reduction Methods for Estimation of Sugar.*—It is contended that sometimes one method and sometimes the other is the most convenient, and that no general rule as to the method to be used can be adopted. For clinical purposes, however, the polarimetric method would appear generally to be the more convenient.

*Substance causing the so-called Cammidge Reaction.*—Various substances can cause this reaction, including glycuronic acid, pentose, and hexoses. The first-named substance gives the naphtharesorcinol and also the orcinol reactions. Pentose gives a positive orcinol reaction only, whereas hexoses give a negative reaction with both reagents. In this way they can be distinguished from one another. Out of seven human urines examined, five contained glycuronic acid, and one each pentose and a hexose. Animal urines also give a Cammidge reaction. From the urine of a calf, a reaction product with phenylhydrazine was isolated, which had the properties of glyoxylic acid phenylhydrazone. S. B. S.

**Estimation of Galactan.** K. MIYAKE (*J. Coll. Agric. Imp. Univ. Sapporo*, 1912, 4, 337—345).—The substance (3 grams or less) is extracted with ether, treated with nitric acid, and evaporated on a water-bath as in Tollens' method (*U.S. Dept. Agric. Bur. Chem. Bull.* No. 107). It is then filtered, while hot, washed with hot water, and evaporated to one-third of the original volume. After twenty-four hours, water (10 c.c.) is added, and the crystallised mucic acid collected on a filter and washed successively with water, alcohol, and ether, after which it is dried at 100°. The employment of ammonium carbonate is dispensed with. When the amount of galactan is less than 0.8%, the filtrate should be concentrated to one-fifth of its original volume and left for several days if necessary.

Different factors, according to the amount of mucic acid produced, should be employed for calculating the amount of galactose.

N. H. J. M.

**Estimation of Cellulose in Woods and Spinning Fibres.** CHARLES F. CROSS and EDWARD J. BEVAN (*Zeitsch. Farb. Ind.*, 1912, 11, 197—198).—The authors point out certain anomalies in the work of König and Hühn (this vol., ii, 1005) on cellulose, and suggest that portions of the work should be revised with the intent to clear up these points. F. M. G. M.

**Estimation of Cellulose in Woods and Spinning Fibres.** JOSEF KÖNIG and FR. HÜHN (*Zeitsch. Farb. Ind.*, 1912, 11, 209—210).—A reply to Cross and Bevan (preceding abstract). F. M. G. M.

**New Method of Analysis for Citronella Oil.** VICTOR BOULEZ (*Bull. Soc. chim.*, 1912, [iv], 11, 915—917. Compare this vol., i, 880).—Twenty-five or 50 grams of citronella oil are placed in an Erlenmeyer flask with 100 or 200 grams of a solution (35—37° Bé.) of sodium hydrogen sulphite saturated with sodium sulphite, shaken thoroughly, and set aside during two to three hours. One

hundred or 200 grams of water are then added, and the mixture warmed on the water-bath during some hours under a reflux condenser with frequent agitation. The residual oil is withdrawn by means of a separator and weighed, and the citronellal obtained by difference. The "geraniol" in the residual oil can be determined in the usual way by acetylation.

T. A. H.

**The Relative Value of Indicators in the Acid Titration of Wines.** FRANCIS MARRE (*Rev. gén. chim. pur. appl.*, 1912, 15, 242—243).—In the analysis of coloured wines, the following mixture is recommended as an indicator. A cold saturated solution of phenolphthalein in alcohol (7 gram in 90 c.c. of alcohol) and fluorescein (1.2 grams) dissolved in 100 c.c. of cold alcohol. To 5 c.c. of clear (or filtered) wine, 5 drops of the phenolphthalein and 3 drops of the fluorescein solution are added, the mixture is just heated to boiling, diluted with 5 c.c. of water, and subsequently titrated.

F. M. G. M.

**The Iodoform Reaction of Lactic Acid.** CARL NEUBERG (*Biochem. Zeitsch.*, 1912, 43, 500—507).—The statement in certain text-books that the *d*-acid does not give the iodoform reaction is incorrect. Other substances which give this reaction are pyruvic acid, aldol,  $\beta$ -hydroxybutyric acid, quercitol, and inositol. S. B. S.

**Analysis of Commercial Calcium Citrate.** I. BARBONI (*Ann. Lab. Gabelle*, 1912, 6, 311—341).—The author has investigated a number of methods which have been proposed for the analysis of commercial calcium citrate. Analysis by any method must be preceded by a qualitative examination for tartrates, oxalates, and other adulterants. Spica's method is convenient and rapid, and it gives good results in practised hands; the author has simplified the apparatus employed in it. Patanè's method (*Intorno dell' analisi del citrato di calcio*, Acireale, 1909) is very exact in the absence of tartrates, and is better than the methods of Warington, and of Soldaini and Berté, but is lengthy and difficult.

R. V. S.

**The Detection of Conjugated Glycuronic Acid in Normal Urine.** CARL NEUBERG and OMER SCHEWKET (*Biochem. Zeitsch.*, 1912, 44, 502—504).—The orcinol and naphtharesorcinol tests for glycuronic acid derivatives are given by other substances contained in urine, such as nucleic acid. These, unlike glycuronic acid derivatives, are insoluble in ether. If the ethereal extract of urine is used, more certain conclusions as to their presence can be drawn when the two above-named tests are applied. For the purpose of the reaction, to 10 c.c. of urine, acidified with 2 c.c. of dilute sulphuric acid, are added 10 c.c. of alcohol and 20 c.c. of ether. The ethereal layer, after separating, is washed with water or saline solution, and, after addition of water, the ether is evaporated off. The tests are carried out with the residue.

S. B. S.

**The Nature of Peroxydase.** ALBERT HESSE and W. D. KOOPER (*Zeitsch. Nahr. Genussm.*, 1912, 24, 301—309. Compare Abstr., 1911, i, 592, 596).—In view of a recent investigation, the authors are of the opinion that the peroxydase reaction of milk is not due solely to the alkaline constituents of the milk, but to the presence of certain inorganic substances. They draw the conclusion that the reaction is brought about by the catalytic action of iron compounds, such as ferrous lactate. This salt is very sensitive towards Rothenfusser's and Arnold's reagents, and gives a coloration in concentrations containing less iron than does albumin which has been five times precipitated. Ferrous lactate solution no longer gives the reaction when boiled, either alone or in the presence of milk, or when it is mixed with boiled milk. Whilst the presence of mercuric chloride or chloroform does not interfere with the reaction, the latter is inhibited by lactic acid, sodium thiosulphate, and methyl, ethyl and amyl alcohols. W. P. S.

**Proposed Modifications of Robin's Method for the Analysis of Butter.** LUCIEN ROBIN (*Ann. Chim. anal.*, 1912, 17, 330—332).—The author points out that alcoholic  $N/2$ -hydrochloric acid does not alter in strength when kept for some length of time, and that, for various reasons, its use is preferable to that of an aqueous acid solution, as has been proposed by Marion. There is no necessity to employ absolute alcohol in the process, 95% alcohol being equally suitable, provided that less water is added subsequently to reduce the strength to 46.5%. The filtration of the fatty acids soluble in dilute alcohol may be carried out at a temperature of 15—18°. W. P. S.

**Simplified Apparatus for the Estimation of the Reichert-Meissl and Polenske Numbers [of Fats].** A. GOSKE (*Zeitsch. Nahr. Genussm.*, 1912, 24, 274—276).—A small filter-tube is attached to the lower end of the condenser employed in this estimation, and the distillate is filtered before it enters the usual 110 c.c. receiver. The insoluble volatile fatty acids are dissolved from the filter at the end of the distillation, and titrated in the usual way. W. P. S.

**Rapid Estimation of Fat in Cocoa by means of Zeiss' Refractometer.** OTTO RICHTER (*Zeitsch. Nahr. Genussm.*, 1912, 24, 312—319).—The process consists in shaking the cocoa with sodium phosphate solution and a mixture of alcohol and ether, separating the ethereal solution of the fat, and determining its refraction. The phosphate solution is prepared by dissolving 65 grams of trisodium phosphate in 1 litre of water, and preliminary experiments are made to ascertain what volume of the alcohol-ether mixture (equal volumes) must be added to 100 c.c. of the phosphate solution so that exactly 5 c.c. of ether shall separate; the proportion of alcohol to ether may be varied somewhat in order that about 25 c.c. of the mixture are required. Ten grams of the cocoa are shaken with this quantity of the alcohol-ether mixture, and 100 c.c. of the phosphate solution are added. The whole is shaken for a further five minutes, allowed to settle, and the ethereal layer is examined in the refractometer. All the

measurements and reading are made at 17.5°. The percentage quantity of fat ( $F$ ) present is calculated from the reading observed by means of the equation:  $F = (n - n_1/n - n_2) - 1.(100xy)/z$ , where  $n$  is the refractive index of the fat (1.4653),  $n_1$  that of the solvent (1.3543),  $n_2$  that of the fat solution,  $x$  the excess of the solvent (5 c.c.),  $y$  the density of the fat, and  $z$  the quantity of substance in grams (10 grams). Tables are also given showing the quantity of fat corresponding with any observed reading.

W. P. S.

**Halphen's Reaction for Cottonseed Oil.** E. GASTALDI (*Ann. Lab. Gabelle*, 1912, 6, 601—609. Compare Rosenthaler, *Abstr.*, 1910, ii, 1123).—This reaction is not due to a specific action of the amyl alcohol employed. The coloured substance produced when amyl alcohol is employed is not the same as that formed in the absence of this alcohol. In further experiments the author finds that the reaction occurs when, instead of amyl alcohol, traces of pyridine, quinoline, aniline, potassium hydroxide, sodium hydroxide, or ammonium hydroxide are added. Amyl alcohol which has been carefully purified gives hardly any reaction when the process is carried out in glass vessels, and none at all when a platinum dish is used. It is therefore probable that the contradictory statements which have been made regarding this reaction are to be explained by the presence of alkali in the reaction mixture derived from the glass of the vessels in which the test was carried out. In regard to the function of bases in the reaction, the author favours the view that it is catalytic, and this is supported by the fact that the same coloration is obtained, whatever base is employed.

The author carries out the test as follows: 5 c.c. of oil are treated with 1 drop of pyridine and about 4 c.c. of carbon disulphide containing 1% of sulphur, and the mixture is heated on the water-bath. This test is more delicate than the original one of Halphen.

R. V. S.

**Njave Nuts and Njave Butter.** H. WAGNER and H. OESTER-MANN (*Zeitsch. Nahr. Genussm.*, 1912, 24, 327—334).—A description of these West African nuts is given. Specimens examined by the authors yielded 65.17% of fat; only the fat from the sound nuts was examined fully, and this may explain the differences between the results found and those recorded by other observers (compare *Abstr.*, 1907, ii, 315). The characteristics of the fat were:  $D_{20}^{25}$  0.9137; acid number, 13.1; saponification number, 186.7; iodine number, 56.2; acetyl number, 12.9; Reichert-Meissl number, 0.8;  $n_D^{40}$  1.4601. The fatty acids had m. p. 53.0°, and a neutralisation number of 195.6.

W. P. S.

**Characteristic Colour Reaction of Soja Bean Oil.** L. SETTIMI (*Ann. Lab. Gabelle*, 1912, 6, 461—465).—When 5 c.c. of this oil are treated with 2 c.c. of chloroform and 3 c.c. of a 2% aqueous solution of uranium nitrate, the mixture yields on shaking an intensely lemon-yellow-coloured emulsion. Some samples of olive oil give a faintly yellow emulsion, but in the case of all the other oils tried the emulsion

was white. Soja bean oil gives the usual colour reactions of seed oils, whilst olive oil does not.

R. V. S.

**The Estimation of Fats and Lipoids in Blood, and the So-called Lipolysis.** L. BERCZELLER (*Biochem. Zeitsch.*, 1912, 44, 193—200).—The Liebermann-Székely and the Kumagawa-Suto methods were applied to the estimation of the fats in blood. If the latter method is employed, it is found that after hydrolysis with alkali and acidification, a very bulky precipitate is obtained, from which constituents soluble in ether could be only extracted with difficulty. Another method tried was the extraction of the blood with alcohol. The alcoholic extract was then extracted with ether both before and after hydrolysis with alkalis. In the latter case, a larger extract was obtained, and the figures obtained varied only slightly with individuals of different species (0.5—0.6% in a dog, and 0.3—0.4% in a horse). The numbers obtained this way, furthermore, were higher than those obtained by direct hydrolysis of the whole fluid by the Kumagawa-Suto method.

The author has repeated Mansfeld's experiments on the effect of leading air through blood on the disappearance of fat. The author estimated this by the method of hydrolysis of the alcoholic extract. By this method no disappearance of fat could be detected. If, however, the fat is directly extracted by the Soxhlet method, the quantity diminishes after the passage of air. The author draws the conclusion that the action of air renders certain constituents insoluble when treated with ether. Alcohol, however, changes them in some way that they again become soluble.

S. B. S.

**Theory of Indicators in Relation to the Estimation of the Acidity of Lecithin.** CARLO CASANOVA (*Boll. chim. farm.*, 1912, 41, 145—148).—The custom of determining the acidity of lecithin preparations by means of litmus paper is criticised. In lecithin the free phosphoric and glycerophosphoric acids are in a condition of extreme dilution, in which, not only are the hydrogen ions of the group  $H_2-HPO_4$  insensitive to litmus paper, but those of the group  $H-H_2PO_4$  do not react to a sufficient extent to prevent dissociation of the indicator to some extent. The acidimetric test may be carried out with phenolphthalein, but better criteria for the therapeutic evaluation of lecithin products are the date of preparation, etc.

T. H. P.

**The Estimation of Lecithin in Medicinal Tablets.** C. VIRCHOW (*Chem. Zeit.*, 1912, 36, 906—907. Compare Abstr., 1911, ii, 945).—Two grams of material are extracted with three successive quantities of 25 c.c. of boiling alcohol, the filtrate is distilled, and the dried residue then extracted with dry ether as before. Thorough extraction with alcohol is necessary. The best fusion mixture consists of 2 grams of dry sodium carbonate and 2 grams of a mixture of two parts of potassium nitrate and one part of crystallised sodium carbonate.

C. H. D.

**Proximate Analysis of Lipoids by Alcoholysis.** ERNEST FOURNEAU and MAURICE PIETTRE (*Bull. Soc. chim.*, 1912, [iv], 11, 805—810).—The method used is that devised by Haller for the

investigation of fats by esterification of the fatty acids with methyl alcohol (Abstr., 1907, i, 9).

Commercial lecithin examined in this way gave the following percentages of products: choline hydrochloride, 14; calcium glycerophosphate, 24; methyl esters, 68; compared with 17, 26 and 76, which are the respective theoretical yields. The methyl esters were separated into three fractions: (a) b. p. 205°/20 mm., iodine number 42.49; (b) b. p. 217°/20 mm., iodine number 79.41, and (c) a small fraction boiling above 217°. Fraction (a) was probably a mixture of methyl oleate and stearate, whilst (b) consisted of methyl oleate with possibly a little stearate and linoleate. No methyl palmitate appeared to be present. The calcium glycerophosphate was separated into two fractions, one crystalline, anhydrous and sparingly soluble in water.

The same method has been applied to the mixed product obtained by successive extraction of dry egg-yolks with boiling acetone, methyl alcohol, and light petroleum. This was found to contain cholesterol 1.75, lecithin 19, and neutral fat 30%. Suprarenal capsules and sheep-skin are being examined.

T. A. H.

**Microchemical Detection of Juglone in Walnuts (*Juglans regia*).** OTTO TUNMANN (*Pharm. Zentr.-h.*, 1912, 53, 1005—1010).—When a section of the green shell of an unripe walnut is immersed in copper acetate solution, crystalline needles of the juglone-copper compound begin to form almost immediately in the cells, whilst the hydrojuglone which exudes from the cut cells forms a precipitate with the reagent. If the section is now washed with water and treated with chloral hydrate solution, the masses of crystals which at first appeared black become red. On subjecting a section of the tissue to the action of nitric acid vapours, black crystals (juglonic acid?) form in the cells. A further test consists in treating a section on a microscope slide with a drop of aniline and placing a cover-glass over it; after the lapse of a few minutes, reddish-brown crystals form in the aniline near the edges of the cover-glass. The sections may be also subjected to micro-sublimation and the sublimate tested with the above mentioned reagents. The crystals yield a red coloration with sulphuric acid, violet-blue with ammonia vapour, and a reddish colour with dilute potassium hydroxide solution, a violet coagulum forming at the edge of the drop (compare Abstr., 1907, i, 839).

W. P. S.

**Estimation of Mustard Oil in Mustard Preparations.** H. PÉNAU (*J. Pharm. Chim.*, 1912, [vii], 6, 160—164).—The author has compared the following methods for the estimation of mustard oil: (1) weighing the silver sulphide formed by the addition of silver nitrate to mustard oil in presence of ammonia; (2) estimating the unused silver nitrate in the above reaction, gravimetrically as silver chloride; (3) estimating the unused silver nitrate volumetrically (a) by *N*/10-potassium cyanide, (b) by *N*/10-ammonium thiocyanate. He finds that (2) gives the best results, that (3a) gives results that are sufficiently accurate (compare Roeser, Abstr, 1902, ii, 483), and that methods 1 and 3b are untrustworthy. Detailed instructions for carrying out the estimations are given.

T. A. H.

**Analysis of Calcium Cyanamide.** A. KIRCHOFF (*Chem. Zeit.*, 1912, 36, 1058).—In the estimation of the total nitrogen in this substance, it is recommended that the weighed portion of the sample be mixed with a small quantity of water before the sulphuric acid is added (Kjeldahl method); a small loss of nitrogen may result if the concentrated acid is added to the dry substance. For the estimation of the calcium carbide which may be present in cyanamide, a portion of the substance is weighed into a flask which is attached to a gas-measuring apparatus. Sodium chloride solution, saturated previously with acetylene, is admitted to the flask from a tapped funnel, and the liberated gas is collected and its volume ascertained, the measuring apparatus being also filled with a solution saturated with acetylene.

W. P. S.

**Detection and Estimation of the Xanthine Bases in Cocoa, Tea, Coffee, and their Derivatives.** S. CAMILLA and C. PERTUSI (*Ann. Lab. Gabelle*, 1912, 6, 611—626).—Traces of the xanthine bases may be recognised by the fact that they yield carbylamines when treated with potassium permanganate and potassium hydroxide in aqueous solution.

The following method is recommended for the estimation of the xanthine bases. Chocolate or cocoa (10 grams) is boiled with dilute sulphuric acid, and half the filtered solution is neutralised with magnesium oxide, evaporated to about 80 c.c., acidified with dilute sulphuric acid, and extracted with carbon tetrachloride in an apparatus which the authors describe. The extract (which contains the caffeine, a little theobromine, and the fat) is evaporated in the presence of a piece of paraffin, and the residue is extracted repeatedly with small quantities of boiling water acidified with sulphuric acid. The solution is added to the liquid remaining in the extractor, and the whole is evaporated to dryness with magnesium oxide. The residue is extracted with boiling chloroform. Tea and coffee products can be dealt with by a similar process.

R. V. S.

**Detection of Colouring Matters and Turmeric in Mustard.** E. SIEVERS (*Zeitsch. Nahr. Genussm.*, 1912, 24, 393—394).—The presence of added colouring matters (aniline dyes) in mustard may be detected by heating 20 grams of the sample with 100 c.c. of water for thirty minutes, filtering the liquid, and testing a portion of the filtrate with hydrochloric acid. Another portion of the filtrate is treated with potassium hydrogen sulphate and heated on a water-bath, a few woollen threads being immersed in the solution. The capillary test with filter-paper may also be applied to the filtrate. Turmeric may be detected by shaking a few grams of the mustard with a drop or two of alcohol and 10 c.c. of ether; the ethereal layer is then transferred to a piece of filter-paper, the latter is dried, and tested with boric acid in the usual way.

W. P. S.

**Detection of Minimal Traces of Blood Mixed with Rust.** ANGELO DE DOMINICIS (*Boll. chim. farm.*, 1912, 41, 181—182).—By means of a needle, the rust is distributed throughout a spot of egg

albumin, not larger than a grain of wheat, on a microscope slide. The dry residue on the slide is treated successively with a drop of pyridine, a drop of saturated aqueous hydrazine sulphate, and a drop of potassium hydroxide solution (1:3), the cover-slip being then applied. Under the microscope the slide shows a more or less marked purple-red coloration, whilst the micro-spectroscope reveals the spectrum of hæmochromogen. The latter test should be carried out with slides containing different amounts of the rust, as it answers only with medium concentrations of blood, too much or too little giving negative results. If the spectrum is not seen distinctly in ordinary light, artificial light should be employed. When sealed with Canada balsam, the slides undergo change but slowly. This method gives good results even with old material.

T. H. P.

**Detection of Blood in Urine and Other Physiological Liquids.** FRANZ MICHEL (*Chem. Zeit.*, 1912, 36, 994—995. Compare this vol., ii, 400).—As some specimens of urine hinder the test, the blood may be precipitated by calcium chloride and sodium phosphate, this precipitate being then heated with water, pyridine, and potassium hydroxide until the blood is dissolved. An excess of potassium hydroxide solution is then added, and the pyridine layer is separated by placing the vessel in boiling water. The reagents are then applied as recommended.

C. H. D.

**Estimation of Extract in Worts and Beers.** WILHELM FRESSENIUS and LEO GRÜNHUT (*Zeitsch. anal. Chem.*, 1912, 51, 643—658).—The authors recommend that in the densimetric determination of the extract in beer, the table of Windisch (for sucrose solutions) should be referred to.

For worts and malt infusions, the table of Rüber (*Abstr.*, 1898, ii, 463) is the more serviceable. This table is reproduced in a more convenient form.

L. DE K

**Errors in the Indirect Method for the Estimation of Total Solids and Alcohol.** H. SERGER (*Pharm. Zentr.-h.*, 1912, 53, 855—858).—The chief source of error of this method lies in the fact that the specific gravity of a solution depends on the nature of the dissolved substances, and, consequently, tables showing the relation between specific gravity and amount of total solids of a solution are only correct for the solutions for which they have been compiled. For instance, the total solids of lemon juice cannot be correctly ascertained by reference to tables dealing with solutions the chief constituents of which are saccharine matters. A simple curve may, however, be plotted, showing the relation of total solids to specific gravity in the case of this juice, a few determinations giving the essential points of the curve. The pycnometer gives the most trustworthy results as regards the specific gravity of a solution; when this determination is made with a Westphal balance the error in the amount of total solids may be 0.025%, or when made with a hydrometer, 0.65%.

W. P. S.

## General and Physical Chemistry.

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**Refraction and Magnetic Rotation of Mixtures.** PAUL TH. MULLER and (Mlle.) V. GUERDJIKOFF (*Compt. rend.*, 1912, 155, 774—777).—Some of the refractive indices given in a previous paper (this vol., ii, 325) were wrong, having been calculated from tables for a different instrument from the one used. The correct figures are now given, and it is shown that, for aqueous solutions of lithium chloride and ammonium nitrate, the angle of rotation is practically a linear function of the refractive index. This does not hold good for such mixtures as aniline-alcohol. The variation of  $B$  in Becquerel's formula:  $R/n^2(n-1)=B$ , is different for different mixtures, and it is not possible to formulate any general rule. With the mixture aniline-alcohol it increases nearly 50% of its value as the concentration of the aniline increases from 0 to 100%. For an aqueous solution of ammonium nitrate, on the other hand, it diminishes to about the same extent, as the percentage of the nitrate increases from 0 to 62% W. G.

**A Powerful Stigmatic Grating Spectrograph without Glass, and its Application to the Photographic Determination of the Red and Ultra-red Iron Arc Spectrum between  $\lambda=6750$  and  $\lambda=9809$ .** LUDWIG GEIGER (*Ann. Physik*, 1912, [iv], 39, 752—788).—A form of grating spectrograph is described in which errors resulting from astigmatism and selective absorption in glass are avoided, and which at the same time gives higher order spectra of considerable intensity. With this apparatus the author has measured the wavelengths of 216 lines in the arc spectrum of iron between  $\lambda=6750$  and  $\lambda=9809$ . The estimated mean error of the measurements amounts to a few hundredths of an Ångström unit.

A method of obtaining ultra-red sensitive plates, in which dicyanin is employed as sensitiser, is also described. H. M. D.

**Emission of the  $D$ -Lines by Different Sodium Compounds.** KONSTANTIN IWANOFF (*Physikal. Zeitsch.*, 1912, 13, 1112—1118).—A comparison has been made of the intensities of the yellow light emitted by flames when equivalent quantities of different sodium salts are introduced. The  $D$ -lines in the grating spectrum of the second order were allowed to act on photographic plates for a measured interval of time, and the intensities of the photographic records were then determined by means of a micro-photometer.

Observations were made with sodium iodide, bromide, chloride, nitrate, and carbonate. In the case of a coal-gas flame, supplied with air insufficient for the complete combustion of the coal-gas, the intensity of the yellow light emitted decreases from the iodide to the carbonate in the order given above. In this series, the heat of formation increases regularly from the iodide to the carbonate. When the ratio of air to coal-gas supplied to the flame is increased, the differences in the intensity of the  $D$ -line emission are found to be

much smaller, and in the case of a Meker burner flame are almost inappreciable.

Curves are plotted to show the distribution of the intensity in the region of the *D*-lines, and these indicate that the distribution is independent of the nature of the sodium salt.

From these observations, the conclusion is drawn that the emission of yellow light by sodium salts is essentially determined by purely thermal factors, and that chemical and electrical changes are of comparatively little importance.  
H. M. D.

**Determination of the Optical Parameters of the  $D_1$ -Line.** KONSTANTIN IWANOFF (*Physikal. Zeitsch.*, 1912, 13, 1119—1123).—New methods are described for determining the parameters characteristic of the electronic vibrations, which, according to Drude's theory, determine the optical properties of a substance. Measurements, made with flames supplied with equivalent quantities of sodium chloride, bromide, iodide, nitrate, and carbonate, afford values which agree within the limits of experimental error.  
H. M. D.

**Measurements in the Spark Spectrum of Palladium.** PETER E. DHEIN (*Zeitsch. wiss. Photochem.*, 1912, 11, 317—346).—A detailed examination of the lines in the spark spectrum of palladium has been made by means of a large concave grating. The wave-length and relative intensity measurements, extending from  $\lambda = 6785$  to  $\lambda = 1972$ , are tabulated and compared with the data obtained by previous observers.  
H. M. D.

**The Spectrum of Magnetic Rotation of Bromine Vapour.** G. RIBAUD (*Compt. rend.*, 1912, 155, 900—903).—The author has studied the Righi effect (compare *Compt. rend.*, 1898, 127, 216) with more powerful magnetic fields up to 24,000 Gauss. The re-establishment of the light observed longitudinally in the magnetic field cannot be attributed to a Zeeman effect. All the absorption rays of bromine exhibit the phenomenon of magnetic rotatory polarisation, provided that, for any given ray, a suitable vapour pressure is chosen. The appearance of the magnetic rotation spectrum changes completely when the pressure is modified. These results are in accord with the work of Wood on iodine (compare Abstr., 1906, ii, 714; this vol., ii, 1018).  
W. G.

**Ultra-Red Absorption Spectra of Gases.** NIELS BJERRUM (*Festschrift W. Nernst*, 1912, 90—98).—On the assumption that ultra-red rays may be absorbed not only by vibrating electrically charged atoms, but also by rotating polar molecules, it is shown that the absorption phenomena exhibited by various gases in the ultra-red region can be accounted for on the basis of the combination of the two effects. The absorption due to molecular rotation is situated in the region of very long wave-lengths, and the influence of this on the absorption due to the atomic vibrations is to produce absorption on both sides of the band, which is characteristic of the atomic oscillation. If the frequency of vibration is  $\nu_1$ , and that of molecular

rotation  $\nu_2$ , absorption may be expected to occur at the three frequencies  $\nu_1 - \nu_2$ ,  $\nu_1$ , and  $\nu_1 + \nu_2$ . By reference to the actual observations on hydrogen chloride, carbon dioxide, and water vapour, it is found that the effects anticipated by this theory agree fairly well with experiment. When the frequency of molecular rotation is small as compared with that of atomic vibration, the apparent effect is a broadening of the band in the higher frequency region ( $1\mu$  to  $10\mu$ ).

By application of the hypothesis of energy quanta to the phenomenon of molecular rotation, it is shown that the frequencies of rotation must vary in a discontinuous manner. In the case of water vapour, the frequencies corresponding with the bands in the region  $10\mu$  to  $20\mu$  form a series with a constant difference equal to  $1.73 \times 10^{12}$ , and this is regarded as evidence that the bands are due to the rotation of the water molecules. From the value of the constant frequency difference, it is calculated that the radius of the water molecule is  $0.4 \times 10^{-8}$  cm., and that the energy of rotation amounts to 1400 cal. per gram molecule.

H. M. D.

**Absorption of Ultra-violet Radiation by Saturated Aliphatic Alcohols.** GUSTAVE MASSOL and A. FAUCON (*Bull. Soc. chim.*, 1912, [iv], 11, 931—935).—The transparency of the various classes of saturated aliphatic alcohols to ultra-violet radiation has been compared.

Among normal primary alcohols, methyl and ethyl alcohols are remarkably transparent in layers up to 10 cm. thick. Propyl alcohol is rather less transparent, and the transparency diminishes slowly with increasing thickness of the layer examined. In the cases of butyl, amyl, hexyl, heptyl, octyl, cetyl, and melissyl alcohols, the transparency diminishes rapidly as the thickness of layer examined increases from 1 to 10 mm., and slowly as the thickness is increased beyond 10 mm. In general, transparency diminishes as the molecular weight is increased (compare Hartley, *Trans.*, 1881, 39, 153), but heptyl alcohol is more transparent than hexyl alcohol. Normal secondary alcohols are on the whole rather more transparent, and the tertiary alcohols much more transparent, than the corresponding normal primary alcohols.

Primary alcohols with branched chains are less transparent than the corresponding normal primary alcohols, and in thicknesses below 10 mm. show two absorption bands about  $\lambda = 2500$ — $2600$  and  $\lambda = 3100$ , but these disappear when thicker layers are examined, because then all the rays inferior to  $\lambda = 3100$  are absorbed.

T. A. H.

**Colloidal Chlorophyll and Certain Colloidal Derivatives of Chlorophyll.** AMEDEO HERLITZKA (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 171—179).—A comparison has been made of the absorption bands in the spectra of (1) chlorophyll in alcohol and acetone solution, (2) colloidal chlorophyll, (3) chlorophyll in sap extract, and (4) chlorophyll in the living plant. The positions of the bands are practically the same in the three last-mentioned cases, but are displaced towards the red in comparison with the bands in the solution spectrum. A similar agreement is found when other properties of colloidal chlorophyll are

compared with those of chlorophyll in sap extract. In view of this similarity, experiments were made to ascertain whether colloidal chlorophyll is capable of assimilating carbon dioxide, but negative results were obtained.

The properties of phäophytin, and of zinc- and copper-phäophytin, which are obtained by the interaction of phäophytin with the corresponding metallic acetates, have been also examined with similar results. The substances represent in all cases electro-negative colloids, and similar differences are found when the optical properties of the substances in solution are compared with those of the colloidal forms.

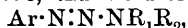
H. M. D.

**Optical Investigation of Diazo- and Azo-compounds.** ARTHUR HANTZSCH and ISRAEL LIFSCHITZ (*Ber.*, 1912, 45, 3011—3036. Compare Baly, *Trans.*, 1906, 89, 982; Dobbie and Tinkler, *Trans.*, 1905, 87, 273).—Diazonium and azo-compounds differ very considerably from one another in their optical behaviour. All benzenediazonium salts are characterised by a single deep absorption band in the ultra-violet, the length and persistence of which may be varied a good deal by substituting other groups; the character, however, remains unchanged. Even in the polynuclear and coloured diazonium salts the absorption band is only slightly altered, eventually partly displaced towards the visible spectrum. Coloured diazonium salts therefore cannot have an abnormal structure. The selective absorption of the diazonium salts is caused by the partial valency relationship between the benzene residue and the tervalent nitrogen as expressed by the symbol  $N:NXAr$ , which, however, cannot be written, as Cain suggests, as a quinoneimide, since such compounds, for example, the quinonediazides, have an entirely different absorption.

It follows from the optical identity of acid and greatly diluted alkaline diazo-solutions that these contain practically exclusively diazonium hydrates and not diazohydrates.

Azo-compounds as distinct from diazonium salts are optically extremely variable. The azo-group in itself is not a chromophore, but its optical effect is influenced by the nature of the groups attached to it. The most simple azo-compounds optically,  $R^1 \cdot N:N \cdot R^2$ , are those in which the azo-group is attached to oxygen or nitrogen, for the hyponitrites,  $MeO \cdot N:N \cdot OMe$ , and the tetrazones show general absorption with the exception of a tiny band in the extreme ultra-violet. Of the azo-carbon compounds with the grouping  $C \cdot N:N \cdot C$ , the azo-paraffins, for example,  $MeN:NMe$ , show a broad absorption band in concentrated solution, which is somewhat similar to that of acetone, but lies at the limit of the visible spectrum. Benzeneazomethane exhibits two bands, which can be distinguished as the ultra-violet and the colour band. The coloured azocarbonyl compounds behave similarly, although somewhat weaker.

The azotates,  $Ar \cdot N:N \cdot OMe$ , and the diazoamino-compounds,



are placed optically intermediate between the azobenzenes and the hyponitrites or tetrazones. Diazomethane derivatives, for example, ethyl diazoacetate, are optically so similar to the open-chain azocarbonyl

compounds and so unlike the diazonium salts that this is interpreted in favour of the old ring formula with the group  $C \begin{smallmatrix} N \\ \diagup \\ N \end{smallmatrix}$ .

Of the isomeric azo-compounds, the two series of the azocyanides,  $Ar \cdot N_2 \cdot CN$ , and the azosulphonates,  $Ar \cdot N_2 \cdot SO_3Me$ , are amongst themselves so similar that their stereoisomerism is confirmed. On the other hand, the *syn*-azotates lack the ultra-violet band of the *anti*-azotates, and the free *anti*-azohydrates in presence of certain negative substituents are optically identical with their salts, but altogether different from the isomeric arylnitrosoamines. This confirms both the usual formula for the *anti*-azotates,  $Ar \cdot N : N \cdot OMe$ , as against the suggested nitrosoamine salt formula,  $Ar \cdot NMe \cdot NO$ , and the isomerism between free *anti*-diazohydrates,  $Ar \cdot N : N \cdot OH$ , and primary arylnitrosoamines,  $Ar \cdot NH \cdot NO$ , which has been disputed latterly.

The latter in solution, according to the nature of the solvent, are probably present either as diazohydrates or as nitrosoamines, whereas in the aliphatic series, at all events for the tautomeric urethane derivative,  $CO_2Et \cdot N_2 \cdot OH$ , the equilibrium  $R \cdot N : N \cdot OH \rightleftharpoons R \cdot NH \cdot NO$  has been demonstrated. Free *anti*-diazohydrates and *anti*-diazotates are also identical optically with the diazo-esters.

The following rules for chromophore and auxochrome are deduced from the spectroscopic behaviour of the azo-, carbonyl, and nitroso-compounds, and to some extent also of the nitro-compounds.

Chromophores are such unsaturated negative complexes as either by themselves (for example,  $C_6H_6$ ), or in combination with saturated alkyls, absorb selectively, for example,  $NO_2$  in  $NO_2 \cdot CH_3$ ,  $NO$  in  $NO \cdot Alph.$ ,  $CO$  in  $CH_3 \cdot CO \cdot CH_3$ ,  $N_2$  in  $CH_3 \cdot N_2 \cdot CH_3$ . This selective absorption of the chromophore is increased by direct combination with itself and with other chromophores, but not by direct combination with the hydroxyl and amino-groups acting as auxochrome ( $OH$ ,  $OMe$ ,  $ONa$ ,  $NH_2$ ,  $NR_2$ ). This auxochrome action on direct combination is observed only with benzene and analogous unsaturated carbon compounds. On direct combination between auxochrome and any of the other chromophores, the absorption, on the other hand, is greatly weakened. Benzene thus behaves towards auxochromes in exactly the opposite manner to all other chromophores. The so-called auxochromes function only in benzene compounds, as their name would denote; in compounds with real chromophoric groups they act in the opposite way, and their name is inappropriate. E. F. A.

**Phototropy of Certain Phosphorescent Metallic Sulphides.** JOSÉ RODRIGUEZ MOURELO (*Anal. Fis. Quim.*, 1912, 10, 231—245).—The property of phototropy observed in some phosphorescent sulphides (calcium, strontium, and barium) is due to manganese. The colour change is induced by intense light and is reversible, and the property remains unimpaired by time. In order to secure active preparations, the carbonates of the alkaline-earth metals must be very pure, the presence of iron being particularly prejudicial. Mixtures of the carbonate with 0.001% of the photogenic element, 1% of sodium carbonate, and 0.5% of sodium chloride are heated for from three to five hours with flowers of sulphur at  $900^\circ$  to  $1000^\circ$ . Manganese, bismuth,

antimony, copper, and zinc were tested, but phototropy is only displayed by the solid solution of manganese in the alkaline-earth sulphides.

G. D. L.

**Cause of the Sensitiveness of Selenium Preparations to Light.** ALFREDO POCHETTINO (*Nuovo Cim.*, 1912, [vi], 4, 189—203).—Ries (compare *Physikal. Zeitsch.*, 1911, 12, 480) has recently suggested an electronic explanation of the sensitiveness of selenium to light as follows: The light penetrating into the superficial layers of selenium liberates electrons from the atoms; these electrons have not sufficient energy to escape from the metal, and, therefore, they add themselves to those already serving to transport the current, with the result that the conductivity is increased. The present author brings forward a number of arguments against the theory of Ries and in favour of the view that the light displaces the equilibrium between two forms of the element *A* and *B* of very different electrical conductivity. In this connexion it is pointed out that light can provoke allotropic changes in selenium and increase the velocity of such changes due to other causes. The fact that the conductivity of selenium is not of metallic character is also opposed to the electronic theory. Other cases where light causes an alteration in the electrical resistance of a substance, such as the iodides of silver and copper, granular silver, antimonite, and sulphur, are also discussed, and are shown to lend no support to Ries's theory.

G. S.

**Action of Light on Water Vapour and Electrolytic Gas.** ALFRED COEHN and GUSTAV GROTE (*Festschrift W. Nernst*, 1912, 136—167).—The decomposition of water vapour and the combination of hydrogen with oxygen under the influence of ultra-violet light has been examined. The apparatus employed is similar to that used in previous experiments on photochemical equilibria (compare Abstr., 1910, ii, 173, 373). In experiments with water vapour at 150° and 240°, a condition of equilibrium is reached after about two hours' exposure to the ultra-violet rays, and over this interval the equilibrium is independent of the temperature. As the intensity of the light increases, the amount of water decomposed in the condition of equilibrium also increases and diverges more and more from that corresponding with the equilibrium set up in the absence of ultra-violet rays. The extent of the decomposition also increases with falling pressure, the variation being greater than that calculated from the law of mass action.

Ultra-violet light has a similar accelerating effect on the combination of hydrogen and oxygen. From experiments with dry mixtures of hydrogen and oxygen in the volume ratio 2:1, it is found that the union takes place in accordance with the requirements of the equation for a unimolecular change. The data observed at 150° and 240° gave for the temperature-coefficient:  $k_{t+10}/k_t = 1.04$ , which value agrees with those found in the case of other photochemical reactions.

From the examination of the equilibrium gas mixture it is found that small quantities of hydrogen disappear, and this has been traced

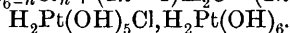
to the reduction of silica by moist hydrogen under the influence of the active light rays.

Although there is no evidence of the presence of hydrogen peroxide in the equilibrium mixture obtained from hydrogen and oxygen, this is readily detected when a mixture of the two gases is made to pass through the apparatus with considerable velocity. From this, it is inferred that hydrogen peroxide is an intermediate product in the formation of water from hydrogen and oxygen under the influence of ultra-violet light. The reaction therefore occurs in two stages: (1)  $2\text{H}_2 + \text{O}_2 = \text{H}_2\text{O}_2 + \text{H}_2$ ; (2)  $\text{H}_2\text{O}_2 + \text{H}_2 = 2\text{H}_2\text{O}$ .

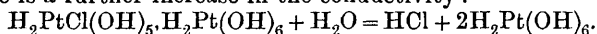
The work done by the light in the displacement of the equilibrium  $2\text{H}_2\text{O} \rightleftharpoons 2\text{H}_2 + \text{O}_2$  is calculated to be 44570 cal. per gram-molecule.

H. M. D.

**Photochemical Hydrolysis of Very Dilute Solutions of the Chloroplatinic Acids.** PAUL JOB and MARCEL BOLL (*Compt. rend.*, 1912, 155, 826—828. Compare this vol., ii, 384, 407).—A further study of the reaction which takes place in aqueous solutions of these acids (0.0001*N*) on exposure to light, by measuring the increase in electrical conductivity, shows that, in every case, one atom of chlorine remains combined with the platinum. As the compound formed will probably contain two atoms of platinum in the molecule, all the monoplatic acids being unstable under the given conditions, the authors suggest that the hydrolysis may be best represented by the equation:  $2\text{H}_2\text{Pt}(\text{OH})_{6-n}\text{Cl}_n + (2n-1)\text{H}_2\text{O} = (2n-1)\text{HCl} +$



The solutions obtained remain unaltered for some time, but finally deposit a reddish-brown, flocculent precipitate of platinum hydroxide, and there is a further increase in the conductivity:



W. G.

**Action of Sunlight on Methyl Alcohol.** HARRY D. GIBBS (*Philippine J. Sci.*, 1912, 7, 57—74).—The principal products of the action of methyl alcohol on *p*-benzoquinone in the presence of sunlight are formaldehyde and quinol. Methyl alcohol alone in the presence of oxygen and sunlight is oxidised to formaldehyde, oxidation proceeding more rapidly with increasing concentration of the methyl alcohol. Little or no formic acid appears to be simultaneously formed. Similarly, formaldehyde is produced when hydrogen peroxide acts on methyl alcohol or its aqueous solutions.

When conductivity water is exposed to sunlight in the presence of air or oxygen, hydrogen peroxide appears to be formed in small quantity. For the detection of the latter substance, Bach's reagent was found to be more sensitive than titanous and vanadic acid solutions.

H. W.

**Methyl Salicylate. III. Coloration of Methyl Salicylate and Some Allied Compounds in Sunlight.** HARRY D. GIBBS, R. R. WILLIAMS, and DAVID S. PRATT (*Philippine J. Sci.*, 1912, 7, (2), 79—96. Compare Abstr., 1908, ii, 906; 1909, i, 231).—Methyl

salicylate alone, in the presence of water, of dilute acids, or of alkalis becomes coloured on exposure to air and sunlight, the tint varying from light yellow for short exposures to reddish-brown for protracted exposure. Active oxidising agents, such as ozone, hydrogen peroxide, oxygen liberated at the anode, persulphuric acid, chromic acid, etc., can effect this change in the dark. Similar results were obtained with *o*-, *m*- and *p*-cresols, the second of which colours most rapidly. *p*-Methoxytoluene was unaffected by light. The esters of the three hydroxybenzoic acids coloured more rapidly than the free acids, the meta-compounds being the most rapidly changed, whilst the para-compounds were practically unaffected. Gentisic acid and its esters were found to be the most susceptible of all the substances employed to the action of light, benzoquinonecarboxylic acid or its esters being probably formed. The latter substances could not be obtained in a pure condition, but by cautious oxidation of methyl gentisate by means of hydrogen peroxide in the presence of hydroxylamine hydrochloride, the corresponding *monoxime* was prepared as an amorphous, dark chocolate-coloured powder.

All the substances investigated, which become coloured in sunlight, contain a labile hydrogen atom, and the behaviour in sunlight is intimately connected with the absorption band in the ultra-violet, indicating ketoenolic tautomerism.

H. W.

#### Physico-chemical Studies of Photographic Developers.

I. NIKOLAI SCHILOFF and S. FEDOROFF. II. NIKOLAI SCHILOFF and BORIS BERKENSTEIN.—See this vol., i, 937, 966.

Different Methods of Photochemical Decomposition of Dextrose and Galactose according to the Wave-length of the Radiations. DANIEL BERTHELOT and HENRY GAUDECHON (*Compt. rend.*, 1912, 155, 831—833. Compare Abstr., 1910, ii, 813).—Unlike the ketones (compare this vol., i, 750), the aldoses, dextrose, galactose, and mannose, are practically unaffected on exposure in aqueous solutions to sunlight. They are, however, decomposed under the influence of medium ultra-violet rays ( $\lambda = 0.30$  to  $0.25\mu$ ). Carbon monoxide and hydrogen are evolved, and the corresponding alcohol, with one carbon atom less than the sugar used, is formed. As in the case of the ketones, secondary reactions occur when they are exposed to the extreme ultra-violet rays, carbon dioxide and methane being evolved. The liquid becomes acid and capable of reducing Fehling's solution and ammoniacal silver nitrate.

W. G.

Retardation of Photochemical Reactions by Oxygen. FRITZ WEIGERT [in part, with D. SAVEANU] (*Festschrift W. Nernst*, 1912, 464—487).—When an aqueous solution of quinine sulphate in contact with air is exposed to the light emitted by a quartz mercury vapour lamp, oxygen is absorbed and experiments have been made to elucidate the nature of this reaction. The progress of the change could be readily followed by measurements of the volume of gas absorbed.

The reaction velocity increases with increasing concentration of the

quinine sulphate, but is diminished by addition of acid. From experiments with gas mixtures containing variable proportions of oxygen, it is found that the reaction velocity increases continuously as the partial pressure of the oxygen diminishes. For a mixture of oxygen and nitrogen containing 0.6% of oxygen, the velocity is about thirty times as large as for pure oxygen. The nature of the oxidation process appears to vary, however, with the proportion of oxygen in the gas mixture, for a larger proportion of the absorbed oxygen was found to have been activated when the gas mixture was rich in oxygen. The activated oxygen is only present to a small extent in the form of hydrogen peroxide, the major portion existing in a loosely combined form, which may be removed by a current of carbon dioxide or nitrogen.

To account for the observations, it is supposed that the quinine sulphate is acted on by the light rays, giving rise to a heterogeneous system in which the nuclei formed play the part of a catalyst. The reaction nuclei are then acted on by the dissolved oxygen, with the result that the stationary concentration of the catalyst will diminish as the concentration of the dissolved oxygen, and therefore the proportion of oxygen in the gas mixture, increases.

A similar influence of the oxygen concentration on the reaction velocity has also been observed in the photochemical oxidation of fluorescein and tetraiodofluorescein.

H. M. D.

**$\delta$ -Rays Produced by  $\beta$ -Rays.** NORMAN CAMPBELL (*Phil. Mag.*, 1912, [vi], 24, 783—788. Compare this vol., ii, 1027).—In order to establish the identity of the  $\delta$ -rays produced by  $\beta$ -rays by impact on solids with those produced by  $\alpha$ -rays, they were investigated under similar conditions. The apparatus consisted of two parallel electrodes, one pierced with a hole and covered with thin foil, through which the exciting rays enter, exciting  $\delta$ -rays in both electrodes.  $\alpha$ -Rays from polonium and  $\beta$ -rays produced by  $X$ -rays were employed as exciting rays, the current between the electrodes being measured with different potential differences. The quality of the  $\delta$ -rays produced by the  $\beta$ -rays was found to be independent of the penetrating power of the  $\beta$ -rays, and of the material they strike. Saturation was reached at 40 volts, and when the ratio of the ionisation current to the saturation current was plotted against the potential difference, identical curves were obtained for the experiments with  $\alpha$ - and with  $\beta$ -rays. The conclusion was drawn that the  $\delta$ -rays owe their properties neither to the ionising rays nor to the material ionised, but to some mechanism concerned in all ionisation. When the electrodes are covered with paper, practically no  $\delta$ -rays are produced, for since it is generally conceded that  $X$ -rays do not ionise save through the intermediate production of  $\beta$ -rays, it is to be expected that no  $\delta$ -rays will be produced by  $X$ -rays apart from  $\beta$ -rays. The  $\beta$ -radiation generated by  $X$ -rays falling on paper is very small.

F. S.

**Recoil Atoms in Ionised Air.** ALOIS F. KOVARIK (*Phil. Mag.*, 1912, [vi], 24, 722—727).—The effect was investigated of strongly ionising the air (by means of a tube containing radium emanation and

thin enough to allow  $\alpha$ -rays to escape) between the plates in collecting recoiled actinium-*D* from the actinium active deposit. The amount of actinium-*D* collected rose from 12 to 100 as the radium emanation (10 millicuries initially) decayed, showing that the recoiled atoms, initially positively charged, lose their charge like positive ions by recombination with negative ions in the gas. Increasing the electric field between the plates kept at constant difference apart, or decreasing the distance keeping the field constant, produces an increase in the amount of actinium-*D* collected by recoil. With highly polished plates more actinium-*D* was collected than from rough plates, but under the most favourable conditions the amount collected was less than half the theoretical. If all the atoms of actinium-*D* were equally capable of recoiling, 50% of the atoms formed should be collected, whereas the maximum obtained was 23%.  
F. S.

**Excitation of the Phosphorescent Alkaline-earth Metal Sulphides by Canal Rays.** HANS BAERWALD (*Ann. Physik*, 1912, [iv], 39, 849—886).—Experiments have been made to ascertain whether charged or uncharged canal rays exhibit any difference in regard to their power of exciting phosphorescence. Observations were made with hydrogen and air canal rays, alkaline-earth metal sulphides, containing bismuth or copper as metallic "impurity," and impure zinc sulphide being employed as phosphorescent substances. The beam of canal rays was made to pass through an electric field before reaching the phosphorescent screen, and the intensities of the phosphorescence excited by the undeflected and deflected beams were measured by means of a special form of photometer. From these data and the measured intensities of the charged and uncharged rays, it is possible to compare the activities of the different beams. The results show that the specific activity of the charged rays is greater than that of the uncharged rays, but that there is no difference between the effects produced by positively and negatively charged rays.

The observations indicate that the excitation of phosphorescence and the chemical activity of the canal rays are not interdependent, for the chemical activity is solely determined by the number of the canal ray particles irrespective of whether they are electrically charged or not.

H. M. D.

**Mobility of the Negative Ion at Low Pressures.** GEORGE W. TODD (*Proc. Camb. Phil. Soc.*, 1912, 16, 653—657. Compare Abstr., 1911, ii, 245, 1050).—The dependence of the mobility of the negative ions, produced by a beam of Röntgen rays, on the pressure of the gas has been examined in air, carbon dioxide, hydrogen sulphide, sulphur dioxide, and hydrogen. The curves obtained by plotting the product of pressure and mobility against the pressure show that at low pressures the negative ions have greater mobilities than the inverse pressure law requires, and that the pressures at which the mobilities begin to deviate from the inverse pressure law are approximately proportional to the normal mobilities in the different gases.

The relationship between the normal mobility and the critical pressure appears to be the same for both positive and negative ions.

H. M. D.

**Dissymmetry of Positive and Negative Ions Relatively to the Condensation of Water Vapour in an Atmosphere of Carbon Dioxide.** E. BESSON (*Compt. rend.*, 1912, 155, 711—713).—Using *X*-ray ionisation the phenomenon observed is much clearer than in the case of air (compare Abstr., 1911, ii, 839). Here, as with air, the cloud formed is always much more intense when the negative ions are in excess. When the gas is ionised but there is no field, the cloud seems to be identical with that obtained when the negative ions are in excess. If the ionisation of the gas is produced by radium, the cloud without field is much more intense than where the negative ions are in excess. The value 7.27 which the author finds for the supersaturation relative to carbon dioxide is in close agreement with Wilson's value of 7.3 for air, when dissymmetry ceases to exist (compare Abstr., 1898, ii, 372). W. G.

**Number of  $\alpha$ -Particles Expelled when an Atom of Thorium Emanation Disintegrates.** JOHN SATTERLY (*Proc. Camb. Phil. Soc.*, 1912, 16, 667—673).—It is shown that the ratio of the number of  $\alpha$ -particles which are expelled in the disintegration of an atom of radium emanation to the number expelled in the disintegration of an atom of thorium emanation can be calculated from the rates of disintegration and the ionising powers of the quantities of radium and thorium emanation which are in equilibrium with known quantities of radium and thorium respectively.

The ionisation data obtained indicate that the transformation of an atom of thorium emanation into thorium-*A* and of an atom of thorium-*A* into thorium-*B* is in each case accompanied by the expulsion of only one  $\alpha$ -particle. H. M. D.

**The Radioactive Constituents of the Sediments from the Springs of Hokuto, Taiwan.** MASATARO HAYAKAWA and TOMONORI NAKANO (*Zeitsch. anorg. Chem.*, 1912, 78, 183—190).—The sediment consists of anglesobarite, together with small quantities of other substances, including 0.2% of ceria and lanthana. The activity is very variable, values ranging from 1/16 to 1/90 of that of pitchblende being obtained from different samples. Ionium, polonium, and radium have been recognised, but uranium and radio-lead are absent. C. H. D.

**Radioactivity of the Waters of Monte Amiata and Experiments on the Atmospheric Dispersion of that District.** RAFFAELLO NASINI and C. PORLEZZA (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 475—478. Compare this vol., ii, 525).—A repetition of the previous experiments confirms the results then recorded. R. V. S.

**The Affinity Constants of Hydrogen Peroxide.** R. A. JOYNER (*Zeitsch. anorg. Chem.*, 1912, 77, 103—115).—The electrolytic dissociation of hydrogen peroxide into ions  $H^+$  and  $HO_2^+$  has been studied by several methods. The conductivity of its solutions, measured by means of iron electrodes coated with tin, leads to uncertain results, as the conductivity is comparable with that of

water. The hydrolysis of ethyl acetate by the sodium salt gives the constant  $0.77 \times 10^{-12}$ ; the extraction of solutions of the sodium salt with amyl alcohol gives  $0.59 \times 10^{-12}$ , and the conductivity of the salt,  $0.64 \times 10^{-12}$ . The molecular heat of ionisation at  $0^\circ$  is about 8600 cal.

C. H. D.

**Electrical Conductivity of Solid and Molten Silver and Thallous Haloids.** CARL TUBANDT [with ERICH LORENZ] (*Festschrift W. Nernst*, 1912, 446—458).—In reference to the view that the haloids of silver and univalent thallium occur in forms which may be regarded as crystalline-liquids, an examination has been made of the electrical conductivity of these substances at temperatures extending considerably above and below the respective melting points. In all cases there is an abrupt change in the conductivity at a perfectly definite temperature, and the conductivity curves furnish no evidence of the existence of crystalline-liquid modifications.

Except in the case of silver iodide, there is a large drop in the conductivity on solidification. The comparatively small increase which is observed with silver iodide is probably due to the contraction which accompanies solidification. When the solidified silver iodide is gradually cooled, an abrupt fall in conductivity is found at  $144^\circ$ , and this evidently corresponds with the transition of the regular into the hexagonal modification.

H. M. D.

**Conductivity and Negative Viscosity Coefficients of Certain Rubidium and Ammonium Salts in Glycerol and in Mixtures of Glycerol and Water from  $25^\circ$  to  $75^\circ$ .** P. B. DAVIS and HARRY C. JONES (*Zeitsch. physikal. Chem.*, 1912, 81, 68—112. Compare Guy and Jones, *Abstr.*, 1911, ii, 863).—The electrical conductivity of solutions of ammonium iodide and of rubidium chloride, bromide, and iodide in glycerol and in mixtures of glycerol and water, and also the viscosities of these solutions, have been measured at intervals of temperature from  $25^\circ$  to  $75^\circ$ . The experimental data are given in detail in the paper.

The conductivities of solutions of salts in glycerol are very small, but increase with rising temperature and also, with very few exceptions, on dilution. In the case of salts which cause a pronounced lowering in the viscosity of the solvent there is a minimum in the conductivity curves of saturated solutions, and the change of conductivity is parallel to the change of fluidity.

Conductivities in mixtures of glycerol and water are always smaller than those calculated according to the mixture rule. Rubidium salts have a very pronounced effect in diminishing the viscosity of glycerol, more so than the corresponding potassium salts, and in this respect ammonium salts behave more like rubidium than potassium salts. The percentage elevation of the viscosity of the solvent by dissolved salts diminishes with increase of temperature and with increasing dilution. The curves representing the variation of the electrical conductivity and fluidity of mixtures of glycerol and water are very similar in appearance.

G. S.

**Conductivity and Dissociation of Certain Organic Acids in Aqueous Solution at Different Temperatures.** A. SPRINGER, jun., and HARRY C. JONES (*Amer. Chem. J.*, 1912, 48, 411—453. Compare White and Jones, *Abstr.*, 1910, ii, 13, 821; Wightman and Jones, 1911, ii, 689; this vol., ii, 1035).—In continuation of the study of the conductivity and dissociation of organic acids in aqueous solution, measurements have now been made at several temperatures between 0° and 65° of the conductivity of dichloroacetic, phenylacetic, ethylmalonic, isopropylmalonic, butylmalonic, allylmalonic, benzylmalonic, dimethylmalonic, methylethylmalonic, diethylmalonic, dipropylmalonic, bromosuccinic, dibromosuccinic, pyromucic, phenylpropionic, salicylic, acetylsalicylic, sulphosalicylic, anisic, vanillic, aniline-*m*-sulphonic, sulphanilic,  $\beta$ -phenylpropionic, cinnamic, *o*-coumaric, *o*-phthalic, and naphthionic acids, and also of 4:6-dinitro-2-aminophenol.

In general, the results confirm those of the earlier work. The percentage temperature-coefficients of conductivity are generally small and of the same order of magnitude, and decrease with rise of temperature. Expressed in conductivity units, the temperature-coefficients increase rapidly with dilution and decrease with rise of temperature. The stronger the organic acid the larger are the conductivity units. The percentage temperature-coefficients of the amino-acids are particularly large, and the coefficients expressed in conductivity units increase with rise of temperature. This behaviour is explained by the inner salt-forming power of the compounds. The relative strengths of organic acids do not seem to be influenced by change of temperature. Strong organic acids do not obey Ostwald's dilution law. Most dibasic organic acids dissociate like monobasic acids. The migration velocities of the anions of organic acids are a function of the number of atoms present in the anions, and  $\mu_{\infty}$  values for dibasic acids may be found by means of this principle. The relation of the dissociation to the temperature seems to be irregular. In general, the maximum dissociation was reached at the temperatures employed, and only in the case of the amino-acids does the dissociation increase at temperatures above 50°. Isomeric acids do not behave similarly with regard to change in their dissociation. A relation has been found between the behaviour of certain isomeric acids and their structure and power of forming inner salts and anhydrides.

E. G.

**Measurements of the Electrical Conductivity of Acetophenone Solutions of Certain Organic Bases and Acids.** HENRY J. M. CREIGHTON (*Trans. Nova Scotia Inst.*, 1912, 13, 154—161).—Measurements have been made of the electrical conductivity of 0.5*N* solutions of a number of organic bases and of the salts formed by these with camphorcarboxylic acid in acetophenone. The data show that the degree of ionisation of both bases and salts is very small, although the conductivity of the salts is from twenty to several hundred times greater than that of the corresponding bases. The order assumed by the bases when arranged according to their conductivity in acetophenone is different from that furnished by the conductivity data for aqueous solutions.

Measurements of the conductivity of piperidine, camphorcarboxylic acid, bromocamphorcarboxylic acid, and piperidine camphorcarboxylate at different dilutions show that the molecular conductivity increases with the dilution in all cases.

H. M. D.

**Silent Electric Discharges in Gases at Atmospheric Pressure.** ERNST H. RIESENFELD (*Festschrift W. Nernst*, 1912, 374—382. Compare *Zeitsch. Elektrochem.*, 1911, 16, 925).—Further experiments have been made to ascertain the minimum potential required for the passage of the silent discharge through hydrogen, oxygen, carbon dioxide, and nitrogen, and its dependence on the dimensions of the "ozoniser," the nature of the glass, and the frequency of the alternating current. The silent discharge potential is appreciably smaller than the sparking potential in continuous current discharge. In both cases, however, the order of the gases, arranged according to the minimum discharge potential, is the same.

For "ozonisers" of the same dimensions the silent discharge potential increases with the electrical resistance of the glass, and appears to vary with the cube-root of the frequency of alternation. No silent discharge could be obtained with an "ozoniser" of quartz glass, and this is attributed to its insulating properties.

The minimum potentials for the different gases, when referred to hydrogen as standard, are not invariable, but the relative values increase with increasing size of the "ozoniser," and fall with increasing frequency of alternation.

In the case of oxygen and carbon dioxide, the passage of the silent discharge is attended by hysteresis effects, and in consequence of this, it is only possible to obtain the values of the minimum potential by gradually lowering the applied potential.

H. M. D.

**Formation of Ozone by the Silent Electric Discharge and the Estimation of Ozone by Absorption Measurements in the Ultra-violet.** FRIEDRICH KRÜGER (and M. MOELLER) (*Festschrift W. Nernst*, 1912, 240—251).—According to Warburg's measurements, the number of coulombs required for the production of a gram-equivalent of ozone varies with the nature of the electrical discharge through the oxygen, but is in all cases very much smaller than the quantity (96540 coulombs) required in the electrolytic production. The formation of ozone by the silent discharge cannot be due, therefore, to electrolytic action, and it is suggested that the liberation of secondary rays by the action of high speed cathode rays on the oxygen molecules is the determining factor in the formation of ozone. The emission of a secondary electron causes the oxygen molecule to decompose into atoms, which then combine with unaltered molecules to form ozone. According to this, two molecules of ozone result from the emission of a single secondary electron. From the number of coulombs required per gram-equivalent by the different methods of discharge, the number of secondary electrons produced from each primary electron can be calculated. These numbers, varying from 17 in the case of positive point discharge to 287 for silent discharge in a metal apparatus, correspond with velocities of the primary rays between 1000 and

50,000 volts. This result is quite consistent with the experimental conditions.

The part of the paper dealing with the photometric estimation of ozone has been published previously (this vol., ii, 821).

H. M. D.

**Becquerel Effect for Complex Iron and Uranium Salts.** HERBERT SCHILLER (*Zeitsch. physikal. Chem.*, 1912, 80, 641—668. Compare Baur, Abstr., 1908, ii, 790 ; Titlestad, Abstr., 1910, ii, 379 ; Schafer, *ibid.*, 380).—It is proposed to term the phenomenon of the alteration of electric potential under the influence of light the "Becquerel effect." The potential of cells containing a solution of ferrous and ferric potassium oxalates becomes more negative on exposure to light, and an alteration of potential also occurs when a solution of potassium ferrous oxalate alone is used. As reduction of the ferric salt takes place on exposure to light, also causing an alteration of potential, the change of potential is the sum of the Becquerel effect (without chemical action) and the reducing effect.

The potential increases the more rapidly on exposure to light, and the maximum is the greater the greater the proportion of ferric salt in the solution. The initial rate of rise of potential is proportional to the light intensity. The rate of fall of potential on placing in the dark is the more rapid the greater the proportion of ferrous salt in the mixture. The existence of maximum values of the Becquerel effect which depend on the light intensity and on the composition of the solutions has been established.

Mixtures of uranyl and uranous formates and oxalates give results in qualitative agreement with those for ferric and ferrous salts just described, the change of potential on exposure to light varying from 6 to 300 millivolts.

The nature of the Becquerel effect is discussed, and evidence in favour of Baur's "energetic" explanations (*loc. cit.*) is adduced.

EMIL BAUR, in a note to the foregoing paper, contends that the statement of Usher and Priestley (compare Abstr., 1906, ii, 299), according to which carbon dioxide is reduced to formic acid on exposure to light in the presence of uranyl sulphate, is erroneous G. S.

**Potential of Hydrogen Peroxide.** KARL BORNEMANN (*Festschrift W. Nernst*, 1912, 118—131).—Systematic measurements have been made of the potential difference at a platinum electrode immersed in 1*N*-sulphuric acid containing varying quantities of hydrogen peroxide. This electrode was combined with a hydrogen electrode, also in contact with 1*N*-sulphuric acid, and observations were made after anodic and cathodic polarisation, and also with the electrode in a non-polarised condition. The data obtained show that for a solution containing one gram-molecule of hydrogen peroxide per litre,  $-0.69$  volt may be taken as a lower limit for the reduction potential when measured against hydrogen in contact with a solution of the same hydrogen ion concentration. Previous measurements (*Zeitsch. Elektrochem.*, 1909, 15, 673) indicate that  $-0.63$  volt may be taken as the upper limiting value, and since these limits only differ to the extent of  $0.06$  volt, the

value of the reduction potential may be taken as  $-0.66 \pm 0.03$  volt. From this, the value of the oxidation potential is  $-1.80 \pm 0.03$  volt, this also being referred to hydrogen in contact with the same hydrogen ion concentration.

H. M. D.

**Electrolytic Potentials and the Periodic System.** WILHELM PALMAER (*Festschrift W. Nernst*, 1912, 332—340).—If the electrolytic potentials of the elements are plotted against the atomic weights, a series of discontinuous curves are obtained, which afford strong evidence of the periodic character of the electrolytic potential. In the diagram thus produced, the positive elements of high and the negative elements of low electrolytic solution pressure are situated above the line of abscissæ, whilst the positive elements of low and the negative elements of high electrolytic solution pressure lie below this line.

The position of certain elements on the electrolytic potential curves is discussed in reference to the usual groupings in the periodic table, and it is pointed out that the diagram affords a means of estimating approximately the electrolytic potentials of elements for which the values have not yet been determined.

H. M. D.

**Tantalum Electrodes.** OTTO BRUNCK (*Chem. Zeit.*, 1912, 36 1233—1234).—The author has investigated the use of tantalum as a substitute for platinum, owing to the high price of the latter metal. Below  $200^{\circ}$  tantalum behaves as a noble metal, being attacked neither by the oxygen of the air, nor by acids, with the exception of concentrated hydrofluoric acid; even aqua regia is without action. It is also completely resistant towards aqueous solutions of the alkalis, although it is attacked by the fused alkalis. On heating in the air, it commences to oxidise at a temperature considerably below red heat.

As cathode, tantalum can replace platinum in all cases. When used as anode, however, it quickly becomes coated with a layer of dark blue oxide, probably  $Ta_2O_4$ , which offers a great resistance to the passage of the current. It is readily plated with platinum, and then can be used as anode in the ordinary way, a deposit of a few centigrams of platinum being sufficient.

Using a tantalum cathode, quantitative deposits of silver, copper, platinum, and cadmium were obtained from the acid sulphate solutions, zinc from an alkaline zinc oxide solution, nickel and cobalt from an ammoniacal solution, and tin and antimony from solutions of their thio-salts. The deposits are readily removed from the electrode by means of acids, leaving the tantalum in a bright condition. There is no tendency for zinc and cadmium to alloy with tantalum, as is the case with platinum. Deposits of platinum and gold can be removed with aqua regia.

The price of tantalum is only 40% of that of platinum. There is also a further saving in cost owing to the facts that the density is less than that of platinum, and that the electrodes can be made thinner than platinum electrodes, owing to the greater rigidity of tantalum.

Tantalum electrodes may also replace platinum in the electrolysis of alkaline solutions, and can be used in the manufacture of electrolytic bleach.

T. S. P.

**Lead Sulphide Electrode and the Passivity of Lead.** PETER P. LEBEDEFF (*Zeitsch. Elektrochem.*, 1912, 18, 891—896).—The *E.M.F.* of the cell  $\text{Pb} \mid \text{PbS}, \text{NaHS}, \text{H}_2\text{S} \mid \text{KCl} \mid \text{KCl}, \text{Hg}_2\text{Cl}_2 \mid \text{Hg}$  has been measured by Bernfeld (compare Abstr., 1898, ii, 150), and it has been found that the solubility of lead sulphide calculated from the results does not agree with the value as determined by other methods. As it appeared that there must be some source of error in Bernfeld's experiments, the measurements have been repeated and his results confirmed. The explanation of the discrepancy indicated above has been found in the fact that the electrode is not reversible; the lead becomes passive and behaves like a noble metal. The chief evidence of this is that almost exactly the same potential is observed when the lead electrode is displaced by one of platinum, and, further, that lead does not liberate hydrogen from a normal solution of sodium hydrogen sulphide, as it should do if it remains in the active form. No satisfactory explanation has been found for the fact that a lead or platinum electrode immersed in a solution of sodium hydrogen sulphide saturated with hydrogen sulphide shows a well-defined reproducible potential.

G. S.

**Determination of the Solubility of Slightly Soluble Salts by means of Electrodes of the Third Kind.** JAMES F. SPENCER (*Zeitsch. physikal. Chem.*, 1912, 80, 701—708. Compare Abstr., 1911, ii, 364).—In electrodes of the third kind there are two slightly soluble depolarisers, the first containing the same cation as the metal with which it is in contact, whilst the second, more soluble than the first, contains the same anion as the first depolariser.

An example is the electrode  $\text{Hg}[\text{Hg}_2(\text{IO}_3)_2]\text{TI}[\text{IO}_3]\text{TI}'$ . The single potential difference at such an electrode depends primarily on the  $\text{Hg}^{++}$  ion concentration, and the two equilibria hold:  $[\text{Hg}_2^{++}][\text{IO}_3]^{-2} = L$  and  $[\text{TI}'][\text{IO}_3]^{-1} = L'$ , where  $L$  and  $L'$  are solubility products. From expressions for the single potential differences at electrodes containing  $\text{Hg}_2^{++}$ ,  $\text{IO}_3^{-}$ , and  $\text{TI}'$  ions respectively, which have to be specially determined when not known, the concentrations of the  $\text{IO}_3^{-}$  and  $\text{TI}'$  ions, and therefore the solubility of thallous iodate, can be calculated. The calculation is still simpler when the solubility of one of the depolarisers is known.

The first method is illustrated by measuring the solubility of thallous iodate, for which the value  $2.12 \times 10^{-3}$  mols. per litre at  $25^\circ$  is obtained, in fair agreement with the results of conductivity determinations. The solubility of thallous iodide, as determined by the second method from measurements with the electrode  $\text{Hg}[\text{Hg}_2\text{I}_2]\text{TI}$ , and the use of Sherrill's data for the solubility of mercurous iodide (compare Abstr., 1903, ii, 534), is  $1.76 \times 10^{-4}$  mols. per litre at  $25^\circ$ .

G. S.

**Iodine Coulometer and the Value of the Faraday.** EDWARD W. WASHBURN and STUART J. BATES (*J. Amer. Chem. Soc.*, 1912, 34, 1341—1368).—A review is given of the work which has been done on the silver, copper, iodine, and oxyhydrogen coulometers, and the values obtained for the faraday by different authors are compared.

The results of this comparison indicate that the silver coulometer gives too low a value, but is superior to all the other types in reproducibility.

The present investigation was undertaken with a view to the production of a form of iodine coulometer which should equal the silver coulometer in reproducibility, and be free from all sources of error, amounting to more than 0.001%. The apparatus devised consists essentially of two vertical limbs connected by a V-tube, and furnished with electrodes of platinum-iridium foil. It is filled with 10% potassium iodide solution to a little above the level of the V-tube. Concentrated solution of potassium iodide is then added to the anode limb, and solution of iodine in potassium iodide to the cathode limb. A comparison of the amount of iodine liberated at the anode with the amount which disappears at the cathode has shown that within the limits of error in analysis, the same quantity of iodine is formed from iodide ions at the anode as is converted into iodide ions at the cathode. The coulometer is free from any constant source of error, amounting to more than 0.002%, and the reproducibility of the reaction at the anode fulfils the requirements necessary for a trustworthy determination of the faraday within 0.005%.

This iodine coulometer has been compared with the silver coulometer, and has been applied to the determination of the faraday. A mean value for the faraday of 96,538 coulombs was obtained (see next abstract), which agrees closely with the value 96,535 obtained by Richards, Collins, and Heimrod (*Abstr.*, 1900, ii, 256) with the copper coulometer. The former figure corresponds with a value 1.1174 mg. per coulomb for the true electrochemical equivalent of silver. E. G.

**Iodine Coulometer and the Value of the Faraday. A Correction.** STUART J. BATES (*J. Amer. Chem. Soc.*, 1912, 34, 1515).—In a paper by Washburn and Bates (preceding abstract) an error was made in the calculation. On making the necessary correction, the electrochemical equivalent of iodine becomes 1.31491 mg. per coulomb and the faraday 96,524 coulombs per equivalent ( $I = 126.92$ ). If the ratio of silver to iodine as found by Baxter (*Abstr.*, 1911, ii, 112) is employed instead of the international atomic weights, the results give 1.11755 for the electrochemical equivalent of silver. E. G.

[Theory of the Electrolytic Thermo-cell  $\text{Sn} \mid \text{CrCl}_3 \mid \text{Pt}$ .] ROBERT KREMAN (and F. NOSS) (*Festschrift W. Nernst*, 1912, 234—239).—In view of the observations of Case, which indicate that tin, dissolved at higher temperatures, separates out when the temperature is lowered, the authors have made a further investigation of the behaviour of this cell. The *E.M.F.* of the cell was found to be 1.02 volt at 30° and 1.03 at 96° with a solution containing 0.054 mol. chromic chloride per mol. water. If the chromic chloride solution is saturated with tin at room temperature, the *E.M.F.* falls to 0.44 volt. The fall in potential is confined to the indifferent electrode, and apparently the cell behaves as an ordinary oxidation-reduction element.

When the chromic chloride is saturated with tin at higher temperatures the *E.M.F.* falls to nearly zero, 0.027 volt having been found at

temperatures from 27° to 94°. Rise of temperature increases the extent to which the chromic chloride is reduced, and by operating the cell at about 90° and then cooling to the ordinary temperature so as to allow tin to separate out from the solution, the cell affords a means of converting heat energy directly into electrical energy. The cells  $\text{Cu} \mid \text{CrCl}_3 \mid \text{C}$  and  $\text{Sn} \mid \text{VdCl}_3 \mid \text{C}$  behave quite similarly, but the current yields are in all three cases too small for technical purposes.

H. M. D.

**Molecular Condition and Ionisation of Aqueous Solutions of Hydrofluoric Acid.** HANS PICK (*Festschrift W. Nernst*, 1912, 360—373).—The freezing point and electrical conductivity data for solutions of hydrofluoric acid afford no evidence of the presence of unionised double molecules in appreciable concentration. The fact that the ionisation constant, when calculated in the ordinary way from the conductivity at different dilutions, increases very considerably with the concentration, is shown to be due to the formation of complex ions,  $\text{HF}_2'$ . In very dilute solutions this effect is negligible, and the ionisation constant is found from the conductivity of these solutions to be  $k = 7.2 \times 10^{-4}$  at 25°. The constant which determines the formation of the complex ions can also be calculated from available data, and  $k' = [\text{HF}_2'] [\text{F}'] [\text{HF}]$  is thus found to be 5.5 at 25°. With the aid of these constants, it is possible to calculate the concentration of the various components,  $\text{HF}$ ,  $\text{H}'$ ,  $\text{F}'$ , and  $\text{HF}_2'$ , in any solution, and such data are recorded for solutions varying in concentration from 1*N* to  $\frac{1}{64}$ *N*.

The above view of the constitution of hydrofluoric acid solutions is shown to be in agreement with Jaeger's data for the solubility of mercuric oxide, according to which the solubility is proportional to the concentration of the acid.

H. M. D.

**Influence of Colloids on the Electrolytic Deposition of Lead.** HERBERT FREUNDLICH and J. FISCHER (*Zeitsch. Elektrochem.*, 1912, 18, 885—891).—It is known that in the presence of gelatin or other organic substances, lead separates from solution in hydrofluosilicic and certain other strong acids in a finely crystalline, dense, coherent form. A possible explanation of this effect is that the organic substances are absorbed by the surface, whereby they retard the rate of crystallisation and permit of the deposition of the metal in a more coherent form. In order to test this suggestion, the smallest concentrations of certain colloids (gelatin, agar agar, etc.) which are sufficient to cause the electrolytic separation of lead to take place in coherent form from solutions in hydrofluosilicic and perchloric acids have been determined. The activity of colloids in this connexion is not parallel to their protective effect on solutions of colloidal gold, but this may be due to the very different conditions of the two sets of phenomena. The assumption that it is mainly the velocity of crystallisation which is influenced by the colloids is supported by the fact that colloids exert a very similar effect on the form of the lead deposited from solution by means of zinc.

G. S.

**Anodic Behaviour of Niobium [Columbium].** U. SBORGI (*Gazzetta*, 1912, 42, ii, 331—345).—The author has investigated the electrolytic valve action of columbium (compare Bolton, *Abstr.*, 1907, ii, 478; Schulze, *Abstr.*, 1908, ii, 350) in various electrolytes. Some differences were observed in the results according to the degree of compactness of the specimen of columbium used as anode. Columbium which is not very compact, when used as anode in sulphuric acid ( $N/5 - N$ ), gives a momentary current with 1—2 volts; the current then becomes almost zero, and if the voltage is increased up to 112 volts, each increase is attended by the passage of a current which is only momentary. Some bubbles of gas appear, and the electrode becomes covered with a greenish-yellow or blue iridescent film, which is insoluble in the common acids and alkalis, but dissolves in hydrofluoric acid. The same results are obtained with phosphoric acid, potassium hydroxide, sodium hydroxide, potassium carbonate, sodium sulphate, sodium oxalate, oxalic acid, and ammonium fluoride. In no case could a permanent passage of current be observed. In other electrolytes, however (hydrochloric acid, sodium chloride, nitric acid, sodium nitrate, acetic acid, potassium bromide and iodide), the metal dissolves with valency 5, columbic acid being precipitated; the electrode becomes disintegrated. The same occurs in hydrofluoric acid, but in this case columbic acid is not precipitated. An anode which has been used in sulphuric acid, and is covered with the film already mentioned, dissolves when made the anode in nitric acid; after a time the film disappears, and the electrode becomes grey from disintegration. When it is again placed in sulphuric acid, no current passes.

A compact block of columbium behaves somewhat differently, for with it no current passes in any of the solutions already named except hydrofluoric acid, potassium bromide, sodium bromide, and potassium iodide. Except in the case of hydrofluoric acid, however, the current soon tends to decrease.

The author considers that these and other experiments show that the columbium anode in all electrolytes (except hydrofluoric acid) becomes covered at the very beginning of electrolysis with a layer which hinders the passage of ions, although the degree of impermeability varies in different electrolytes. The behaviour of this metal differs from that of the ordinary passive metals in these respects, and also because solution occurs when the current does pass. R. V. S.

**New Lamp with very Powerful Ultra-violet Radiation, and its Use in Sterilising Large Quantities of Water.** VICTOR HENRI, ANDRÉ HELBRONNER, and MAX VON RECKLINGHAUSEN (*Compt. rend.*, 1912, 155, 852—854).—The lamp consists, in its luminous portion, of a quartz U-tube, the two limbs of which almost touch; the internal diameter of the tube is 14 mm., and the length of each limb 160 mm., the two electrodes being of mercury. The lamp burns in a 500 volt circuit, taking 3 amperes, consuming 1150 watts, and having a luminosity of 8000 candle power. The intensity of its ultra-violet radiation has been compared with that from lamps constructed for 110 volts by measuring the rapidity of their action in

various chemical reactions, such as the hydrolysis of starch (compare Bielecki and Wurmser, this vol., i, 538) and the polymerisation of hydrocarbons (compare Landau, this vol., ii, 986), and comparison has also been made in sterilisation experiments. It is found that the ultra-violet radiation from the 500 volts lamp is fifty to sixty times as intense as that from a 110 volts lamp, whilst the power consumption is only 4.6 times as great. A method is described by which this new lamp can be used for sterilising large quantities of water. W. G.

**Magnetic Researches. VI. Paramagnetism at Low Temperatures.** H. KAMERLINGH ONNES and E. OOSTERHUIS (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 322—329. Compare Abstr., 1911, ii, 694; this vol., ii, 228, 425).—From measurements of the magnetic susceptibility ( $\chi$ ) over a wide interval of temperature, it appears that gadolinium sulphate follows Curie's law, according to which  $\chi T = \text{constant}$ , down to  $14^\circ$  abs., and may therefore be regarded as a normal paramagnetic substance. Over the same range, dysprosium oxide is found to satisfy the relation  $\chi(T + \Delta) = \text{constant}$ . Anhydrous manganous chloride behaves normally down to about  $65^\circ$  abs., but at lower temperatures its behaviour approximates to that of dysprosium oxide. In the case of anhydrous ferrous and ferric sulphates, the change of magnetic susceptibility with temperature is very similar, deviations from Curie's law of the same kind being found at temperatures below  $65^\circ$  abs. H. M. D.

**Thermal Expansion of Liquids between Boiling Point and Critical Point.** JULIUS MEYER (*Festschrift W. Nernst*, 1912, 278—301).—The literature relating to the influence of temperature on the coefficient of expansion of liquids has been examined and new experiments made with the object of obtaining values for the coefficient of expansion at zero pressure.

If the coefficient of expansion between absolute zero and the critical point be plotted against the temperature, a curve is obtained which exhibits neither maximum nor minimum in the case of a normal liquid. If the change in temperature, however, is accompanied by changes in the molecular condition, then curves are obtained which show maxima or minima, or both. The recorded data for the thermal expansion of nitrogen peroxide, water, and nitrous oxide indicate that these liquids furnish examples of the three abnormal types referred to.

For the examination of the thermal expansion of liquids above their boiling points, an apparatus was employed which permitted of superheating the liquids to a considerable extent. With this it was possible to determine the expansion of water at negligibly small pressures up to  $200^\circ$ , of benzene to  $168^\circ$ , ethyl alcohol to  $155^\circ$ , methyl ethyl ether to  $85^\circ$ , ethyl ether to  $115^\circ$ , and isopentane to  $95^\circ$ . In order to obtain the corresponding data for temperatures up to  $200^\circ$ , measurements were made of the expansion under different pressures and the results extrapolated to zero pressure.

In all cases, the coefficient of expansion increases very considerably with the temperature, and the data for methyl ethyl ether, ethyl ether, and isopentane indicate that the expansion coefficient changes in a

perfectly continuous manner when the transition from liquid to gas occurs at the critical temperature.

The range covered by the observations on water, benzene, and ethyl alcohol does not extend to the critical temperature, but the form of the expansion temperature curves affords evidence of similar behaviour in these cases.  
H. M. D.

**The Critical Temperature of Mercury.** J. KOENIGSBERGER (*Chem. Zeit.*, 1912, 36, 1321).—The mercury was heated in sealed capillary tubes of clear quartz glass, suspended in a spiral of platinum wire. The temperature was determined optically from the glowing platinum.

At 1200° the meniscus is very flat, and only the liquid mercury is luminescent. At about 1400° the luminosity of the liquid decreases very rapidly, and soon the whole tube becomes non-luminous. The pressure was estimated at more than 1000 atmospheres. The tubes withstand the critical temperatures for a few seconds only, then exploding with a sharp report, although they contain only about 0.5 mg. of mercury.  
T. S. P.

**Theory of Specific Heats.** P. DEBYE (*Ann. Physik*, 1912, [iv], 39, 789—839).—As a consequence of the influence exerted by neighbouring atoms, the motion of a vibrating atom cannot be of a simple periodic character corresponding with a single frequency, but must be represented as giving rise to a complete spectrum, corresponding with a large number of component vibrations. It is shown that the distribution of the lines in this spectrum may be deduced, and on this basis the author derives an equation expressing the relation between the specific heat and the temperature in terms of the theory of quanta.

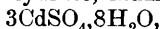
According to this, the specific heat of a monatomic substance at the temperature,  $T$ , is determined by the ratio  $T/\theta$ , where  $\theta$  denotes a temperature which is characteristic of the substance. When, for different monatomic substances, temperatures are expressed as multiples or submultiples of the respective characteristic temperatures, the dependence of the specific heat on the temperature can be represented by a single curve which holds for all such substances. At low temperatures, the formula further indicates that the specific heat is proportional to the cube of the absolute temperature.

By reference to the available data for the specific heat of diamond, aluminium, copper, silver, and lead over a wide range of temperature, it is shown that the above equation affords a satisfactory account of the observed variation of the specific heat with temperature.

The characteristic temperature,  $\theta$ , may be calculated from the elastic constants of the substance. For diamond,  $\theta = 1830^\circ$ , aluminium  $396^\circ$ , copper  $309^\circ$ , silver  $215^\circ$ , and lead  $95^\circ$ .  
H. M. D.

**Specific Heats of Crystallised Salts.** FREDERICK GRAY JACKSON (*J. Amer. Chem. Soc.*, 1912, 34, 1470—1480).—This investigation was undertaken with the object of elucidating the physical structure of double salts and salts containing water of crystallisation. The

specific heats have been determined adiabatically of copper sulphate pentahydrate, anhydrous copper sulphate, copper ammonium sulphate hexahydrate, copper sodium sulphate hexahydrate, copper potassium sulphate hexahydrate, ammonium sulphate, sodium sulphate, potassium sulphate, zinc sulphate heptahydrate, cadmium sulphate,



ferrous sulphate heptahydrate, and ice between  $-190^\circ$  and  $+22^\circ$ , and  $-78.4^\circ$  and  $+22^\circ$ . From the results the molecular heats have been calculated between  $-190^\circ$  and  $-78.4^\circ$ , and  $-78.4^\circ$  and  $+22^\circ$ . It is shown that the sum of the molecular heats of the factors agrees with the molecular heat of the product in the case of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . Similar comparisons are made between the molecular heats of the other hydrated and double salts and those of their factors, and it is shown that these are almost the same, except in the case of copper sodium sulphate, in which the factors have a greater heat-energy content than the product. It is suggested that this may be connected with the fact that sodium sulphate is capable of crystallising with water of crystallisation, whilst potassium and ammonium sulphates are not.

E. G.

**Specific Heat of Liquids at Constant Pressure for Different Pressures and Temperatures.** SILVIO LUSSANA (*Nuovo Cim.*, 1912, [vi], 4, 207—232).—The measurements were made by a modification of the ordinary calorimeter method, and also by supplying a known amount of electrical energy to the system and observing the rise of temperature. The apparatus is figured and described in detail.

The observations were made with mercury, methyl, and amyl alcohols, acetone, ether, and petroleum. Pressures up to, and in some cases exceeding, 1000 atmospheres were used. The specific heats of the liquids examined diminished in general with increase of pressure. With increase of temperature the diminution became less, and in some cases changed to an increase; in the case of mercury only it became greater with rise of temperature. Some of the data are as follows, where  $\gamma$  denotes the coefficient of variation of the specific heat with the pressure: Mercury  $\gamma \times 10^8$  at  $63.4^\circ$  is  $-1890$  at  $90.5^\circ - 2581$ ; amyl alcohol,  $\gamma \times 10^8$  at  $52.2^\circ$  is  $-5189$  at  $77.4^\circ + 7238$ ; methyl alcohol,  $\gamma \times 10^8$  at  $11.9^\circ - 8331$  at  $44.7^\circ + 32551$ ; acetone  $\gamma \times 10^8$  at  $12.5^\circ$  is  $-14728$  at  $42.3^\circ - 4665$ ; ether  $\gamma \times 10^8$  at  $9.4^\circ$  is  $-14719$  at  $46.6^\circ - 12908$ .

G. S.

**The Determination of Fusion Curves for Substances of Low Melting Point.** GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1912, 81, 187—203).—A method is described by which the fusion curves of ethyl ether, methyl alcohol, and carbon disulphide were determined. The substances were cooled to the temperature of liquid air, and subjected to pressures up to 3000 kilograms. The results are given in curves, from which it is visible that the number of centres of crystallisation is so small that it is impossible to deduce the influence of pressure on spontaneous crystallisation. In some experiments with ether, crystallisation did not occur at all, or only to a small extent, but on warming, as the melting point was approached, crystallisation

occurred suddenly. The results with methyl alcohol were similar. In the case of carbon disulphide only can the conclusion be drawn that the number of centres of crystallisation decrease with increasing pressure. Tables are given containing the temperature and pressure data, as well as the increase in pressure on melting at constant temperature ( $\Delta p_T$ ), the volume change on melting at constant temperature and pressure ( $\Delta v_p$ ), and the volume change on melting at constant temperature with change of pressure ( $\Delta v_T$ ). The values of  $\Delta v_p$  for methyl alcohol and ether decrease with increasing pressure. The fusion curves up to a pressure of 3000 kilogrammes can be expressed by the equation:  $\Delta T = ap - bp^2$ , where  $\Delta T$  is the temperature change by pressure, and  $a$  and  $b$  constants. For the substances investigated the expressions are: ether,  $156^\circ + \Delta T = 156^\circ + 0.0134p$ ; methyl alcohol,  $178^\circ + \Delta T = 178^\circ + 0.0060p$ ; carbon disulphide,  $160^\circ + \Delta T = 160^\circ + 0.0160p$ , and the value of  $b$  in every case is less than 0.00001. The results are only regarded as preliminary, and a more accurate and exact method is indicated. J. F. S.

**Cryoscopy in Decahydrated Sodium Sulphate.** A. BOUTARIC and C. LEENHARDT (*Compt. rend.*, 1912, 155, 825—826. Compare Abstr., 1911, ii, 1060; this vol., ii, 234).—By dissolving carbamide in the fused salt,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ , the authors obtained the value 32.05 for the molecular depression of the freezing point, as compared with 32.2 obtained by Loewenherz (Abstr., 1896, ii, 149). Using van't Hoff's formula and the figure they obtained for the heat of transformation,  $L = 57.7$  calories at  $31.5^\circ$ , they found for  $K$  the value 32.08, this being in very close agreement with the experimental figure.

W. G.

**Connexion between Boiling Point and Molecular Weight of Substances.** J. C. T. (*Chem. News*, 1912, 106, 187—188).—The absolute boiling point ( $T$ ) and the vapour density ( $\rho$ ) of a number of non-metallic elements are found to be connected by the equation:  $T/\sqrt{\rho} = n \times \text{constant}$ , in which  $n$  represents an integer. The value of the constant is 10, and for hydrogen, argon, krypton, xenon, nitrogen, oxygen, and fluorine,  $n$  is equal to 2, whilst for chlorine, bromine, and iodine,  $n = 4$ .

In a similar way, the boiling points and vapour densities of a number of trihalogen compounds are found to satisfy the relation:  $T/\sqrt{\rho} = 30\sqrt{2}$ .

From the equation:  $T/\sqrt{\rho} = n \times \text{constant}$  and the kinetic theory, it is deduced that the attraction pressure due to each molecule of a liquid varies as  $n/\sqrt{m}$ , where  $m$  denotes the molecular weight of the substance. H. M. D.

**Sulphur Trioxide, Sulphuryl Chloride, Sulphuryl Oxide, and Chromyl Chloride as Ebullioscopic Solvents.** ERNST BECKMANN (*Zeitsch. anorg. Chem.*, 1912, 77, 90—102).—The liquid sulphur trioxide is obtained by heating the commercial asbestos-like product in a glass cylinder to  $150^\circ$ , cooling to  $30^\circ$ , and distilling

from phosphoric oxide. The liquid must not be allowed to cool below 30°. A portion is then distilled into the boiling tube, which is heated electrically. Most organic compounds are blackened by sulphur trioxide; arsenious oxide is very sparingly soluble, and molybdenum and tungsten trioxides are insoluble.

For molecular-weight determinations, a jacket of boiling carbon disulphide, which has the same b. p. as sulphur trioxide, is used. Sulphonal and trional give satisfactory results, and lead to the constant 13.5, whilst sulphuric acid leads to the same constant in dilute solutions, diminishing to one-half in concentrated solutions.

Sulphuryl chloride does not dissolve the metallic oxides examined. Sulphonal, trional, and camphor give the constant 45, whilst aluminium chloride gives a lower result.

Sulphuryl oxychloride always loses hydrogen chloride when boiled. Chromyl chloride gives the constant 55 with chromium trioxide. The constants thus found are in good agreement with those calculated by Trouton's formula.

C. H. D.

**Thermo-chemistry of Silicon.** H. VON WARTENBERG (*Festschrift W. Nernst*, 1912, 459—463).—From measurements of the heat of solution of amorphous and crystalline silicon in hydrofluoric acid in presence of different oxidising agents, the conclusion is drawn that the heat of transformation of one form into the other is less than 2000 cal. The value (6900 cal.) obtained by Troost and Hautefeuille is much too high.

The heat of combustion of amorphous silicon was found to be 195,000 cal., the possible error attaching to this being estimated at 2%. Previously recorded values are 184,500 cal. by Berthelot and 191,000 cal. by Mixter.

H. M. D.

**The Explosion Method. I. The Molecular Heat of Ammonia.** HANS BUDE (*Zeitsch. anorg. Chem.*, 1912, 78, 159—168).—The apparatus used is that of Pier (*Abstr.*, 1909, ii, 789), but the bomb has a capacity of only 10 litres in place of 35 litres. Still smaller bombs give low results. The ammonia is mixed with electrolytic gas, and exploded. The best results are obtained in presence of an excess of hydrogen. It is in this way possible to heat ammonia far above its temperature of dissociation, on account of the slowness of the reaction. The dissociation is favoured by the presence of water vapour. The specific heat of ammonia between 1400° and 2300° is found to be:

$$\begin{aligned} C_v (\text{mean}) &= 11.82 + 0.0059 (t - 1400^\circ) \\ C_v (\text{true}) &= 11.82 + 0.012 (t - 1400^\circ). \end{aligned}$$

C. H. D.

**The Heat of Vaporisation of Mixtures.** HUGO MASING (*Zeitsch. physikal. Chem.*, 1912, 81, 223—245).—A mathematical paper, the object being to develop more fully the formula for the heat of evaporation of mixtures, and to show some applications of this formula.

J. F. S.

**Tempering of Metals.** MAURICE HANRIOT (*Compt. rend.*, 1912, 155, 828—831).—The author extends the definition of a tempered

metal to include any metal which, after sufficient annealing, changes its physical properties, chemical changes being excluded. He determines the tempering by measuring, under a microscope, the diameter of the impress produced on the metal in fifteen seconds by a ball of steel, 3 mm. in diameter, under a weight of 30 kilos. By this means he has determined the hardness of metals like bismuth and antimony which break under a pressure of 1000 kilos. For bismuth he obtained the value 4.6—4.8, and for antimony 42—58. Mechanical properties of metals, such as breaking strain and elongation, do not appear to vary regularly with the hardness. W. G.

**New Densivolumeter for Determining the Density of Solids.** JEAN ESCARD (*Ann. Chim. anal.*, 1912, 17, 368—370).—The density ( $d = w/v$ ) is determined by observing the volume of water displaced by a known weight of the substance. The apparatus is fully described and figured. L. DE K.

**Unusual Case of Specific Gravity.** A. L. HYDE (*J. Amer. Chem. Soc.*, 1912, 34, 1507—1509).—When *p*-nitrotoluene is dissolved in carbon disulphide, the specific gravity of the solution is less than that of carbon disulphide itself, in spite of the fact that *p*-nitrotoluene has a higher specific gravity than carbon disulphide. The decrease in the specific gravity is nearly proportional to the percentage of *p*-nitrotoluene in the solution, the relation being expressed approximately by the formula  $D = 1.2660 - 0.0013a$ , where  $a$  is the percentage of *p*-nitrotoluene present.

Further experiments have shown that both carbon disulphide and *p*-nitrotoluene always tend to increase the volume of solutions into which they enter, although the specific gravity of the solution is not in all cases less than that of the pure solvent. *o*-Nitrotoluene seems to have a similar effect. E. G.

**Isotherms of Diatomic Gases and of their Binary Mixtures. X. Control Measurements with the Volumometer of the Compressibility of Hydrogen at 20°.** W. J. DE HAAS (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 295—299. Compare Abstr., 1911, ii, 203, 467, 854; this vol., ii, 900).—The compressibility of hydrogen at 20° may be expressed by the equation  $pv_A = 1.07258 + 0.000667 d_A + 0.00000099 d_A^2$ , in which  $v_A$  represents the volume in terms of the normal volume, and  $d_A$  is the reciprocal of  $v_A$ . At low pressures, the third term on the right-hand side may be entirely neglected.

The numerical coefficient in the second term is shown to agree fairly well with the values deduced from the experiments of previous workers on the compressibility of hydrogen at low pressures.

H. M. D.

**Isotherms of Diatomic Substances and of their Binary Mixtures. XII. Compressibility of Hydrogen Vapour at and below the Boiling Point.** H. KAMERLINGH ONNES and W. J. DE HAAS (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 405—416).—The range of temperature covered by previous investi-

gations on the equation of state for hydrogen has been extended by measurements over the interval  $-252^{\circ}$  to  $-258^{\circ}$ . From these observations, the value of the second virial coefficient  $B_A$  in the equation  $pv_A = A_A + B_A d_A + C_A d_A^2$  has been found equal to  $-0.00047$  at  $-252.47^{\circ}$ ,  $-0.00049$  at  $-255.32^{\circ}$ , and  $-0.00055$  at  $-257.10^{\circ}$ . These temperatures refer to the absolute scale. From the values of this coefficient, the corrections required for the reduction of hydrogen thermometer temperatures to the absolute scale are found to be  $+0.118$ ,  $0.125$ , and  $0.144$  for the above three temperatures respectively.

H. M. D.

**Composition and Pressure of the Vapour of Binary Liquid Mixtures.** M. S. VREVSKY (*Zeitsch. physikal. Chem.*, 1912, 81, 1—29. Compare Abstr., 1910, ii, 1038; 1911, ii, 256; this vol., ii, 132).—The composition and the pressure of the vapour given off from aqueous solutions of methyl, ethyl, and propyl alcohols of different concentrations have been determined at different temperatures, and the results are represented in tabular form and also graphically. The method adopted was that of Zawidzki (compare Abstr., 1901, ii, 6) with some modifications.

Constant boiling mixtures are obtained both with ethyl and propyl alcohols. In the former case, the relative proportion of alcohol in the constant boiling mixture is the greater the lower the temperature of vaporisation, as shown by the following numbers: proportion of alcohol, 95.7% by weight at  $74.79^{\circ}$ , 96.5% at  $54.81^{\circ}$ , and 97.6% at  $39.76^{\circ}$ . With propyl alcohol, on the other hand, the lower the temperature of vaporisation the smaller is the proportion of alcohol in the mixture. The data are as follows: 71.4% by weight of alcohol at  $79.8^{\circ}$ , 70.5% at  $65.94^{\circ}$ , 69.8% at  $49.92^{\circ}$ , and 68.2% at  $30.35^{\circ}$ . Young found 71.69% at  $97.19^{\circ}$ .

G. S.

**Theory of Contraction on Mixing Normal Liquids.** EUGEN VON BIRON (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1264—1312).—This paper has been to some extent published previously (Abstr., 1910, ii, 393, 394), but contains a number of further consequences of the author's theory, and experimental data in support of them.

Investigation of the contraction shows that isotherms of liquids may be expressed by a formula of the form:  $v = A + B/(C + p)$ , where  $p$  is the manometric pressure and  $C$  is an arbitrary constant, which, however, corresponds theoretically with the internal pressure  $P$ . From this expression and those already given (*loc. cit.*), the author derives the equation:  $k = (V_1 \beta_1 P_1 / P_2 - V_2 \beta_2 P_2 / P_1)(P_2 - P_1)$ , which he shows may be used to calculate the contraction constant in all cases where no anomaly is exhibited by either of the components of the mixture or by their mutual actions on mixing.

From the expression  $v = A + B/(C + p)$  and van der Waals' equation, the author derives the equation,  $P = -Ta/\beta - p$ , which was first obtained by Dupré (*Ann. chim. phys.*, 1864, [iv], 2, 185, and 1865, [iv], 6, 274), and gives results in agreement with the experimental  $p, v, T$ -surfaces for liquids.

The formula  $v = A + B/(C + p)$  or  $v = A^1 + B^1(P + p)$ , where  $P$  is the internal pressure calculated either from Dupré's equation or from the

contraction, is a correct expression for the isotherms of liquids, at any rate up to values of 500 atmospheres for  $p$ .

The expression  $a_{1,2} = \sqrt{a_1 a_2}$ , assumed by Galizine (Abstr., 1891, 378) and by D. Berthelot (*Compt. rend.*, 1898, 126, 1703, 1857), is to be applied only in cases where the external signs of isofluidism are apparent, the most important of these being the absence of any change in volume on mixing the component liquids. Mixtures of liquids which are not isofluid are also considered.

T. H. P.

**Simple Apparatus for Layering Two Miscible Liquids of Different Densities.** SIEGFRIED WIECHOWSKI (*Chem. Zeit.*, 1912, 36, 1234).—Inside a glass tube of 10 mm. bore a longer tube of 3 mm. bore is fitted by means of a piece of india-rubber tubing, which slips over one end of the wider tube, and allows the narrow tube to slide through it. At the opposite (bottom) end to the rubber tubing, the narrow tube projects a short distance beyond the wider tube. The top end of the narrow tube is connected with a funnel by means of rubber tubing and a pinchcock.

In order to layer two liquids of different densities, a glass cylinder is partly filled with the lighter liquid, and the apparatus immersed until it nearly touches the bottom. The heavier liquid is then put in the funnel, and, by squeezing the pinchcock, allowed to run gently into the bottom of the cylinder, taking care that it does not rise as high as the outer, wider tube. When sufficient liquid has been run in, the pinchcock is closed, the narrow tube drawn up within the wider one, and then the apparatus carefully lifted out of the cylinder.

T. S. P.

**The Behaviour of Hydrates and Hydrogels in Dry Air.** GUSTAV TSCHERMAK (*Monatsh.*, 1912, 33, 1087—1163).—As is well-known, the vapour tension of many hydrated salts and hydroxides remains constant at a definite temperature so long as two solid phases of definite composition are present; when one of these phases is replaced by another of a lower stage of hydration, as happens during the process of dehydration, there is a sudden fall to a lower vapour pressure, and so on. It was probable, therefore, that the velocity with which the vapour is evolved should remain constant during the stages where the vapour pressure is constant, and change abruptly with the sharp change in the vapour pressure. The author has measured this velocity of dehydration (vapour evolution) by determining at intervals, the temperature being maintained constant, the loss in weight of a definite amount of the substance when preserved over sulphuric acid solutions of known concentrations. The velocity is not found to be constant, but to diminish towards the end of each stage of the dehydration. However, it was found that a well-marked retardation of the velocity takes place at certain points during the dehydration, and these points of retardation correspond with the abrupt fall in the vapour pressure when a change in the solid phase takes place. It follows that by observing such points of retardation the existence

and composition of hydrated compounds can be determined. Experiments with such hydrated salts as sodium sulphate, barium chloride, sodium phosphate, and with hydrated hydroxides, such as strontium hydroxide, gave satisfactory results.

When totally or partly dehydrated salts are exposed to the action of water vapour, the original water-content is attained, but the velocity of hydration is smaller than that previously observed for the dehydration, owing to the occurrence of structural changes.

Certain hydrated salts are known, for example, the zeolites, strychnine sulphate, cerium oxalate, in which there is a gradual diminution in the vapour tension during dehydration. Even with these, the velocity of dehydration shows a retardation at the change from one hydrate to another, that is, at definite stoicheiometrical ratios.

Experiments with unsaturated and supersaturated solutions of sodium sulphate, sodium phosphate, and strontium chloride showed that the velocity of dehydration could be used to determine the composition of the crystals which first separate, there being a definite retardation at the point where all the solvent water disappears.

The above experiments with hydrated salts form the basis of further investigations on hydrogels. When the freshly made hydrogels are gradually dehydrated, retardations of the velocity take place at certain points, which correspond with definite stoicheiometrical ratios, as shown by the following results:  $\text{WO}_3 \cdot 2\text{H}_2\text{O}$ ,  $\text{WO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{Al}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3 \cdot 4\text{H}_2\text{O}$ ,  $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ ,  $\text{SnO}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{SnO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{TiO}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{SiO}_2 \cdot \text{H}_2\text{O}$ . Further considerations lead the author to the conclusion that some of these hydrogels at the point where the first retardation takes place are to be considered as hydroxides with one molecule of water of crystallisation, for example,  $\text{WO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}$ ,  $2\text{Al}(\text{OH})_3 \cdot \text{H}_2\text{O}$ ,  $2\text{Fe}(\text{OH})_3 \cdot \text{H}_2\text{O}$ , whilst the remainder, which belong to the silicon group, are hydroxides (acids), which decompose at the ordinary temperature, for example,  $\text{Sn}(\text{OH})_4$ ,  $\text{Ti}(\text{OH})_4$ ,  $\text{Si}(\text{OH})_4$ , which readily give the lower and more stable state of hydration (meta-acids):  $\text{H}_2\text{SnO}_3$ ,  $\text{H}_2\text{TiO}_3$ ,  $\text{H}_2\text{SiO}_3$ .

The author further discusses the changes which take place on the rehydration of hydrogels, and the structure of hydrogels.

T. S. P.

**A New Hypothesis Relating to the Nature of Different States of Aggregation and of [Allotropic] Modifications.** LÉON SCHAMES (*Ann. Physik*, 1912, [iv], 39, 887—896. Compare this vol., ii, 738).—The assumption that a change in the state of aggregation is accompanied by a change in the molecular complexity of a substance is modified to the extent that the energy ratio is supposed to be equal to the square of the ratio of the numbers of atoms in the molecule. The hypothesis is applied to van der Waals' equation in its relation to the critical phenomena, and also to the question of the surface tension of liquids and the specific heat of gases.

H. M. D.

**Surface Tension of Solutions and Suspensions of Soaps.** FILIPPO BOTTAZZI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 365—378. Compare Bottazzi and Victoroff, *Abstr.*, 1910, i, 537).—Potassium and sodium stearates do not lower the surface tension of water, and the addition of alkali to the suspensions does not alter this result. The author records experiments with solutions and suspensions of sodium oleate (6%) and potassium oleate (2%), which were dialysed until they had about doubled in volume. The results indicate that the undissociated molecules of oleate lower the surface tension, whilst the products of dissociation are much less active, or are inactive. Hence addition of sodium hydroxide lowers the surface tension until a point is reached at which precipitation begins. When to the solution so obtained, containing excess of alkali, hydrochloric acid is added, the surface tension first diminishes (neutralisation of excess of alkali), then increases (precipitation of fatty acid, and consequent diminution in the number of molecules of undissociated soap). The addition of sodium hydroxide to the original 6% solution of sodium oleate, first increases the surface tension (aggregation or incipient precipitation of soap), then apparently decreases it, because it increases the viscosity and consequently the number of drops from the stalagmometer.

R. V. S.

**Significance of Nernst's Formula Relating to Ideal Concentrated Solutions for the Phenomena of Swelling.** J. R. KATZ (*Festschrift W. Nernst*, 1912, 201—214).—The relationship between the vapour pressure and the heat of mixing of the components of a binary mixture, one of which is volatile and the other non-volatile, deduced by Nernst (*Abstr.*, 1894, ii, 444), represents a special case of the general thermodynamic equation for the vapour pressure of binary mixtures. This simplified equation, representing the behaviour of ideal concentrated solutions, is applied to the case of aqueous solutions of sulphuric acid, phosphoric acid, and glycerol. The curves obtained by plotting the vapour pressure ( $p$ ) as a function of the dilution ( $i$ ) expressed in grams of water per gram of non-volatile substance are shown to be in agreement with the equation connecting the vapour pressure and the heat of mixing. The equation is also applicable to the binary solutions formed by the absorption of water by swelling substances, such as casein, cellulose, and potassium ferrocyanide.

With reference to the applicability of the simple law of distribution to swelling substances, it is pointed out that the distribution law depends on the validity of the laws regulating the vapour pressures of ideal dilute solutions, and deviations may be anticipated when one of the phases represents an ideal concentrated solution, the behaviour of which is expressed by Nernst's equation. In many cases, divergences from the law of distribution have led to the assumption that adsorption is involved, but the author believes that the actual behaviour may frequently be interpreted on the basis of the equation referred to.

H. M. D.

**The Forces Acting between the Atoms of Solid Substances.** F. A. LINDEMANN (*Festschrift W. Nernst*, 1912, 258—263).—On the assumption that the forces between two atoms of a solid

substance depend only on the distance of separation, and that the attractive and repulsive forces vary inversely as the  $m^{th}$  and  $n^{th}$  power of the distance respectively, an expression is deduced which gives  $(m-1)(n-1)$  in terms of the atomic weight, the distance of separation of the atoms, the vibration frequency, and the heat of sublimation. The data for copper, silver, and lead give  $(m-1)(n-1) = 10.7, 11.6,$  and  $7.5$  respectively. Since  $n$  must be greater than  $m$ , it follows that  $m$  must be between 1 and 4, and  $n$  must be greater than four.

If it is assumed that the tensile strength is equal to the maximum force between two layers of atoms,  $n$  may be calculated from this, but the value obtained is such as to lead to the conclusion that the tensile strength does not represent the forces between the atoms, but the forces between small, crystalline conglomerates. H. M. D.

**Tensile Strength of Materials at Low Temperatures.** F. A. LINDEMANN and C. L. LINDEMANN (*Festschrift W. Nernst*, 1912, 264—265).—Measurements of the tensile strength of aluminium, iron, nickel, copper, silver, gold, platinum, and lead have been made at the temperature of liquid hydrogen and liquid air, and at the ordinary temperature. Excepting aluminium, the tensile strength increases regularly as the temperature falls. If the metals are arranged in the order of the temperature coefficients, the sequence is the same as that given by the arrangement according to atomic volumes. H. M. D.

**Relations between Viscosity and Other Physical Properties.** III. The Influence of Neighbouring Unsaturated Groups. THOMAS P. HILDITCH and ALBERT E. DUNSTAN (*Zeitsch. Elektrochem.*, 1912, 18, 881—885. Compare this vol., ii, 435).—In order to throw light on the reciprocal influence of neighbouring unsaturated groups, the esters of a number of dibasic acids, certain dichloro- and dibromo-paraffins, and diphenylparaffins have been prepared, and their viscosities determined in the pure state, or in amyl acetate solution (the esters were examined under both conditions). The molecular refractivities of the esters have also been measured. For the pure substances the data obtained indicate a definite reciprocal influence of the neighbouring unsaturated groups, but a similar effect in solution was not proved with certainty. G. S.

**Physico-chemical Properties of Sulphur Hydrosols.** SVEN ODÉN (*Zeitsch. physikal. Chem.*, 1912, 80, 709—736).—Sulphur hydrosols present certain advantages from the point of view of the physico-chemical investigation of colloids, as they can be prepared in a very concentrated and stable form. The density of the solutions is represented approximately by the formula:  $d_{sol} = d_{medium} + KA$ , where  $A$  represents the weight of sulphur in grams per 100 grams of sol, and  $K$  is a constant;  $K$  is not, however, quite constant, but varies with the concentration in the more concentrated solutions in such a way that the increase of density for a definite increase in the proportion of sulphur becomes progressively smaller. The mean expansion coefficient of a solution containing amicroscopic particles is

0.000229 between  $10^{\circ}$  and  $25^{\circ}$ , and the curve obtained by plotting the expansions as ordinates against the temperatures as abscissæ is somewhat flatter than the corresponding curve for water. Reversible coagulation causes no change of volume.

An extensive series of viscosity measurements has been made at different temperatures. The relationship between viscosity and temperature is represented approximately by the formula  $1/\eta = Kt + C$ , where  $K$  and  $C$  are constants; but the influence of temperature becomes relatively smaller as the temperature rises, and relatively greater with the increasing concentration of sulphur. Theoretically, the viscosity of suspensoids should be independent of the degree of dispersion of the colloid, but the experimental results appear to show that, in the case of sulphur, the viscosity increases with increased dispersion of the particles. The viscosity shows a marked increase as soon as a visible coagulation of the solution occurs.

The presence of colloidal sulphur does not affect the surface tension of water. The refractivity of the solutions is represented by the formula  $n_{\text{sol}} = n_{\text{medium}} + Kp$ , where  $p$  represents the sulphur content of the solution, and  $K$  is a constant which amounts to about 3.30 at  $17.5^{\circ}$ .  
G. S.

**Fluidity and the Hydrate Theory.** EUGENE C. BINGHAM and GEORGE F. WHITE (*Zeitsch. physikal. Chem.*, 1912, 80, 670—686).—The paper consists mainly of the detailed description of a new form of viscometer by means of which the viscosity of water at a series of temperatures between  $0^{\circ}$  and  $100^{\circ}$  has been measured. The capillary is placed horizontally, and the ends fit by ground glass joints into the tubes connected with the two vertical tubes in which the volume of liquid passing through the capillary is observed. Every precaution, including the effect of the shape or the ends of the capillary on the rate of flow, and of the deviation of the capillary from a true cylindrical form, has been taken to ensure the accuracy of the results. The data for the change of viscosity of water with temperature, which are in fair agreement with those of previous observers, are as follows:

Temperature ...	$0^{\circ}$	$10^{\circ}$	$20^{\circ}$	$30^{\circ}$	$40^{\circ}$	$50^{\circ}$
Viscosity $\times 100$	1.797	1.301	1.006	0.7998	0.6563	0.5500
Temperature ...	$60^{\circ}$	$70^{\circ}$	$80^{\circ}$	$90^{\circ}$	$95^{\circ}$	
Viscosity $\times 100$	0.4735	0.4075	0.3570	0.3143	0.2993	

G. S.

**Adsorption by Heated Charcoal.** KURT ARNDT and GEORG SCHRAUBE (*Festschrift W. Nernst*, 1912, 46—52).—Experiments are described which show that carbon dioxide and carbon monoxide are both adsorbed by carefully purified wood charcoal. At the ordinary temperature, the volume ratio of the adsorbed gas was found to be 3.4 : 1, carbon dioxide being adsorbed the more readily.

When a mixture of the gases is exposed to the action of the charcoal and the adsorbed gas removed in successive fractions, it is found that the ratio of carbon dioxide to carbon monoxide increases very considerably as the fractionation proceeds. Similar results were obtained

when a mixture of carbon dioxide and nitrogen was brought into contact with the charcoal at 200°, 300°, and 400°.

Analysis of the successive fractions removed from the charcoal which had been in contact with carbon dioxide for several hours at 750—800° showed a similar variation in the ratio of dioxide to monoxide. At this temperature the equilibrium condition corresponding with the reversible changes,  $C + CO_2 \rightleftharpoons 2CO$ , is readily attained, and the fractionation experiments seem to show that the adsorbed gas is under considerable pressure, for this will tend to displace the equilibrium in favour of the dioxide. H. M. D.

**Adsorption by Animal Charcoal and Chemical Reactions in Aqueous Solutions of Potassium Permanganate.** TADEUSZ ORYNG (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 169—171).—Potassium permanganate is readily adsorbed by animal charcoal from aqueous solutions. At the same time reduction of the permanganate occurs, and the solution becomes alkaline. According to measurements of the rate at which permanganate disappears from the solution, this occurs very quickly during the early stages, and the rate then falls off considerably. The period of rapid change is probably chiefly due to the adsorption effect, whilst the subsequent slow change is due to the chemical reduction of the permanganate. The addition of acids increases the rate of disappearance of the permanganate from its solutions, the effect increasing with the strength of the acid.

H. M. D.

**The Adsorptive Power of the Hydroxides of Silicon, Aluminium, and Iron.** V. PAUL ROHLAND (*Zeitsch. anorg. Chem.*, 1912, 77, 116—118. Compare Abstr., 1909, ii, 27, 551; 1910, ii, 104).—The adsorptive power of clay is limited to colloidal colouring matters. Such dyes as aniline-red and -blue, malachite-green, and carmin, although crystalloidal in dilute solution, are polymerised and colloidal in concentrated solution, and are hence adsorbed.

C. H. D.

**The Explosion Method. II. The Dissociation into Atoms of Sulphur Vapour.** HANS BUDDE (*Zeitsch. anorg. Chem.*, 1912, 78, 169—177. Compare this vol., ii, 1137).—Hydrogen sulphide is exploded with electrolytic gas, and above 1500° molecules larger than  $S_2$  are not present. Even a small quantity of hydrogen sulphide prevents the explosion of dry electrolytic gas. Even in the presence of moisture, 1.5 mol. of hydrogen sulphide to 1 mol. of hydrogen burnt is the maximum proportion permitting explosion to take place.

It is found that the dissociation of  $S_2$  into single atoms amounts to one-half at 2450° under atmospheric pressure. Between 1800° and 2300° the heat of reaction amounts to 120,000 cal. The constant of the reaction-isochore is 8.58.

C. H. D.

**Gas Pressure Measurements by means of a Quartz-glass Spiral Manometer.** Isotherms of Selenium, Sulphur, Arsenic, Phosphorus. Dissociation of Copper Sulphide and of Hydrogen Selenide. GERHARD PREUNER and I. BROCKMÖLLER (*Zeitsch. physikal. Chem.*, 1912, 81, 129—170).—By means of a modified form

of the quartz-glass manometer described by Preuner and Schupp. (Abstr., 1910, ii, 118), the authors have investigated the dissociation of gaseous sulphur, selenium, arsenic, and phosphorus at different pressures and temperatures.

The values for the dissociation of sulphur vapour, up to  $800^{\circ}$ , obtained by Preuner and Schupp (*loc. cit.*) are confirmed, and use is made of the dissociation constants of sulphur in the investigation of the equilibrium :  $4\text{CuS} \rightleftharpoons 2\text{Cu}_2\text{S} + \text{S}_2$ . From this reaction at temperatures  $450$ — $500^{\circ}$  it is calculated that  $2\text{Cu}_2\text{S} + \text{S}_{2(\text{gaseous})} = 4\text{CuS} + 41,000$  cal., and using the result of Wartenburg (Abstr., 1909, ii, 794),  $2\text{Cu}_2\text{S} + 2\text{S}_{(\text{rhombic})} = 4\text{CuS} + 8500$  cal., they calculate that the passage of 64 grams of solid rhombic sulphur into gaseous  $\text{S}_2$  molecules is accompanied by the absorption of 32,500 cal.

The dissociation of hydrogen sulphide is also discussed in connexion with the dissociation constants of sulphur. Selenium is shown to exist chiefly as  $\text{Se}_6$  and  $\text{Se}_2$  up to a temperature of  $900^{\circ}$ , a small quantity of  $\text{Se}_1$  molecules exist, however, at this temperature, and  $\text{Se}_3$  probably at lower temperatures than  $550^{\circ}$  (see also Wartenberg, Abstr., 1908, ii, 86). Dissociation isotherms and vapour pressure curves of selenium are given. The change of gaseous  $\text{Se}_6$  into  $3\text{Se}_2$  absorbs 55,960 cal. Arsenic is shown to exist as  $\text{As}_4$ ,  $\text{As}_2$ , and  $\text{As}_1$  molecules in the gaseous condition at temperatures between  $600^{\circ}$  and  $1200^{\circ}$ , and phosphorus as  $\text{P}_4$ ,  $\text{P}_2$ , and  $\text{P}_1$  between the same temperatures. The change from gaseous  $\text{P}_4$  molecules to  $2\text{P}_2$  molecules is accompanied by a heat absorption of 31,500 cal., and  $\text{P}_2$  molecules into  $2\text{P}_1$  molecules by an absorption of 45,500 cal. Dissociation isotherms of both phosphorus and arsenic are given.

J. F. S.

**Method of Fractionation by Diffusion, and its Application to the Study of Colloidal Solutions.** I. STÉPHANE DABROWSKI (*Bull. Acad. Sci. Cracow*, 1912, A, 485—526).—Fractional diffusion is suggested as a means of ascertaining the uniformity of fine suspensions or the homogeneity of colloidal solutions. For experiments of this nature a new type of diffusimeter is described, in which the disturbing influence of convection currents is more or less completely eliminated. In this apparatus, the solution under examination is separated from the supernatant water by a special diaphragm consisting of a system of narrow vertical tubes, about 1 mm. in diameter and 4 cms. long. The two compartments of the diffusimeter are provided with stirrers, so that the contents of each are mixed continuously during the progress of the diffusion.

The theory of the method is described, and it is shown that the observed changes in the concentration of the liquid contained in the upper compartment after measured intervals of time may be employed to calculate the coefficient of diffusion.

To test the apparatus, experiments were made with aqueous solutions of carbamide and mannitol. The values obtained in the case of carbamide are smaller than those yielded by the ordinary method of free diffusion. For solutions of different concentrations the product of the diffusion coefficient and the coefficient of viscosity

remains constant, indicating the validity of Einstein's formula for the coefficient of diffusion.

The diffusion of crystallised ovalbumin in ammonium sulphate solution has also been examined, the coefficient obtained being much greater than the coefficient for pure aqueous solutions of this substance. This result is in harmony with the general behaviour of the two solutions. From Einstein's equation it is calculated that the volume occupied by a molecule of ovalbumin in a 3.6% solution of ammonium sulphate is only about one-sixth of the volume occupied in pure aqueous solution.

H. M. D.

**Extension of the Theory of Allotropy, Monotropy, and Enantiotropy for Liquids.** [ANDREAS] SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 361—369. Compare Abstr., 1910, ii, 195, 400; 1911, ii, 263, 871).—A theoretical paper, in which the possibility of the occurrence of monotropy and enantiotropy in liquid substances is discussed.

H. M. D.

**Concentrated Solutions.** ÉMILE BAUD (*Ann. Chim. Phys.*, 1912, [viii], 27, 89—116).—The relation  $\Delta t = K \log x \cdot T_2$  already deduced (Abstr., 1910, ii, 689) is now shown to hold for mixtures of bromoform and toluene, naphthalene and ethylene dibromide, in addition to the binary mixtures already examined (*loc. cit.*), and also for the ternary mixture, ethylene dibromide, benzene and toluene. These are all normal mixtures, that is, mixtures of liquids, which do not interact. The modified equation  $T_2 = T_1(1 - q/Q)/(1 + k \log x)$  deduced for partly miscible liquids has been verified for mixtures of naphthalene and acetic acid in addition to those already given (Abstr., 1911, ii, 581; this vol., ii, 233, 331).

T. A. H.

**Deduction of the Law of Dilution.** C. VAN ROSSEM (*Chem. Weekblad*, 1912, 9, 848—854).—A theoretical paper in which the author deduces Arrhenius's law of dilution from the dynamic theory of dissociation equilibrium.

A. J. W.

**Velocity of Crystallisation. IV.** GUSTAV TAMMANN (*Zeitsch. physikal. Chem.*, 1912, 81, 171—186. Compare Abstr., 1897, ii, 445; 1898, ii, 425; 1899, ii, 548).—A theoretical paper, in which the main points deduced are: The maximum velocity of crystallisation in strongly supercooled liquids is independent of the temperature. As a method of determination of the true relationship between the velocity of crystallisation and temperature, the author suggests the study of the influence of molecular quantities of soluble substance on the velocity of crystallisation. The velocity of crystallisation for solutions of benzoic anhydride in benzophenone is calculated by means of the formula  $KG_{T_1} = KG_{T_0} e^{A \frac{T_1 - T_0}{T_0 T_1}}$ , in which  $T_1$  is the freezing point of the solution, calculated by the Raoult formula,  $T_0$  the temperature at the surface of crystallisation of pure benzophenone which gives the velocity  $KG_{T_0}$ , and  $A$  is a constant. The calculated results agree well with the experimental results of Pickhardt (Abstr., 1903, ii, 66). For

isomorphous mixtures, the temperature of the crystallising surface and the maximum velocity of crystallisation depend on the concentration of the mixture. The results of Bogojawlensky and Sacharoff are quoted, and from them it is shown that the temperature at the surface of crystallisation is not the equilibrium temperature for isomorphous mixtures, but generally lies somewhat below it. The surface of crystallisation of a 50% mixture of  $\alpha$ -bromocinnamaldehyde and  $\alpha$ -chlorocinnamaldehyde, supercooled  $24^{\circ}$ , is  $1.9^{\circ}$  below the equilibrium temperature. Substances with a velocity of crystallisation of more than 3 mm. per min. reach a maximum velocity when supercooled  $20$ – $30^{\circ}$ , and this remains constant until a supercooling of  $70^{\circ}$  has been reached, after which by greater supercooling the velocity slowly decreases. Substances with velocities of crystallisation less than 3 mm. per min. have velocities which increase with supercooling and reach a sharply defined maximum and then slowly decrease. Some substances are abnormal, and their abnormalities are stated to be due to the presence of more than one kind of molecule. They are to be regarded as associated, whilst the normal substances are generally composed of simple molecules, although this is not necessarily so, for they may be associated but with rates of change into the simple molecules so slow as not to affect the velocity of crystallisation. It is suggested that the study of the rate of change of the velocity of crystallisation with supercooling offers a method of determination of the association of liquids.

J. F. S.

**Nature of the Electrical Synthesis of Colloids.** MICHAEL KUTSCHEROFF (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 165–169).—The product obtained as a result of the electrical disintegration of metals immersed in ethyl alcohol by means of an alternating discharge is found to consist of two kinds of particles, one of which forms a more or less stable colloidal solution, whilst the other consists of much larger particles of approximately the same diameter. On the assumption that the fine and coarse particles are the products of essentially different processes, the author has examined the electrical disintegration of various binary alloys.

When the two metals are of different valency, the ratios of the components in the original alloy, in the colloidal solution, and in the deposit of coarser particles, are found to differ appreciably. The observed ratio in the case of the colloidal solution is approximately equal to that given by  $pn'/p'n$ , where  $p$  and  $p'$  are the percentages of the two metals in the original alloy, and  $n$  and  $n'$  are the corresponding valency values.

The colloidal solutions, obtained by the passage of an alternating discharge between electrodes of different metals in alcohol, have also been examined. In a large number of cases the ratio of the two metals in the colloidal solution is approximately equal to that of the chemical equivalents. In other cases, these ratios diverge considerably, but a satisfactory explanation is obtained when the assumption is made that disintegration occurs at both anode and cathode, and that the equivalents of metals of variable valency, such as tin, lead, and

bismuth, vary according to whether disintegration occurs at the anode or at the cathode.

For other pairs of metals, for example, calcium and aluminium, nickel and aluminium, the composition of the colloid solutions seems to show that, although aluminium is pulverised at both electrodes, the effect is unipolar for calcium and nickel.

Whereas the formation of relatively coarse particles may be due to a thermo-mechanical or electro-mechanical process, the above observations show that the primary change involved in the formation of the colloidal metals is electro-chemical in character. In this stage of the process, the passage of the current liberates the metals in the atomic form, and the colloidal metal is then formed as the result of a subsequent condensation process.

H. M. D.

**Camphorylphenylthiosemicarbazide Jellies and Observations on the Structure of Jellies.** EMIL HATSCHKE (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 158—165).—The gelatinisation of solutions of camphorylphenylthiosemicarbazide (*Trans.*, 1907, 91, 1888) in ethyl alcohol and toluene has been examined, together with the properties of the resulting jellies. The two solvents show considerable differences in their behaviour.

If a 5% solution in boiling alcohol is slowly cooled, the substance separates in well-formed crystals, but a transparent jelly is obtained if the cooling is sufficiently rapid. The jelly is unstable, and crystals begin to separate after a short time. These crystals exhibit twinning to a very marked extent. Less concentrated jellies are more stable, especially at low temperatures, but after some time crystallisation sets in. The observations suggest that the gelatinisation process consists in the separation of the semicarbazide in a highly disperse condition. The net-work structure, which would appear to be characteristic of the jellies, is considered to be the result of the twinning of the crystal constituents.

In the case of toluene jellies, the rate of cooling appears to be without influence. Jellies containing less than 2.5% of the semicarbazide are comparatively stable, but more concentrated jellies soon exhibit signs of change in that the jelly becomes cloudy at certain points, and the gradual development of more or less spherical aggregates round these centres may be followed quite readily. This process comes to an end before the jelly is completely transformed, and the residual jelly appears to be quite stable.

H. M. D.

**Jellies. Ultramicroscopic Study of Soap Solutions and Jellies.** RICHARD ZSIGMONDY and W. BACHMANN (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 145—157).—The fact that apparently homogeneous gelatin jellies give rise to a bluish-white strongly polarised beam when examined by means of the ultra-microscope indicates a very high degree of dispersity. The heterogeneity thereby disclosed is very much less coarse than would correspond with Bütschli's honey-comb structure, and the evidence thus furnished by the ultra-microscopic examination of such jellies is in favour of Nägeli's micellary theory.

The morphological changes which occur in the transition of the

alkali oleates, palmitates, and stearates from the hydrosol to the hydrogel condition have been examined in detail. These changes are described in reference to micro-photographs, which show the dependence of the jelly structure on the nature of the soap, the concentration of the hydrosol, and the conditions under which the hydrogel is formed.

H. M. D.

**New Method for the Determination of the Concentration of Colloidal Solutions and the Investigation of Drainage Waters.** ROBERT MARC (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 195—199).—The interferometer may be applied with advantage in the estimation of the concentration of dilute solution. Equally satisfactory results are obtained whether the dissolved substances are in the form of true or pseudo-solutions. The adsorption of colloids from solution by solid substances can also be determined by means of interferometer observations, and the data obtained in experiments on the adsorption of albumin by strontium carbonate and lead carbonate and of starch by strontium carbonate are shown to agree with the exponential adsorption formula.

The use of the interferometer is further recommended in connexion with the estimation of the colloids in drainage waters. For this purpose observations may be made on the original water, and also after the water has been thoroughly shaken with finely divided barium carbonate and then centrifuged. The difference in the interferometer readings affords a measure of the colloidal substances present.

H. M. D.

**The Isoelectric Point of Electro-amphoteric Colloids.** LEONOR MICHAELIS (*Festschrift W. Nernst*, 1912, 308—318).—The conclusions, to which a theoretical consideration of the influence of the hydrogen ion concentration on the condition of albumins lead, are the same whether the albumin solutions be regarded as true or pseudo-solutions. The two conceptions cannot therefore be regarded as fundamentally antagonistic. Whether the isoelectric point is determined from observations on the cataphoretic migration in a series of solutions of gradually varying hydrogen ion concentration, or from the measurement of the hydrogen ion concentration which is most favourable to the coagulation of the albumin, the results are identical within the limits of error of the respective methods.

A table is given, in which the hydrogen ion concentrations corresponding with the isoelectric point, as determined by both methods, are recorded for a number of albumins.

H. M. D.

**Action of Hydroxyl Ions on Suspensions of Kaolin.** PAUL ROHLAND (*Zeitsch. Chem. Ind. Kolloide*, 1912, 11, 193—195).—The rate of sedimentation of kaolin suspensions is unaffected by neutral salts, but is accelerated by bases, and to a smaller extent by the alkali metal salts of weak acids. These facts indicate that the hydroxyl ion is the active agent. For small hydroxyl ion concentrations the velocity of sedimentation is almost exactly proportional to the OH'

concentration, but as this is continuously increased, the rate of sedimentation reaches a maximum and then diminishes. H. M. D.

**Significance of the Elementary Quantum for the Theory of Gases and the Calculation of Chemical Constants.** OTTO SACKUR (*Festschrift W. Nernst*, 1912, 405—423. Compare this vol., ii, 145).—A theoretical paper in which the conception of elementary quanta is applied to the transfer which accompanies molecular collision. It is shown that this hypothesis may be employed with success in the calculation of the chemical constants of different gases and of the equilibria in gas reactions. The particular gas reactions considered are those represented by the equations:  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$ ,  $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ , and  $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ . H. M. D.

**Quadruple Points and the Continuities of the Three-Phase Lines.** F. F. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 389—405).—A theoretical paper in which various types of systems possessing quadruple points are analysed. H. M. D.

**The Law of Mass Action. Its Contradictory Verifications and its Defence by Le Chatelier.** ALBERT COLSON (*Compt. rend.*, 1912, 155, 719—721).—A reply to Le Chatelier (this vol., ii, 631), in which the author gives further figures from Bodenstein (*Abstr.*, 1897, ii, 252) showing a large variation in the value of  $k$  for the dissociation of hydrogen iodide. In further support of his position, he quotes the views of van't Hoff and Nernst on the equilibrium of nitrogen peroxide. W. G.

**The Law of Mass Action.** HENRY LE CHATELIER (*Compt. rend.*, 1912, 155, 753).—Reply to Colson (preceding abstract) declining to continue the discussion. W. G.

**The System Ether-Water.** F. E. C. SCHEFFER (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 380—389).—The conditions under which three phases coexist have been investigated by experiments with a series of binary mixtures containing the components in different proportions. H. M. D.

**Influence of Substitution in the Components on the Equilibrium of Binary Solutions. VI. Naphthalene and the Three Isomeric Dihydroxybenzenes.** ROBERT KREMANN and E. JANETZKY (*Monatsh.*, 1912, 33, 1055—1062. Compare *Abstr.*, 1911, ii, 871).—Freezing-point curves of the mixtures of naphthalene with the three isomeric dihydroxybenzenes show that in no case is a compound formed between the components. Naphthalene and resorcinol give a eutectic containing 5% of resorcinol, the eutectic temperature being  $76.5^\circ$ .

Naphthalene and catechol give a eutectic containing 19% of the latter component, the eutectic temperature being  $72.5^\circ$ ; in the case of naphthalene and quinol the eutectic composition is about 0.5% quinol, the corresponding temperature being  $79^\circ$ .

In all three cases the part of freezing-point curve lying between the eutectic temperature and the freezing point of the pure dihydroxybenzene shows a point of inflexion, which is most marked in the case of the meta- and para-compounds, resorcinol and quinol. The authors consider that this peculiarity may be due to the formation of a compound between the components, which is dissociated to such an extent in the fused state that only the one component, the dihydroxybenzene, is deposited from the fusion. The fact that the inflexion of the curve is most marked with the meta- and para-compounds agrees with the rule put forward by Kremann and Rodinis (Abstr., 1906, ii, 268) that of three disubstitution isomerides the meta- and para-isomerides have a greater tendency to form compounds than the ortho-isomeride.

T. S. P.

**Synthesis of the Natural Fats from the Point of View of the Phase Rule. I. The Ternary System: Tristearin-Tripalmitin-Triolein.** ROBERT KREMANN and R. SCHOULZ (*Monatsh.*, 1912, 33, 1063—1076).—The melting points of stearin, palmitin, and olein were found to be  $56^{\circ}$ ,  $62.6^{\circ}$ , and  $-7^{\circ}$  respectively. The binary mixtures of these three compounds each give freezing-point curves indicating the existence of a continuous series of solid solutions. In the case of the system stearin-palmitin, the freezing-point curve rises to a maximum and then falls to a minimum with increasing percentage of palmitin. The system stearin-olein gives a curve with a maximum, whilst the system palmitin-olein gives a curve with neither maximum nor minimum.

The maxima observed in the stearin-palmitin and stearin-olein curves are extended into the ternary system, as also, but to a much greater extent, the minimum in the stearin-palmitin system.

T. S. P.

**Distribution Law.** WALTER HERZ (*Festschrift W. Nernst*, 1912, 190—195).—Experiments have been made on the distribution of substances between two non-miscible liquid layers, one of which is a pure substance and the other a binary mixture. Data are recorded for the distribution at  $25^{\circ}$  of (1) iodine between water and mixtures of carbon disulphide and carbon tetrachloride; (2) iodine between chloroform and mixtures of glycerol and water; (3) bromine between water and mixtures of carbon disulphide and carbon tetrachloride; (4) ammonia between water and mixtures of amyl alcohol and chloroform; (5) boric acid between water and mixtures of amyl alcohol and carbon disulphide. In the case of the first two systems, the curve showing the relationship between the ratio of distribution and the volume composition of the mixed solvent indicates that the ratios are less than those calculated from the mixture rule, whilst in the fourth and fifth systems the experimental ratios are greater than the calculated values. For the third system the calculated and observed ratios are in approximate agreement.

Measurements were also made of the distribution of acetic acid between water and mixtures of carbon disulphide and carbon tetrachloride for varying acetic acid concentrations. The ratio of distribution varies with the concentration of the acid, but the variation can be

explained to a large extent on the assumption that the acetic acid exists in the form of double molecules in the binary solvent.

H. M. D.

**Solubility and Distribution Coefficients of Thymol.** ATHERTON SEIDELL (*Amer. Chem. J.*, 1912, 48, 453—467).—In view of Meyer and Overton's theory that the activity of a narcotic is proportional to its coefficient of distribution between the blood and the fatty matter of animal cells, a study has been made of the distribution of thymol between water and olive oil as representing the blood and the fatty matter respectively.

The solubility of thymol in water has been determined at temperatures between 10° and 40°, and found to vary from 0.067 gram at the former to 0.141 gram at the latter temperature per 100 grams of solution. The solubility has also been determined in hydrochloric acid of various concentrations up to 5*N*, and it has been found that as the concentration of the acid increases, the solubility of the thymol decreases. It is calculated that the diminution of solubility of thymol in the gastric juice of man is 1.2%, and in that of the dog 11.7%. The solubility of thymol has also been determined between 10° and 40° in olive, peanut, cod-liver, petroleum, castor, cotton-seed, and linseed oils. Experiments have been made on the distribution of thymol between water and each of these oils. The results indicate that for the purpose of studying the distribution of drugs at the temperature of the body, olive oil is fairly representative and its selection for the purpose is justifiable.

E. G.

**Hydrolysis of Iodine.** EMIL ABEL (*Festschrift W. Nernst*, 1912, 1—26).—The hydrolytic equilibrium represented by  $3\text{I}_2 + 3\text{H}_2\text{O} \rightleftharpoons 6\text{H}^+ + 5\text{I}^- + \text{IO}_3^-$  has been investigated in aqueous solutions containing varying amounts of sodium acetate. The hydrolysis takes place very slowly at the ordinary temperature, and equilibrium is not attained until after the lapse of several months. The progress of the change was followed by titrating portions of the solution with sodium thio-sulphate, the end point being determined both before and after the addition of acid. The difference between the two readings affords a measure of the iodate produced by the hydrolysis.

The results obtained indicate that at 18° the equilibrium constant  $K = [\text{H}^+]^6 [\text{I}^-]^5 [\text{IO}_3^-] / [\text{I}_2]^3$  is equal to  $0.38 \times 10^{-48}$ .

From the data, the true solubility of iodine in sodium acetate solutions may be calculated. The numbers show that the solubility is diminished in presence of the acetate, the relative lowering of the solubility per gram-equivalent of sodium acetate being equal to 13.7%.

The observations are also considered in reference to the kinetics of the hydrolysis. Under the conditions of the experiments as carried out by the author, the solutions being saturated with iodine and containing relatively large quantities of sodium acetate, the rate at which iodate is formed is found to be inversely proportional to the square of the iodate concentration. The reaction is therefore auto-catalytic in type.

H. M. D.

**Action of Iodine on Hydrogen Selenide.** LUIGI ROLLA and ANGELO REPETTO (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 463—468).—The paper gives a detailed account of the experimental methods employed, and of the numerical results obtained in connexion with the determination of the equilibrium constant of the reaction  $\text{H}_2\text{Se} + \text{I}_2 = 2\text{HI} + \text{Se}$  recently employed to calculate the heat of formation of hydrogen selenide (compare this vol., ii, 1040). R. V. S

**The Velocity Coefficient of the Chemical Formation of Chlorate Determined by Electrolysis.** ERICH MÜLLER and OTTO MÜLLER (*Festschrift W. Nernst*, 1912, 319—326).—It is shown that the velocity coefficient, which determines the rate of formation of chlorate from hypochlorite, can be ascertained from observations on the rate at which chlorate is formed in the electrolysis of sodium chloride solutions to which varying amounts of acid are added. When the steady state is reached after prolonged electrolysis of sodium chloride solutions, the current yield of chlorate amounts to 66·6% if cathodic reduction is eliminated, and the velocity coefficient of chlorate formation is given by the equation:  $k = i(A - 66\cdot6)/v \times 66\cdot6 \times 96540 \times [\text{HClO}]^2[\text{ClO}']$ , in which  $i$  is the current strength,  $v$  the volume of the solution,  $A$  the yield of chlorate, and  $[\text{HClO}]$  and  $[\text{ClO}']$  the concentration of hypochlorous acid and sodium chlorite respectively.

In different experiments, the ratio  $i/v$  was varied, but this has comparatively little influence on the calculated value of  $k$ .

For a given concentration of hypochlorite, the yield of chlorate varies according to whether the solution is stirred or not; this is probably due to local variations of the hypochlorite concentration in the unstirred solutions. H. M. D.

**Ester Formation in Methyl Alcohol.** HEINRICH GOLDSCHMIDT and ARTHUR THUSEN (*Zeitsch. physikal. Chem.*, 1912, 81, 30—67. Compare Abstr., 1910, ii, 283).—The following acids are used: phenyl-acetic, acetic, propionic, *n*- and *iso*-butyric, *isovaleric*, heptonic, lauric, and benzoic, and as catalysts hydrochloric, picric, and trichlorobutyric acids. The influence of salts of these acids on the rate of reaction was also observed. The earlier results were vitiated owing to the presence of traces of ammonia in the methyl alcohol, originating from the occurrence of a little nitride in the calcium used for dehydration.

The electrical conductivity of solutions of hydrogen chloride, picric acid, and trichlorobutyric acid in methyl alcohol and the effect of small amounts of water on the conductivity have been observed. The addition of water diminishes the conductivity of solutions of hydrogen chloride in methyl alcohol, a result ascribed to the establishment of the equilibrium  $\text{CH}_3\text{OH}_2\text{H}^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{OH}^+$  and the small velocity of the ion  $\text{H}_2\text{O}_2\text{H}^+$  in methyl alcohol solution. The addition of water raises the conductivity of solutions of picric acid and of trichlorobutyric acid in methyl alcohol. The conductivity of aniline salts of the three acids used as catalysts have also been measured in methyl alcohol, and it is shown that more or less "alcohololysis" occurs depending on the strength of the acids.

The main results of the discussion of the kinetic data, which are

given in detail, is that the catalytic effect is not proportional to the  $H^+$  ion concentration of the catalyst, but is exerted in two ways: (1) by means of the  $H^+$  ions; (2) by the non-ionised portion. When the partial velocity due to the  $H^+$  ions is known for one acid, it can be calculated for any other acid the dissociation constant of which is known. The effect due to the non-ionised acid cannot be predicted; all that is known is that it is greater for highly ionised than for slightly ionised catalysts. In methyl alcohol solution, as in ethyl alcohol, the retarding influence of water on esterification is much the same in magnitude for different acids, which supports the view that an intermediate compound of alcohol and catalyst plays the most important part in the change.

G. S.

**Heterogeneous Reactions.** HARRY HEYMANN (*Zeitsch. physikal. Chem.*, 1912, 81, 204—222).—The author shows mathematically, on the basis of Nernst's theory of heterogeneous reactions (Abstr., 1904, ii, 315), that when the velocity of reaction is conditioned by diffusion, and when the velocity of reaction is very rapid in comparison with the diffusion,  $k' = D/\delta$ , in which  $k'$  is the reaction constant,  $D$  the coefficient of diffusion, and  $\delta$  the thickness of the diffusion layer, that is, the layer in which the reaction occurs. Experiments are described on the catalytic decomposition of hydrogen peroxide by platinum and the solution of copper in a potassium iodide solution of iodine, in which the three values  $k'$ ,  $D$ , and  $\delta$  are determined. The values of  $k'$  were obtained by rotating cylinders of platinum and copper respectively in solutions of hydrogen peroxide and iodine in potassium iodide, and titrating the solutions at known intervals of time. The value of  $\delta$  was determined by measuring the residual current by the method of Nernst and Merriam (Abstr., 1905, ii, 674). The value of  $D$  was directly determined by Ostwald and Luther's method. The results in general confirm Nernst's theory of heterogeneous reactions, although a disagreement of 20% is found in some of the results for the solution of copper; this is attributed by the author to the existence of complexes in the potassium iodide solution, which influence the rate of diffusion.

J. F. S.

**Velocity of Decomposition of Ammonia in Quartz Glass.** MAX BODENSTEIN and FRANZ KRANENDIECK (*Festschrift W. Nernst*, 1912, 99—117. Compare Perman and Atkinson, *Proc. Roy. Soc.*, 1904, 74, 110).—The rate of decomposition of ammonia contained in a quartz vessel has been measured at 780° and 880°, the volume being kept constant and the progress of the change followed by determination of the increase in pressure.

At these temperatures the quartz is permeable to hydrogen, and a correction has therefore to be applied to the pressure readings in order to allow for the hydrogen which escapes from the reaction vessel. The rate at which the hydrogen passes through the quartz is proportional to the partial pressure of the hydrogen. It increases very slowly with the temperature, the velocity coefficient,

$$k = 1/t \log a/(a-x),$$

being doubled when the temperature is raised from 730° to 880°. The

volume of hydrogen which passes through a quartz plate, one millimetre thick, amounts to  $8.65 \times 10^{-6}$  c.c. ( $0^\circ$  and 760 mm.) per square cm. per hour when the temperature is  $880^\circ$ . It is probable that the action is due to the porosity of the quartz and not to the formation of a solid solution.

From the data obtained in the observations on the decomposition of ammonia, it is evident that the reaction is a surface reaction and of somewhat complicated character. The values obtained for the unimolecular velocity-coefficient fall very considerably during the progress of the change, whilst the bimolecular coefficient exhibits gradually increasing values. Measurements of the initial velocity at different pressures show that this is proportional to the square root of the ammonia concentration. When the products of decomposition are separately added to the ammonia, the velocity of the change is unaffected, but when both nitrogen and hydrogen are present at the outset, the speed of the reaction is appreciably less. The retarding influence of the products of decomposition varies largely with the temperature, and in consequence of this, the velocity of the reaction, which is practically independent of the temperature in the absence of the reaction products, increases with temperature to an increasing extent as the products of decomposition accumulate.

From the analysis of these observations, the conclusion is drawn that the decomposition of the ammonia takes place in the pores of the quartz glass, and that the velocity of the change is determined by the rate at which the ammonia diffuses into the pores. The actual decomposition probably occurs very rapidly, but the speed of the chemical reaction is determined to some extent by the velocity with which the products of decomposition escape from the pores in the quartz into the space occupied by the gas.

H. M. D.

Valency and the Evolution of the Elements. M. D'A. ALBUQUERQUE (*Chem. News*, 1912, 106, 202—203).—Various lines of evidence support the view that evolution is the clue to the chemistry of the future.

G. S.

The Nature of Atomic Weight. MASAO KATAYAMA (*Sci. Rep. Tôhoku Imp. Univ.*, 1912, i, 171—200).—On the assumption that an atom consists of a positively charged nucleus with which are associated a number of electrons, and that the mechanical and electromagnetic masses of the nucleus are distributed in such a manner that there is no tendency due to the electrical force to change the distribution, a general expression is obtained from which the total mass of the positive nucleus can be calculated. The numbers calculated from the equation are in fairly good agreement with the series of atomic weights, as is shown by a comparison of the values of the fifty-four elements between lithium and lanthanum. The greatest differences are found in the case of elements, the positions of which in the periodic table may be regarded as abnormal.

The theory indicates that there must be an upper limit to the dimensions of the atomic nucleus. If this limit be supposed to correspond with the atomic weight 252, the electromagnetic mass is

then found to agree with the value found experimentally for the electron.

The relation between the radii of the atom and of the atomic nucleus is discussed in reference to the existence of periodicity and to the difference in the behaviour of elements of low as compared with those of high atomic weight.

H. M. D.

**Reactivity of Atomic Groups containing Sulphur.** ARTHUR KÖTZ (*Festschrift. W. Nernst*, 1912, 227—233).—The influence of different groups on the reactivity of a compound is supposed to be due to their varying content of free energy, which will affect the mobility of neighbouring atoms and so give rise to variations in reactivity. From this point of view the author discusses the influence of various groups containing sulphur on the reactivity of neighbouring hydrogen atoms.

H. M. D.

**Reform of Chemical and Physical Calculations.** C. J. T. HANSEN (*Chem. News*, 1912, 106, 215).—In the author's opinion, chemical and physical calculations could be simplified by adopting  $41^{\circ}10'$  northern latitude as the "international circle of gravity" and by taking the atomic weights of the elements as whole numbers.

G. S.

**The Second Virial Coefficient for Diatomic Gases.** W. H. KESOM (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 417—431).—From a consideration of the compressibility data, it is shown that the behaviour of hydrogen at temperatures between  $-100^{\circ}$  and  $100^{\circ}$  is in agreement with Reinganum's hypothesis that the molecules consist of rigid spheres, each having an electric doublet of constant moment at its centre.

As the temperature falls below  $-100^{\circ}$ , the behaviour of the gas deviates in gradually increasing measure from the requirements of this hypothesis, and between  $-180^{\circ}$  and  $-230^{\circ}$  it behaves exactly like a monatomic substance. The variation of the viscosity of hydrogen with the temperature also affords evidence of this change in character.

In so far as the second virial coefficient is concerned, the behaviour of oxygen between  $0^{\circ}$  and  $200^{\circ}$  is also found to correspond with that of a system of rigid spheres with a centralised electrical doublet, whilst nitrogen, within the same limits of temperatures, deviates considerably from the behaviour of such a system.

H. M. D.

**Exact Form of the Law of Molecular Attraction.** RICHARD D. KLEEMAN (*Proc. Camb. Phil. Soc.*, 1912, 16, 658—666. Compare *Abstr.*, 1910, ii, 492 ; 1911, ii, 34).—The form of the function ( $\phi$ ) in the author's expression for the law of molecular attraction has been investigated more closely. According to experiments on the Joule-Thomson effect, the function ( $\phi$ ) must consist of a number of positive and negative terms, and since the attraction between two molecules changes to repulsion when they are separated by a sufficiently large distance, the principal negative term which expresses this repulsion must contain an inverse power of the distance of separation of the

molecules which is less than the fifth. Since it has also been shown that the attraction changes to repulsion for distances of separation of the order of the molecular diameter, there must be a term consisting of an inverse power greater than the fifth. Assuming that these powers are the fourth and sixth respectively, a new expression is obtained for the law of attraction. From this, formulæ are obtained for the intrinsic pressure and for the energy required to separate the molecules by an infinite distance from one another.

By reference to data for ethyl ether, the distances of separation of the molecules at which the force between them changes sign are calculated, and it is then found that, the higher the temperature, the smaller is the distance over which two molecules attract one another.

The equations are also applied in the calculation of the average velocity of a molecule, from which it appears that the average velocity of a molecule in a liquid in the critical condition is about 2.5 times the average velocity in the gaseous state. H. M. D.

**Application of Curves of Neutralising Force to the Determination of the Molecular Magnitudes and Dissociation Constants of Chemical Compounds in General and Proteins in Particular.** E. D'AGOSTINO and G. QUAGLIARIELLO (*Festschrift W. Nernst*, 1912, 27—45).—A method of determining the molecular weights and dissociation constants of weak electrolytes is described.

If the molecular quantity ( $y$ ) of a strong univalent acid or base, added to a litre of a solution containing  $P$  grams of the weak electrolyte (molecular weight  $=p$ ) under investigation, is plotted as a function of the logarithm of the hydrogen ion concentration  $[H^+]$  corresponding with each stage in the process of the addition of the strong acid or base, curves are obtained which exhibit characteristic points of inflexion. If  $y_1, y_2, y_3, \dots$  are values of  $y$  corresponding with such points, at which the tangent to the curve is horizontal, then  $y_2 - y_1 = y_3 - y_2 = y_4 - y_3 = \dots = m$ , where  $m$  is the normality of the solution. The molecular weight of the dissolved substance is then given by  $p = P/m$ .

If the acid dissociation constant is  $k_a$ , then it can be shown that  $\log k_a = \log [H^+] - \log (m - y)/y$ , and this equation may be employed for the determination of  $k_a$  when the corresponding values of  $y$  and  $[H^+]$  have been ascertained by experiment. The basic dissociation constant  $k_b$  can be obtained similarly, and the method is readily applicable to amphoteric electrolytes.

For glycine, the experimental data lead to  $k_a = 0.13 \times 10^{-9}$  and  $k_b = 0.22 \times 10^{-11}$ , which are in agreement with the values obtained by other methods. Measurements on serum-albumin gave  $k_a = 0.91 \times 10^{-9}$  and  $k_b = 0.14 \times 10^{-7}$ , whilst the value of  $\log [H^+]$  for the pure substance was found to be  $-7.56$ . H. M. D.

**The Interaction of Gaseous Molecules.** STANLEY SMITH (*Chem. News*, 1912, 105, 193).—If a mixture of gases be taken such that there is an excess of one gas above the amount required for the formation of a particular compound, this excess will be left after combination has taken place. The author then puts forward the question: What is it that determines which molecules of the gas in excess enter into com-

bination, and which are left unchanged at the end of the reaction? As an answer to this, it is suggested that the molecules which are moving with the greater velocity will be those which enter into combination, whilst the molecules which are moving with the less velocity are left. It would follow (according to the author) that the resulting residue should possess a lower temperature than would be anticipated, since the temperature of a gas depends on the mean velocity of its molecules.

The author suggests experiments by means of which the above ideas could possibly be tested, although it is probable that the differences in temperature to be recorded would be very small.

T. S. P.

**Method for Determining the Molecular Weights of Volatile Liquids.** CHARLES W. PORTER (*J. Amer. Chem. Soc.*, 1912, 34, 1290—1293).—The determination of molecular weights by vapour density methods depends on the gas law which may be written in the form of the equation:  $M = WRT/PV$ , in which  $R$  is a constant and  $W$ ,  $T$ ,  $P$ , and  $V$  are variables. Any three of these variables being known,  $M$  can be calculated from a measurement of the fourth. In the usual methods, either  $V$ ,  $P$ , or  $W$  is the variable measured. A method is now described in which  $P$ ,  $V$ , and  $W$  are fixed, and  $T$  is determined by direct measurement.

A glass bulb, of about 300 c.c. capacity, with a tube of small bore at each end, is immersed in a bath of glycerol and water, which is heated by passing an electric current through coils of nichrome wire. The lower tube from the bulb passes through a stopper in a hole in the side of the jar, near the bottom, and is connected with a mercury reservoir. The upper tube is attached to a short tube of capillary bore which is sealed by a solid glass plug and rubber connexion. The bulb is filled with mercury by means of pressure applied to the mouth of the mercury reservoir with an air-pump. Before the mercury reaches the top of the upper tube of the bulb, a small glass bulb containing a weighed quantity of the liquid to be investigated is dropped on to the surface of the mercury so that the long capillary end of the tube is directed upwards. The tube of capillary bore is then placed in position and held by a heavy rubber tube, securely wired. Pressure is then applied until a drop of mercury appears at the top of the tube of capillary bore. The glass plug is inserted and the rubber connexion wired. The end of the bulb containing the liquid has now been forced into the capillary bore of the upper tube. By slightly bending the connexion between the tube of capillary bore and the upper tube of the bulb, the end of the small bulb is broken, and the vapour of the liquid is free to escape. The bath is then heated and stirred vigorously until the level of the mercury in the bulb is a little below that in the reservoir. The system is allowed to cool slowly, and the temperature read when the level is the same in each vessel. When the rising and falling column of mercury reaches the level at a temperature which is constant within  $0.5^\circ$ , the temperature is recorded. The volume of the bulb must be corrected for the temperature attained and the vapour pressure of mercury at that temperature must be subtracted from the barometric pressure before the calculation is made.

Experiments are recorded in which this method was applied to the determination of the molecular weight of acetone, ether, benzene, and toluene.

The author does not claim that this method is superior to Victor Meyer's, but states that it is as convenient as most of the vapour density methods employed, and yields equally accurate results. Moreover, it completes the possibilities for molecular weight determinations based on the gas law.

E. G.

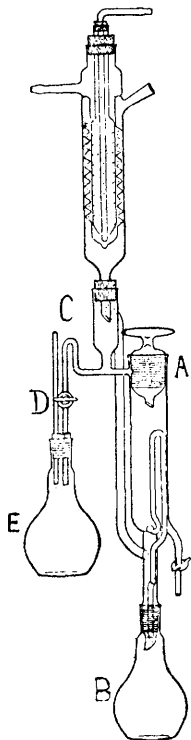
**Laboratory Apparatus of Coloured Glass for Working with Substances Sensitive to Light.** HEINRICH GÖCKEL (*Zeitsch. angew. Chem.*, 1912, 25, 2303).—A claim for priority in the manufacture and use of laboratory apparatus of coloured (brown) glass over Friedrichs (this vol., ii, 933).

T. S. P.

**Electrically-heated Microscope Slide.** F. G. COTTRELL (*J. Amer. Chem. Soc.*, 1912, 34, 1328—1332).—The device described in this paper was designed in connexion with a study of liquid crystals, but is recommended for any case in which a rapid and accurate adjustment of temperature under the microscope is desired. It is particularly useful for studying phenomena of melting and recrystallisation, as any individual crystal may be watched and its melting or crystallisation stopped and held constant, or reversed at will.

Glass slips,  $\frac{1}{2}$ -inch  $\times$  1 inch in size and about 0.6—0.8 mm. thick, are coated with a uniform film of platinum of such tenuity as not seriously to reduce the transparency, but forming a continuous conductor for the electric current. The ends of the slide are gilded or platinised so as to act as terminals for the thinner film between them which serves as the electrical resistance for heating. By connecting the film in series with a suitable rheostat to a convenient source of current, any temperature up to almost the m. p. of the glass can be rapidly established. A full description is given of the method of preparing such slides.

E. G.



**A Modified Soxhlet Extraction Apparatus with Arrangement for Distillation.** FRITZ FRIEDRICH (Zeitsch. angew. Chem., 1912, 25, 2208—2209).—The apparatus is shown in the annexed diagram. When being used for extraction purposes only, the stopper *A* is turned so as to connect the condenser with the Soxhlet tube; the tap *D* is closed. When used for

distillation, *A* is turned to cut off the condenser from the upper part of the Soxhlet apparatus, and *D* is opened; the condensed liquid then syphons over into *E*.

T. S. P.

**Modified Soxhlet Extraction Apparatus.** H. SCHMID (*Chem. Zeit.*, 1912, 36, 1249).—A three-way tap is placed on the stem of an ordinary Soxhlet apparatus immediately below the junction of the stem with the wider portion. While the extraction is proceeding, the tap is turned so as to cut off the connexion between the stem and the wide portion, and the apparatus operates in the usual way. The tap may then be turned so that the solvent runs off through a side-tube. The apparatus may also be used for fractional extractions.

W. P. S.

**Some New Forms of Laboratory Apparatus.** FRITZ FRIEDRICHS (*J. Amer. Chem. Soc.*, 1912, 34, 1509—1514. Compare *Abstr.*, 1911, ii, 268; this vol., ii, 37, 933).—Descriptions are given of (1) a gas-washing bottle with circulating device, (2) a modified Soxhlet extraction apparatus with accessory distilling apparatus, (3) a modified Schiff nitrometer, (4) a yellow glass phosphorus pipette, and (5) a telescope burner.

The modified Schiff nitrometer consists essentially of a gas burette connected by a two-way stopcock with an absorption vessel provided with a glass screw or spiral similar to that employed in Ferry's nitrometer (this vol., ii, 486). The gas enters the absorption vessel through a mercury seal, passes up the glass screw, and collects in the upper part of the vessel which has the form of a bulb. When absorption is complete, the gas is allowed to enter the burette by means of the stopcock and is then measured. The advantage of this form of apparatus is that the gas can be measured over water instead of over the absorbent.

E. G.

**A Safety Siphon.** MARY L. FOSSLER (*J. Amer. Chem. Soc.*, 1912, 34, 1398—1399).—The following apparatus has been devised in order to provide a neat and convenient method for handling and distributing solutions in the laboratory.

The bottle is fitted with an ordinary siphon tube supported by a rack attached to the shelf on which the bottle stands. A rubber connexion with pinchcock is placed on the siphon tube well above the level of the liquid in the bottle. To the lower end of the siphon tube is attached a graduated wide glass cylinder, which ends in a narrow tube carrying a rubber joint and pinchcock. The liquid is first drawn over into the cylinder by opening the upper pinchcock, and, after this has been closed, the lower one is opened and the liquid thus withdrawn from the cylinder.

In another form of apparatus, the graduated cylinder is replaced by an ordinary burette, which is slipped up over the siphon tube and held in position by a piece of rubber tubing. A small hole blown in the side of the burette near the top allows air to enter as the liquid is withdrawn.

E. G.

**Laboratory Hints.** F. A. STEENSMA (*Chem. Weekblad*, 1912, 9, 894—896).—The author describes a simple form of thermometer holder, a method of cataloguing chemicals by number, and a mode of loosening glass stoppers by allowing ether to soak in, and then warm water.

A. J. W.

[Lecture Experiment.] Apparatus to Study the Diffusion of Chlorine Gas. W. R. FORBES (*Chem. News*, 1912, 105, 193).—A jar containing chlorine is inverted over a jar of nitrogen. In the lower jar a small wooden stand is placed containing a row of glass tubes of gradually decreasing height, each of the tubes being filled with a solution of starch and potassium iodide. As the chlorine diffuses it gradually liberates iodine in the series of tubes, giving rise to the usual blue coloration. In this way the diffusion of chlorine can be demonstrated to a large audience.

T. S. P.

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### Inorganic Chemistry.

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**Chemically Active Modification of Hydrogen.** IRVING LANGMUIR (*J. Amer. Chem. Soc.*, 1912, 34, 1310—1325).—In a tungsten lamp, the vacuum gradually improves during use; the removal of the gas in the bulb depends largely on the voltage across the terminals of the filament as well as on its temperature. A study has been made of the behaviour of several gases under these conditions, and some of the results are now recorded.

When a tungsten wire is heated at 1300—2500° K. in hydrogen under a pressure of 0·001—0·020 mm., the hydrogen slowly disappears. If nitrogen or carbon monoxide is used, the gas does not disappear below about 2200° K.; in these cases, the phenomenon seems to be an electrical effect, whilst with hydrogen it appears to be purely thermal. There is a distinct fatigue effect, but the substitution of a new section of wire does not restore the action. The hydrogen is not absorbed by the wire, but is deposited on the glass, especially if the latter is cooled by liquid air. On allowing the wire to cool and then removing the liquid air, hydrogen is liberated, and does not re-condense if the liquid air is replaced. If the hydrogen is now pumped out and oxygen admitted, the oxygen will disappear and be replaced by a small quantity of hydrogen. These effects are much more marked with platinum, and especially with palladium wires, and are not due to the presence of finely divided metal on the surface of the glass. If phosphorus is present on the bulb and hydrogen is introduced and the wire heated, the hydrogen disappears and hydrogen phosphide is produced; this seems to be the first time that hydrogen phosphide has been directly synthesised.

In order to explain these effects, it is suggested that the hydrogen dissolves in the wire in the atomic condition, and that some of the atoms, leaving the wire, diffuse into the tube cooled by liquid air, or become adsorbed by the glass, and remain in the atomic condition, thus retaining their chemical activity. E. G.

**A Cause of Explosion of Tubes Containing a Compressed Mixture of Air and Hydrogen.** LELARGE (*Compt. rend.*, 1912, 155, 914—916).—An enquiry into the cause of the explosion of a tube filled

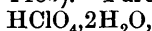
with compressed hydrogen during measurement of its density and pressure, and a description of a means of avoiding its recurrence. The author ascribes the ignition of the air-hydrogen mixture in the cylinder to the rapid compression of air in the manometer tube, and finds that this can be avoided by interposing disks of wire-gauze having sufficient heat capacity, so as not to become heated during the combustion of the mixture in the manometer tube.

W. G.

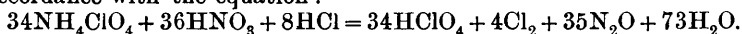
[Hydrogen Peroxide.] FRANZ RICHARZ (*Zeitsch. anorg. Chem.*, 1912, 78, 269—272).—Polemical. A reply to K. Bornemann (compare this vol., ii, 1050).

C. H. D.

**Preparation of Perchloric Acid.** HOBART H. WILLARD (*J. Amer. Chem. Soc.*, 1912, 34, 1480—1485).—Pure perchloric acid,



can be prepared by the following method. In a two-litre flask are placed 500 grams of ammonium perchlorate, 600 c.c. of water, and 410 grams of 68—70% nitric acid. The mixture is heated until it boils, and 105 grams of 37% hydrochloric acid, diluted to 400—500 c.c., are then introduced by means of a long-stemmed dropping funnel. The acid is added rapidly at first, and then more slowly, the whole being added in about twenty-five minutes. Vigorous boiling is continued throughout the operation. Water is added to replace that lost by boiling, the volume being kept nearly constant for about an hour. The solution is then rapidly concentrated by boiling until fumes of perchloric acid appear. When the acid fumes copiously, its composition is nearly that of the dihydrate. The acid is now distilled under 200 mm. pressure. The acid is obtained in theoretical yield in accordance with the equation:



The method is simple, rapid, and economical.

Attention is drawn to some of the principal properties of the acid. It is stated that it yields an excellent standard solution for use in acidimetry, especially for cases in which a non-volatile acid is required and sulphuric acid is unsuitable; it may be added to ferric chloride solutions, instead of sulphuric acid, to ensure the complete removal of chloride by evaporation, and may be employed as a substitute for sulphuric acid in permanganate titrations.

E. G.

**Atomic Weight of Bromine.** H. C. P. WEBER (*J. Amer. Chem. Soc.*, 1912, 34, 1294—1310).—The accepted value for the atomic weight of bromine depends almost entirely on that of silver. Since the atomic weight of chlorine has been satisfactorily determined by the direct comparison of chlorine and hydrogen (Dixon and Edgar, *Abstr.*, 1905, ii, 696; Noyes and Weber, 1908, ii, 371), the method employed by Noyes and Weber has now been applied to the determination of the ratio between hydrogen and bromine.

Experiments have been carried out in which hydrogen bromide was prepared by the direct union of the elements, the hydrogen being weighed absorbed in palladium and the bromine in the form of potassium platinitobromide. The hydrogen was passed over the heated

potassium salt, and the hydrogen bromide was collected and weighed. The methods of preparing and purifying the materials and the precautions observed in carrying out the experiments are described in detail.

In ten experiments, a total weight of 9.00369 grams of hydrogen was combined with 714.05722 grams of bromine and yielded 723.05828 grams of hydrogen bromide. From these figures, the ratio  $H:Br = 79.3067 \pm 0.0022$ , and the ratio  $H:HBr = 80.3064 \pm 0.0018$ . By combining these results, a final value,  $H:Br = 79.3066 \pm 0.0014$ , is obtained. The value for the atomic weight of bromine on the oxygen basis becomes 79.924 ( $H = 1.0079$ ) as compared with 79.920 adopted by the International Committee on Atomic Weights for 1912.

E. G.

**Apparatus for Working with Ozone and for its Quantitative Estimation.** HUGO BRACH (*Chem. Zeit.*, 1912, 36, 1325—1327).—A full description of the apparatus used by the author when working with ozone. The details can be understood only by reference to the original paper.

T. S. P.

**Solubility of Ozone in Dilute Sulphuric Acid.** VICTOR ROTHMUND (*Festschrift W. Nernst*, 1912, 391—394).—The widely divergent numbers obtained by different experimenters for the solubility of ozone in water are due to the rapidity with which the gas is decomposed in aqueous solution. In presence of sulphuric acid, the rate of decomposition is much smaller, and experiments with 0.1*N* acid at 0° have given concordant values. The mean value of the absorption coefficient is 0.487 and since this, which expresses the ratio of the concentrations in the gas and solution, is independent of the absolute concentration, it follows that the molecular weight of the dissolved ozone is the same as that of the gas. When the above value is corrected for the salting-out action of the sulphuric acid, the absorption coefficient in water at 0° is found to be 0.494.

H. M. D.

**Application of the Theory of Allotropy to the System Sulphur.** ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 369—371. Compare Abstr., 1910, ii, 400; this vol., ii, 40).—The diagrammatic representation of the relations between the different forms of sulphur is modified so as to include nacreous sulphur, the melting-point line of which has been determined recently. This is effected by assuming a discontinuity in the monoclinic mixed crystals in the pseudo-binary system  $S_r - S_m$  and  $S_m - S_\alpha$  above the eutectic point.

H. M. D.

**Some Physical Constants of Sulphur Trioxide: Melting and Boiling Points, Density, Coefficient of Expansion, and Molecular Weights.** DAVID M. LICHTY (*J. Amer. Chem. Soc.*, 1912, 34, 1440—1448).—Sulphur trioxide is known to exist in two forms: the  $\alpha$ -form which has a definite m. p., and the  $\beta$ -form which volatilises without melting. The following constants have been determined with material of an exceptional degree of purity: m. p. 16.79°, b. p. about

44.88°/760 mm.,  $D^{11.8}$  1.9457,  $D^{15}$  1.9422,  $D^{20}$  1.9229,  $D^{25}$  1.9020,  $D^{30}$  1.8798,  $D^{35}$  1.8569,  $D^{40}$  1.8324,  $D^{48}$  1.7921. The coefficient of expansion was determined for several intervals of temperature between 11.8° and 45°; it was found to be 0.002005 at 15—20°, and 0.002671 at 35—40°. A slow attainment of constancy of volume at a fixed temperature, such as was observed by Schenck at 35.3° in the case of the  $\alpha$ -trioxide (Abstr., 1901, ii, 380), was not perceived at any point between 11.8° and 45°. The molecular weight of both  $\alpha$  and  $\beta$ -forms was determined cryoscopically with phosphoryl chloride as solvent, and found to be 80 in each case (compare Oddo, Abstr., 1901, ii, 650).

E. G.

**The Preparation of Hydrogen Selenide and Telluride.** WALTER HEMPEL and MAX GUSTAV WEBER (*Zeitsch. anorg. Chem.*, 1912, 77, 48—50).—Hydrogen selenide is best obtained in a pure condition from hydrogen and selenium at 350°, the product being freed from hydrogen by cooling with liquid air. Hydrogen telluride cannot be prepared by direct combination.

For the preparation of hydrogen telluride by electrolysis, a tube bent twice at right angles is used, into one limb of which a narrow glass tube is fixed containing the tellurium cathode. The electrolyte is 50% sulphuric acid, and the tube is cooled externally by solid carbon dioxide and alcohol. The apparatus must be protected from light.

C. H. D.

**Synthesis of Ammonia from the Elements.** JEAN BILLITER (*Festschrift W. Nernst*, 1912, 86—89).—When commercial cerium fluoride is heated strongly with magnesium in the ratio 4 : 1, a product is obtained which is found to accelerate the combination of nitrogen and hydrogen to a very marked extent. If a dry mixture of the two gases is passed over the finely powdered contact substance at the ordinary temperature, ammonia is formed, but the action soon comes to an end. If the temperature is raised, ammonia is again formed, but the activity of the contact substance disappears in the same way at 300° as at the ordinary temperature. By exposure of the contact substance to the air, its activity is temporarily restored.

From experiments with moist and carefully dried gases, and observations relating to the influence of dry and moist air and carbon dioxide on the activity of the contact mass, it appears that the catalytic effect is conditioned by the presence of hydrogen, air, and water vapour, and that the progress of the change is accompanied by the oxidation of the active solid substance.

H. M. D.

**Two-Component System Water-Arsenic Pentoxide.** ALAN W. C. MENZIES and PAUL D. POTTER (*J. Amer. Chem. Soc.*, 1912, 34, 1452—1470).—From time to time various hydrated forms of arsenic pentoxide have been described. Owing to the lack of agreement in the formulæ and properties ascribed to these hydrates, the present work was undertaken.

The results show that only two of these hydrates can be isolated,

namely:  $\text{As}_2\text{O}_5, 4\text{H}_2\text{O}$ , m. p.  $36.14^\circ \pm 0.05$ , and  $3\text{As}_2\text{O}_5, 5\text{H}_2\text{O}$ . The former was prepared by dissolving commercial arsenic acid in water and concentrating the solution until it had b. p.  $150^\circ$ ; after cooling, a small portion of the solution was caused to crystallise by inoculation with phosphoric acid hydrate,  $\text{P}_2\text{O}_5, 4\text{H}_2\text{O}$ , and the crystals so obtained were used to inoculate the remainder of the solution. When this hydrate is left in the superfused state, a hard, white, crystalline scale is produced, consisting of the hydrate,  $3\text{As}_2\text{O}_5, 5\text{H}_2\text{O}$ , which can be prepared satisfactorily by evaporating a solution of arsenic acid to dryness at  $100^\circ$ . The solubilities of these two hydrates have been determined, and are represented by means of curves. The curve of depression of the f. p. of water by arsenic acid has also been constructed. A supersaturated solution of the hydrate,  $3\text{As}_2\text{O}_5, 5\text{H}_2\text{O}$ , at  $9.2^\circ$  was well inoculated with crystals and stirred continuously; supersaturation was not entirely removed until after twenty-seven days. Arsenic pentoxide retains a small quantity of water at high temperatures, and it has been found that its removal can be best and most rapidly effected by heating it in a current of air containing water-vapour.

During the course of this work, the following method was devised for estimating arsenic acid. Arsenic acid is taken in sufficient quantity to require, as a dibasic acid, 30—40 c.c. of *N*-alkali. Saturated barium chloride solution (15 c.c.) is added, the liquid is diluted to 250 c.c., boiled for fifteen minutes to expel carbon dioxide, and then cooled and titrated with *N*-alkali, phenolphthalein being used as an indicator. As the alkali is added, the solution is stirred until the precipitate formed locally redissolves but slowly. The walls of the vessel are now scratched below the surface of the clear liquid until, on stirring, the solution is lustrous with small crystals; the titration is then completed in the usual way. The method has proved very satisfactory, and gives a sharp end-point.

E. G.

The Compound " $\text{P}_4\text{S}_{10}$ ," as described in the German Patent No. 239162. ALFRED STOCK and KURT FRIEDERICI (*Zeitsch. angew. Chem.*, 1912, 25, 2201—2203).—In the German Patent No. 239162, a phosphorus sulphide,  $\text{P}_4\text{S}_{10}$ , is described, which is said to be different from ordinary phosphorus pentasulphide. It is made by mixing the sulphide  $\text{P}_4\text{S}_8$  (1 mol.) with sulphur (7 atoms), treating the mixture with carbon disulphide, and either evaporating the solution or precipitating it with light petroleum; it is then obtained as yellow cakes, or in the form of hexagonal tablets. Its physical and chemical properties are different from those of the sulphides  $\text{P}_4\text{S}_8$  and ordinary  $\text{P}_4\text{S}_{10}$ .

The authors show that the above substance does not contain any compound  $\text{P}_4\text{S}_{10}$ , but that it is essentially a mixture of the sulphide  $\text{P}_4\text{S}_8$  with sulphur, which behaves approximately as a unitary compound owing to it being a eutectic, the components of which are difficult to separate because of their similar solubility relations.

Solutions of the sulphide  $\text{P}_4\text{S}_8$  absorb oxygen very readily, whilst the dry substance can be exposed to the air for months without undergoing oxidation.

T. S. P.

**Methods for the Production of Alkali Metals by means of Calcium Carbide and Aluminium.** HEINRICH SPECKETER (*Festschrift W. Nernst*, 1912, 424—427).—Three methods for the preparation of sodium and potassium are described. According to the first, the alkali metal fluoride is intimately mixed with the calculated quantity of calcium carbide and heated in a retort to about 900°. The reaction corresponds with  $2\text{KF} + \text{CaC}_2 = 2\text{K} + \text{CaF}_2 + 2\text{C}$ .

In the second, the alkali metal fluoride is heated to a temperature somewhat above its melting point with granulated aluminium, when the alkali is set free according to  $6\text{NaF} + \text{Al} = \text{Na}_3\text{AlF}_6 + 3\text{Na}$ . If powdered aluminium is used, the reaction is very violent.

The third method involves the use of anhydrous alkali metal sulphide, which is intimately mixed with finely powdered calcium carbide and heated to about 850°, when reaction occurs according to  $\text{Na}_2\text{S} + \text{CaC}_2 = 2\text{Na} + \text{CaS} + 2\text{C}$ .

Lithium cannot be obtained by these methods, its volatilisation requiring a much higher temperature. H. M. D.

**The Polyiodides. I. Thermal Investigation of the System KI-I<sub>2</sub>.** ROBERT KREMANN and R. SCHOULZ (*Monatsh.*, 1912, 33, 1081—1086).—The method of investigation was to seal up the mixtures of potassium iodide and iodine in known proportions in a glass vessel containing a re-entrant tube. In this tube a small quantity of mercury was placed and a thermo-element introduced, whereby cooling curves from temperatures as high as 300° could be taken, without loss of iodine by vaporisation. Undercooling takes place to a considerable extent, and it was necessary to measure the period of the eutectic arrest in order to be quite sure of the observations.

Two eutectics occur at respectively 20.5 and 50 molar % of potassium iodide, the corresponding temperatures being 76° and 77°. Between these eutectics the curve rises to an indefinite maximum, from which it is difficult to draw conclusions. The eutectic arrests over this portion of the curve, however, become zero at a point corresponding with the composition  $2\text{KI}, 3\text{I}_2 (= \text{KI}_4)$ , which compound therefore exists, although in a highly dissociated state, in the fusion (compare Abegg and Hamburger, *Abstr.*, 1906, ii, 747). There is no evidence for the existence of a polyiodide poorer in iodine.

These results do not, of course, exclude the existence of other polyiodides in aqueous solution, or in equilibrium with solutions of iodine in benzene. T. S. P.

**Thermal Decomposition of Potassium Permanganate.** PAUL ASKENASY and A. SOLBERG (*Festschrift W. Nernst*, 1912, 53—61. Compare Askenasy and Klonowski, *Abstr.*, 1910, ii, 297).—The evolution of oxygen from potassium permanganate begins to be appreciable at about 215°. When decomposition has commenced, oxygen continues to be evolved quite readily even when the temperature is reduced to below 200°. The analysis of the products of the thermal decomposition agrees with the reaction equation suggested by Rudolf:  $10\text{KMnO}_4 = 3\text{K}_2\text{MnO}_4 + 7\text{MnO}_2 + 2\text{K}_2\text{O} + 6\text{O}_2$  (*Abstr.*, 1901,

ii, 388). According to Rousseau (Abstr., 1887, ii, 552), the manganate, which is originally present in the residue, disappears on prolonged heating, but this result was not confirmed by experiments in which the residue was heated for several hours at about 500°.

From a consideration of the dissociation pressure curve of manganese dioxide (Abstr., 1910, ii, 297), it is improbable that the residue contains free manganese dioxide as represented by the above equation. The dissociation pressure of the residue was found to be 50 mm. at 505°, 129 mm. at 560°, 391 mm. at 594°, and 400 mm. at 600°. From a comparison of the dissociation pressure curves of manganese dioxide and potassium manganate, and of the residue resulting from the thermal decomposition of potassium permanganate, the authors infer that the decomposition should be represented by the equation:  $10\text{KMnO}_4 = 2\text{K}_2\text{MnO}_3 + [3\text{K}_2\text{MnO}_4 + 5\text{MnO}_2] + 6\text{O}_2$ . This equation agrees with the chlorine value of the residue. The reversibility of the reaction in which oxygen is evolved by the heated residue suggests that the entire residue or the bracketed constituents represent a chemical compound. It may be, however, that the manganate and the dioxide form a solid solution in which the manganite is dissolved.

H. M. D.

**Potassium Ammoniotitanate,  $\text{N}:\text{Ti}\cdot\text{NHK}$ .** EDWARD C. FRANKLIN and THOMAS B. HINE (*J. Amer. Chem. Soc.*, 1912, 34, 1497—1501).—Franklin (this vol., ii, 451) has shown that the amides and imides, and the nitrides of the non-metallic elements may be regarded as ammonio-acids and acid ammonides, which may be expected to react with ammonio-bases in liquid ammonia solution to form ammonio-salts in a manner analogous to the action of aqueous potassium hydroxide on the oxides and hydroxides of the non-metallic elements.

In order to test this view, siliconamide was treated with excess of potassamide in liquid ammonia solution, and a product was obtained with a composition roughly approximating to  $\text{N}:\text{Si}\cdot\text{NHK}$ . Since it was thought probable that the ammoniotitanate of potassium might be more easily prepared, experiments were made on the action of potassamide on titanium tetrabromide, or, rather, on an ammoniolytic product of the formula  $\text{N}:\text{Ti}\cdot\text{Br}$ . *Potassium ammoniotitanate,  $\text{N}:\text{Ti}\cdot\text{NHK}$* , was thus obtained in an impure state as a dense, brick-red powder; it is not explosive, but is vigorously hydrolysed by water. The reaction is represented by the equation:  $\text{N}:\text{Ti}\cdot\text{Br} + 2\text{KNH}_2 = \text{N}:\text{Ti}\cdot\text{NHK} + \text{KBr} + \text{NH}_3$ .

E. G.

**Combination of Salts with Hydrogen Peroxide.** Y. P. RUDENKO (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1209—1218).—According to Petrenko (Abstr., 1902, ii, 316), the action of hydrogen peroxide on trisodium and triammonium phosphates yields phosphates in which the metal is partly replaced by the residue,  $\text{NaO}$  (or  $\text{NH}_4\text{O}$ ), of a metallic peroxide. The similar compound obtained from trisodium arsenate is regarded by the same author (Abstr., 1902, ii, 499) as a hydrate of sodium arsenate in which part of the water is replaced by hydrogen peroxide,  $3\text{Na}_3\text{AsO}_4\cdot 5\text{H}_2\text{O}_2\cdot 16\text{H}_2\text{O}$ .

The author has investigated the action of hydrogen peroxide on all

the sodium, potassium, and ammonium salts of nitric, phosphoric, and arsenic acids.

Neither in the cold nor on a boiling water-bath does the action of hydrogen peroxide on the nitrates lead to the assumption of active oxygen by these salts. The compounds prepared by Alvarez (*Chem. News*, 1906, 94, 269) and described by him as  $\text{KNO}_4$ ,  $\text{NaPO}_4$ , and  $\text{NaAsO}_4$ , are shown to have compositions in total disagreement with these formulæ, and to be merely mixtures of the respective normal salts with hydrated sodium peroxide. This result is confirmed by examining these compounds by the method employed by Riesenfeld and Reinhold to distinguish real percarbonates from carbonates with hydrogen peroxide of crystallisation (*Abstr.*, 1910, ii, 33).

Trimetallic phosphates and arsenates decompose hydrogen peroxide at  $100^\circ$ , owing to their alkalinity, but in the cold the sodium and ammonium salts take up active oxygen (compare Petrenko, *loc. cit.*). Of the dimetallic hydrogen salts, disodium hydrogen phosphate combines with 10.2% of active oxygen in the hot, and with 3.2% in the cold, diammonium hydrogen phosphate taking up 5.6% in the cold. The monometallic dihydrogen salts do not unite with active oxygen. Sodium pyrophosphate combines with 11% and sodium metaphosphate with 3% of active oxygen in the hot. None of the potassium phosphates or arsenates seem to be capable of entering into combination with active oxygen.

The results of analysis of a number of the products obtained indicate that they represent the normal salts with hydrogen peroxide of crystallisation.

T. H. P.

**Silver Fluoride and Silver Subfluoride.** LOTHAR WÖHLER (*Zeitsch. anorg. Chem.*, 1912, 78, 239—244).—The statement of Vanino and Sachs (*Abstr.*, 1911, ii, 884), that silver subfluoride is a mixture of silver fluoride, silver, and silver oxide, is denied (compare Guntz, this vol., ii, 941). When the exact experimental conditions are observed, the subfluoride is readily obtained in large, octahedral crystals, which are quite stable when dry, even if exposed to light. For analysis, the compound is decomposed by means of water, the residual silver being weighed, whilst the silver in solution is precipitated by means of hydrazine, re-dissolved, and precipitated as chloride. The fluorine is then estimated in the filtrate as calcium fluoride. The total silver is in complete agreement with the formula  $\text{Ag}_2\text{F}$ , but the insoluble silver is always slightly high and the fluorine low, owing to particles of subfluoride becoming coated with silver during the decomposition.

Hydrated silver fluoride,  $\text{AgF}\cdot\text{H}_2\text{O}$ , has also been obtained in crystals.

C. H. D.

**Natural and Artificial Thioantimonites and Thioarsenites.** FRANS M. JAEGER and H. S. VAN KLOOSTER (*Zeitsch. anorg. Chem.*, 1912, 78, 245—268).—Fused mixtures of antimony and sulphur yield only a single compound,  $\text{Sb}_2\text{S}_3$ , which gives rise to a maximum on the freezing-point curve at  $546^\circ$ . The eutectic points are at  $61.3$  and  $55$  atomic % of sulphur, and at  $530^\circ$  and  $519^\circ$  respectively. Beyond

these limits two liquid layers are formed, at  $530^{\circ}$  for the sulphur end of the series, and at  $615^{\circ}$  for the antimony end. There is no indication of the formation of a compound  $\text{Sb}_2\text{S}_5$ .

Silver sulphide melts at  $842^{\circ}$ , and dissociates readily above that temperature. Mixtures containing from 10 to 30 atomic % of sulphur separate into two liquid layers at  $905^{\circ}$ , and there is a eutectic point at  $806^{\circ}$ . Mixtures containing more sulphur than the compound evolve sulphur very rapidly. There is a transformation point at  $179^{\circ}$  (compare Friedrich and Leroux, *Abstr.*, 1906, ii, 751).

Mixtures of antimony sulphide and silver sulphide give a freezing-point curve with two maxima, corresponding with  $3\text{Ag}_2\text{S}\cdot\text{Sb}_2\text{S}_3$  and  $\text{Ag}_2\text{S}\cdot\text{Sb}_2\text{S}_3$  respectively. The first of these, identical with the mineral pyrargyrite, has m. p.  $483^{\circ}$ . The second maximum corresponds with miargyrite, m. p.  $509^{\circ}$ . Eutectic points occur at 81,  $64\cdot5$ , and  $28\cdot2$  mol. %  $\text{Ag}_2\text{S}$  and  $463^{\circ}$ ,  $455^{\circ}$ , and  $449^{\circ}$  respectively. The minerals bolivianite, stephanite, pyrostilpnite, polybasite, and polyargyrite can only have been formed from solution, as they are not represented in the equilibrium diagram.

Lead sulphide and antimony sulphide give a freezing-point curve which is without a maximum. Two compounds are recognised:  $5\text{PbS}\cdot 4\text{Sb}_2\text{S}_3$ , plagionite, and  $2\text{PbS}\cdot\text{Sb}_2\text{S}_3$ , jamesonite, the breaks on the curve occurring at  $609^{\circ}$  and  $570^{\circ}$  respectively. The latter compound also undergoes a transformation at  $523^{\circ}$ . The eutectic point is at 80 mol. %  $\text{Sb}_2\text{S}_3$  and  $495^{\circ}$ . There is no evidence of the formation of zinenite, warrenite, heteromorphite, semseyite, boulangerite, meneghinite, or geocronite under these conditions.

Silver sulphide and arsenious sulphide give a curve with two maxima, corresponding with  $3\text{Ag}_2\text{S}\cdot\text{As}_2\text{S}_3$ , proustite, m. p.  $490^{\circ}$ , and  $\text{Ag}_2\text{S}\cdot\text{As}_2\text{S}_3$ , m. p.  $417^{\circ}$ , which may be called arsenomiargyrite. The two eutectic points are at  $469^{\circ}$  and  $399^{\circ}$ . A prolongation of the curve indicates that pure arsenious sulphate has m. p. about  $300^{\circ}$ .

Solid solutions are not formed to an appreciable extent in the above cases, but mixtures of pyrargyrite and proustite form an unbroken series of solid solutions, the freezing-point curve having a flat minimum at  $473\cdot5^{\circ}$ .

C. H. D.

[Hydration of Calcium Oxide.] W. A. BURDAKOFF (*J. Russ. Phys. Chem. Soc.*, 1912, 44, 1325—1334).—The author points out that in Chumanoff's investigations on the hydration of calcium oxide (this vol., ii, 349), since only the relative quantities of the phases were changed, one and the same solid phase and one and the same saturated aqueous calcium oxide solution should be obtained in all cases. That other results were obtained, the author regards as due to the presence of small proportions of calcium carbonate in the calcium oxide employed by Chumanoff.

Objections are also advanced against the results of Chumanoff's investigation of the equilibria in the systems  $\text{CaX}_2\text{—MeOH—H}_2\text{O}$  (this vol., ii, 543), and it is shown, both theoretically and experimentally, that hydrated calcium oxide could not be precipitated under the conditions employed by Chumanoff.

T. H. P.

**Formation and Decomposition of Calcium Peroxide.** FRIEDRICH BERGIUS (*Festschrift W. Nernst*, 1912, 68—85).—Experiments have been made to ascertain the conditions under which the reversible change  $2\text{CaO} + \text{O}_2 \rightleftharpoons 2\text{CaO}_2$  occurs. On account of the small reaction velocity the dissociation pressure is not attainable when the peroxide is heated by itself. By the use of an indifferent solvent in which the oxide and peroxide are soluble to some extent, the speed of the change can be increased. For this purpose the eutectic mixture of sodium and potassium hydroxides was employed. The apparatus consisted essentially of a steel chamber, into which the peroxide and the solvent were introduced, the chamber communicating with a manometer and a supply of oxygen at high pressure. In this way the following dissociation pressures were determined: 200°, 93·35; 250°, 101·1; 300°, 107·2; 350°, 124; 400°, 151·9 atmospheres.

From the variation of the dissociation pressure with the temperature, the heat of formation of the peroxide may be calculated. The result obtained is  $2\text{CaO} + \text{O}_2 = 2\text{CaO}_2 + 3300$  cal., which differs widely from the directly observed value of 10,800 cal. given by de Forcrand (Abstr., 1910, ii, 479). If the latter value is substituted in Nernst's formula, the calculated dissociation pressure at 400° is over 1000 atmospheres, and the author draws the conclusion that the directly determined heat change is incorrect.

It is also shown that calcium oxide may be transformed into the peroxide under the conditions indicated by the dissociation pressure data.  
H. M. D.

**Influence of Sodium Chloride on the Composition of Calcareous Waters.** CAMILLE GILLET (*Bull. Soc. chim. Belg.*, 1912, 26, 463—465).—When a calcareous water flows through a stratum containing sodium chloride, reversible reactions take place between the calcium carbonate in solution and the sodium chloride, and calcium carbonate is precipitated. In the absence of dissolved carbon dioxide, practically the whole of the calcium carbonate may be removed from solution. Small quantities of calcium chloride and carbonate, as well as sodium hydrogen carbonate, remain in solution, and the water exhibits an alkaline reaction towards phenolphthalein.  
W. P. S.

**Preparation of Calcium Perborate.** CHEMISCHE WERKE VORM. HEINRICH BYK (D.R.-P. 248683. Compare Abstr., 1906, ii, 448).—Calcium perborate has previously been prepared, but was of uncertain composition (Abstr., 1898, ii, 374); it is now obtained in 90% yield and containing 12·3% of active oxygen by the following procedure: crystalline calcium chloride (11 parts) dissolved in water (10 parts) is treated at 50—60° with sodium perborate (15·4 parts); the product separates in clumps, but is stirred into a homogeneous paste and diluted with 5 parts of water, from which the calcium perborate separates in crystalline form. The mother liquor, which contains 9·5% of active oxygen, can be employed for another experiment if desired.

F. M. G. M.

**Preparation of Barium Nitrate.** AKTIEN-GESELLSCHAFT FÜR CHEMISCHE INDUSTRIE and HANS KÜHNE (D.R.-P. 248524).—The

reaction  $\text{BaSO}_4 + \text{Ca}(\text{NO}_3)_2 \rightleftharpoons \text{Ba}(\text{NO}_3)_2 + \text{CaSO}_4$  is a reversible one, but it is found that by employing an excess of calcium nitrate (2 mols.), fusing the substances together, and then suddenly cooling the heated mass, about 75% of the barium sulphate is converted into barium nitrate, which rapidly crystallises from the excess of calcium nitrate in the solution. F. M. G. M.

**Thermal Analysis of Binary Mixtures of Chlorides of Bivalent Elements. III.** CARLO SANDONNINI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 524—530).—The present paper deals with the systems  $\text{ZnCl}_2$ - $\text{SrCl}_2$ ,  $\text{ZnCl}_2$ - $\text{BaCl}_2$ ,  $\text{ZnCl}_2$ - $\text{HgCl}_2$ , and  $\text{ZnCl}_2$ - $\text{MnCl}_2$ .

Zinc chloride and strontium chloride give at  $476^\circ$  a compound,  $\text{ZnCl}_2\cdot\text{SrCl}_2$ , which decomposes on melting.

Barium chloride and zinc chloride give a compound,  $\text{ZnCl}_2\cdot\text{BaCl}_2$ , its temperature of formation being  $470^\circ$ .

Zinc chloride and mercuric chloride are incompletely miscible in the liquid state; two layers are formed, each of which contains traces of the other substance.

Zinc chloride and manganous chloride give a curve which descends from the m. p. of manganous chloride to that of zinc chloride. The temperature of the eutectic pause coincides with the m. p. of zinc chloride, but decreases with increased amounts of manganous chloride.

R. V. S.

**Some Peculiarities of Metal Wools.** O. OHMANN (*Ber.*, 1912, 45, 2973—2976. Compare this vol., ii, 635).—Besides steel wool, zinc, lead, aluminium, magnesium, copper, silver, phosphor bronze, and brass wools can be obtained.

Zinc wool burns with a brilliant flame when lighted with a bunsen burner, giving a coherent mass of oxide. Under the same conditions, lead wool shows only traces of vaporisation and flame formation. With aluminium wool a layer of oxide is formed which prevents further oxidation. Magnesium wool burns with explosive violence.

T. S. P.

**The Corrosion of Lead by Lime Mortar and the Disinfecting Power of Calcium Hydroxide.** WILHELM VAUBEL (*Zeitsch. angew. Chem.*, 1912, 25, 2300—2301).—Lead is readily corroded by mortar, the corroded places becoming covered with a layer of basic lead carbonate. The author ascribes the corrosive action to the presence of calcium hydroperoxide in the mortar. He finds that when dry calcium hydroxide is exposed to the air for some days, the presence of a peroxide can be detected with starch-iodide. The amount of peroxide present is relatively very small, in one case corresponding with 0.125 gram of active oxygen per 100 grams of calcium hydroxide, but as it is probably readily decomposed and re-formed in a cycle of reactions, its corrosive action may be very great.

The marked disinfecting power of slaked lime is ascribed to the presence of calcium hydroperoxide. T. S. P.

**Ultraphosphates. II. Thermal Investigation of the Glassy Lead Phosphates.** ADOLF V. KROLL (*Zeitsch. anorg. Chem.*, 1912, 77, 1—40).—Lead phosphates containing high proportions of phosphoric oxide form glasses, and the freezing-point cannot be determined by thermal methods. The method adopted is that of measuring the temperature at which a certain viscosity is reached.

A thread of the glassy phosphate is prepared by dipping a platinum needle into the molten mixture and drawing it out, a section of the required diameter being found by drawing through capillary openings of known size. The thread is loaded with a definite weight, and heated by means of a fine platinum spiral until rupture takes place. The heating current also passes through a thin platinum spiral which surrounds a straight Nernst filament, the resistance of which is measured by a bridge method, the compensating resistance in the other arm being a second similar Nernst filament. This gives a sensitive means of measuring the temperature. Absolute measurements are not obtained, but the results of a series of tests with different threads of the same size are strictly comparable, the temperature-composition curve being merely displaced as a whole. The apparatus is very complicated, and many devices are required in order to apply the method, for which reference must be made to the original.

The curve has distinct breaks at compositions corresponding with the two ultraphosphates,  $\text{PbO}, 3\text{P}_2\text{O}_5$  and  $2\text{PbO}, 3\text{P}_2\text{O}_5$ . The metaphosphate does not cause a discontinuity, and the next distinct break is due to the well-known compound  $5\text{PbO}, 3\text{P}_2\text{O}_5$ , whilst the existence of a compound  $4\text{PbO}, 3\text{P}_2\text{O}_5$  is possibly indicated. Corresponding differences in the mechanical properties and tendency to devitrify are observed.

Devitrification only takes place in these glasses at temperatures considerably below the melting point, and the viscosity results are held to justify the view that glasses are not undercooled liquids, but colloidal solids, for which the term "cryosol" is proposed, or colloidal solutions of one amorphous solid in another.

C. H. D.

**The Structure, Recrystallisation, and Strength of Electrolytic Copper.** OTTO FAUST (*Zeitsch. anorg. Chem.*, 1912, 78, 201—212).—The crystallites of electrolytic copper are, in general, parallel with the direction of the current. They are smaller the lower the concentration of copper in the electrolyte and the greater the current density. Numerous small crystallites form at first, but only a few of these continue to grow. High current density leads to the formation of irregular and porous deposits. The process of recrystallisation on annealing is described. The orientation of the crystallites is clearly seen by straining a polished specimen until slip-bands are developed. Using a specimen made up of parallel crystallites, the vectorial properties may be observed by crushing in various directions, and observing the principal directions of the slip-bands (compare Faust and Tammann, *Abstr.*, 1910, ii, 1039). Electrolytic copper behaves like worked copper, developing twinning planes on annealing, the assumption of a stress in the metal being in accordance with the

observation that a film of copper deposited on the bulb of a thermometer exerts a considerable pressure. C. H. D.

**Galvanic Deposition of Copper on Plaster.** A. DUFAY (*Chem News*, 1912, 106, 225).—The plaster cast or object is heated at 50°, then put into a paraffin-bath at 50–60° until no more gas is evolved, removed, and allowed to cool. The surface is coated with a thin layer of photographic collodion free from silver salts, dried, and then coated with graphite. The conductors for the current are then attached, a second coat of graphite put on, and the whole immersed for a few minutes in a 10% solution of aluminium sulphate or alum. The plaster cast is then made the cathode to a copper anode in a solution of copper sulphate containing 5–8% of sulphuric acid; a current density of 1 ampere per sq. dcm. at 3 volts is used; a thin layer of copper is rapidly deposited.

According to the author, two reactions occur: firstly, reduction of the alumina to the metallic state, and secondly, combination of the aluminium and copper. It is suggested that this reaction could be used to prepare alloys of copper and aluminium, and also to determine aluminium by electro-analysis, the aluminium being deposited on the cathode as an alloy containing a known weight of copper. T. S. P.

**Action of Potassamide on Cupric Nitrate in Liquid Ammonia Solution.** Cuprous Imide, Cuprous Nitride, and Potassium Ammoniocuprite. EDWARD C. FRANKLIN (*J. Amer. Chem. Soc.*, 1912, 34, 1501–1507).—Fitzgerald (Abstr., 1907, ii, 546) has found that when a solution of cupric nitrate in liquid ammonia is treated with potassamide, a precipitate is produced which redissolves on addition of excess of potassamide. This suggests the formation of a copper compound related to ammonia in the same way as the alkali zincoxides are to water. The present investigation was undertaken with the object of isolating and studying this compound.

By the action of potassamide on a solution of cupric nitrate in liquid ammonia, an ammoniated cuprous nitride,  $\text{Cu}_3\text{N}, n\text{NH}_3$ , is produced in accordance with the equation:  $3\text{Cu}(\text{NO}_3)_2 + 6\text{KNH}_2 = \text{Cu}_3\text{N}, n\text{NH}_3 + 6\text{KNO}_3 + (4-n)\text{NH}_3 + \text{N}$ . When this substance is left in a vacuum at the ordinary temperature, it is converted into a dark brown cuprous imide,  $\text{Cu}_2\text{NH}$ , which, when heated at 160°, yields a black cuprous nitride,  $\text{Cu}_3\text{N}$ . The ammoniated cuprous nitrides,  $\text{Cu}_3\text{N}, n\text{NH}_3$ , dissolve in liquid ammonia solutions of potassamide to form solutions from which a colourless, crystalline *potassium ammoniocuprite*,  $\text{CuNK}_2, 3\text{NH}_3$ , has been obtained. If this salt is placed in a vacuum at the ordinary temperature it loses 1 mol. of ammonia to form the *salt*,  $\text{CuNK}_2, 2\text{NH}_3$ , which when heated to a higher temperature is converted into the *salt*,  $\text{CuNK}_2, \text{NH}_3$ . E. G.

**Action of Ammonia on Mercurous Bromide and Iodide.** HARIDAS SAHA and KUMUDNATH CHOUDHURI (*Zeitsch. anorg. Chem.*, 1912, 77, 41–47. Compare Abstr., 1910, ii, 712; 1911, ii, 804).—Mercurous bromide and strong ammonia yield a black mass containing free mercury, whilst the evaporated filtrate yields a white compound,

$\text{NH}_2\text{HgBr}, \text{HgO}, 2\text{H}_2\text{O}$ . In the case of mercurous iodide, the filtrate deposits white needles of a compound,  $\text{HgI}_2, 2\text{NH}_3$ . The same compound is obtained from ammonia and mercuric iodide. C. H. D.

**Double Sulphites of the Alkalis and Mercury.** HENRI BAUBIGNY (*Compt. rend.*, 1912, 155, 833—836).—The author confirms the results of Barth, that the double sulphites of the alkalis and mercury, unlike those of silver and copper, decompose on warming their solutions, or even on prolonged keeping in the cold, yielding sodium sulphate, sulphur dioxide, and mercury, without any sign of the intermediate formation of dithionic acid. W. G.

**The Odour of Clay.** II. PAUL ROHLAND (*Zeitsch. physiol. Chem.*, 1912, 81, 200—201. Compare Abstr., 1909, ii, 404).—In addition to colloids, such as ferric sucrate, certain crystalloids, for example, ammonia solutions, have the property of acquiring the odour of clay; thus when a mixture of 30% of kaolin and 70% of sand is shaken with ammonia, the solution acquires the characteristic odour of kaolin.

Pure dry kaolin is odourless; when wetted with water, particularly with an alkali, the characteristic odour and taste develop. Kaolin adsorbs dyes, smoke, and odours of all kinds.

It is suggested that the odour is due to bacterial action at the time of formation of the kaolin; this is confirmed by the presence of organic material in the kaolin. E. F. A.

**Crystallisation of Mixed Solutions of Manganous Chloride and Potassium Chloride.** J. SÜSS (*Zeitsch. Kryst. Min.*, 1912, 51, 248—268).—The following double salts are deposited from mixed solutions of manganous and potassium chlorides. Above  $6^\circ$ ,  $\text{MnCl}_2, \text{KCl}, 2\text{H}_2\text{O}$ ; below this temperature, potassium chloride and  $\text{MnCl}_2, 4\text{H}_2\text{O}$  crystallise out side by side. Above  $28.4^\circ$ , the salt,  

$$\text{MnCl}_2, 2\text{KCl}, 2\text{H}_2\text{O},$$

as tetragonal crystals with  $a : c = 1 : 0.815$ ,  $D\ 2.221$ . Above  $62.6^\circ$ , the double salt,  $\text{MnCl}_2, 4\text{KCl}$ , as rhombohedral crystals with  $a : c = 1 : 0.594$ ,  $D\ 2.310$ , which are identical with the Vesuvian mineral chlormanganokalite (Abstr., 1908, ii, 395).

In solutions of manganous chloride the tetrahydrate,  $\text{MnCl}_2, 4\text{H}_2\text{O}$ , passes over into the dihydrate,  $\text{MnCl}_2, 2\text{H}_2\text{O}$ , at  $58.3^\circ$ , but in the presence of potassium chloride this point is lowered to  $52.8^\circ$ . The lower limits of temperature at which these various salts exist were fixed by the dilatometric method. The solubility of potassium chloride and of manganous chloride at each of these fixed temperatures and in contact with the various solid phases were also determined. These points are marked on a temperature-concentration diagram for the system  $\text{KCl}-\text{MnCl}-\text{H}_2\text{O}$ , which is discussed in detail. L. J. S.

**Ternary Alloys of Iron, Nickel and Manganese.** NICOLA PARRAVANO (*Gazzetta*, 1912, 42, ii, 367—379).—The three binary systems included in the ternary system  $\text{Fe}-\text{Ni}-\text{Mn}$  have been studied by other observers, and the author has repeated only certain experi-

ments in connexion with the system Ni-Mn. The results of the present investigation of the ternary system are shown in a table and a number of diagrams. As would be expected from the behaviour of the binary systems, in the ternary system also there is miscibility in all proportions in the solid state. The heterogeneity of composition of the solid solutions which follow from these results is also shown in a number of microphotographs.

R. V. S.

**Inverse Occurrence of Solid Phases in the System Iron-Carbon.** ANDREAS SMITS (*Proc. K. Akad. Wetensch., Amsterdam*, 1912, 15, 371—380).—According to Wittorf (this vol., ii, 259), the separation of solid phases from iron-carbon alloys furnishes an example of inversion, in that the carbon content of successive phases does not diminish in a regular manner, but decreases and then increases. The theory of this phenomenon is examined in detail.

H. M. D.

**The Equilibrium Diagrams of Carbon with Iron, Nickel, Cobalt, and Manganese.** OTTO RUFF (*Ber.*, 1912, 45, 3139—3148. Compare Ruff and Goecke, *Abstr.*, 1911, ii, 897; Ruff and Martin, this vol., ii, 166, 354).—The formation of carbides which are stable at high temperatures, but decompose at lower temperatures, yielding graphite, is not confined to iron. The evidence for the existence of the carbides  $\text{Fe}_3\text{C}$ ,  $\text{Fe}_2\text{C}$ , and  $\text{Ni}_3\text{C}$  is repeated. It has not been found possible to carry the observations with cobalt sufficiently far to observe the corresponding break in the curve. Cobalt with 6.7% C has b. p.  $2475^\circ/20$  mm. Manganese carbide,  $\text{Mn}_3\text{C}$ , is stable within the range investigated.

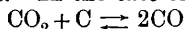
The vapour obtained from the carbide fusions consists either of pure iron or of iron containing a very small quantity of carbon.

C. H. D.

**Reduction of the Oxides of Iron.** MAX LEVIN (*Festschrift W. Nernst*, 1912, 252—257).—The volume percentage of carbon monoxide in the gaseous phase corresponding with the equilibrium between iron, ferrous oxide, carbon monoxide, and carbon dioxide increases continuously over the temperature range  $450$ — $800^\circ$ . There is no evidence of the minimum at  $680^\circ$  indicated by the experiments of Baur and Glaessner (*Abstr.*, 1903, ii, 423). In the case of the system ferrous oxide, ferroso-ferric oxide, carbon monoxide, and carbon dioxide, the volume percentage of carbon monoxide in the gaseous phase increases from about  $350^\circ$  to  $500^\circ$ , and then decreases as the temperature rises.

When the observed carbon monoxide equilibrium concentrations for the two systems are compared, it is found that the curves showing the relationship between the percentage of carbon monoxide and the temperature lie close together below  $500^\circ$ , but show gradually increasing divergence as the temperature rises. From these curves it would appear that at temperatures above  $500^\circ$  the percentage of carbon monoxide requisite for the reduction of ferrous oxide to iron is much greater than that required for the reduction of ferroso-ferric oxide to ferrous oxide, whereas both reduction processes are brought about by the same gas mixture between  $400^\circ$  and  $500^\circ$ .

The ratio of carbon monoxide to carbon dioxide in blast furnace gases is much higher than that corresponding with the equilibrium in either of the above systems. In the case of the equilibrium



the ratio on the other hand is lower up to about 640°, intermediate from this temperature to about 700°, and greater at higher temperatures.

H. M. D.

**Solubility and Heat of Solution of Chromium Trioxide in Water.** ERNST H. BÜCHNER and ADA PRINS (*Zeitsch. physikal. Chem.*, 1912, 81, 113—120. Compare Kremann, Abstr., 1911, ii, 898).—The solubility curve of the system  $\text{CrO}_3\text{--H}_2\text{O}$  has been determined. There were no indications of the separation of a solid hydrate. The eutectic mixture contains about 60.5% of  $\text{CrO}_3$ , but the eutectic temperature could not be accurately determined.

The observed heat of solution of chromium trioxide in water is always positive; in an unlimited amount of water it amounts to about 2467 cal. per mol. The theoretical heat of solution (that amount of heat given out when a mol. of substance is dissolved in an unlimited amount of the saturated solution) has been calculated by Roozeboom's method, and is negative, as would be anticipated from the influence of temperature on the solubility of the trioxide.

The specific heats of solutions of different concentrations has been determined. For  $1\text{CrO}_3$  to  $3.55\text{H}_2\text{O}$  it amounts to 0.506, and for  $1\text{CrO}_3$  to  $9.91\text{H}_2\text{O}$  to 0.665.

G. S.

**Removal of Phospho-tungstic Acid from Aqueous Solutions.** WALTER A. JACOBS (*J. Biol. Chem.*, 1912, 12, 429—430).—The usual procedure is to precipitate with barium hydroxide, but as the precipitate is voluminous much valuable material may be lost by adsorption. Winterstein recommends extracting the solution with ether, but there are difficulties there also, which may be overcome, however, by the substitution of amyl alcohol for the ether.

W. D. H.

**Compounds of Uranium with Hydrazine.** ROBERTO SALVADORI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 455—460).—When hydrazine hydrate (50% solution) is added to an aqueous solution of uranium nitrate a yellow precipitate,  $(\text{N}_2\text{H}_5)_2\text{O}, 5\text{UO}_3, 8\text{H}_2\text{O}$ , is obtained. At 100° it loses almost all its nitrogen. When the hydrazine hydrate and uranium nitrate are boiled for twenty minutes, a green precipitate of the composition  $(\text{N}_2\text{H}_5)_2\text{O}, 5\text{UO}_2, 6\text{H}_2\text{O}, 2\text{UO}_2$  is produced.

If hydrazine uranate is treated with hydrogen sulphide in the presence of excess of uranium nitrate or sulphate, an orange-yellow precipitate,  $5\text{UO}_3, 2(\text{N}_2\text{H}_5)_2\text{O}, \text{H}_2\text{S}_2, 6\text{H}_2\text{O}$ , is formed, which (after removal of the excess of hydrogen sulphide) gives with an excess of hydrazine hydrate a vermilion-red substance, "*hydrazine uranium red*,"



which is the analogue of "uranium red" (compare Kohlschütter, Abstr., 1901, ii, 165). The substance decomposes a little above 100°. In the air it slowly loses one molecule of hydrazine. The compound remaining

readily absorbs a molecule of ammonia, becoming blood-red. "Hydrazine uranium red" is also obtained when "uranium red" is treated with hydrazine.

R. V. S.

**Simple Method for the Preparation of Metallic Oxides.** MAURICE BILLY (*Compt. rend.*, 1912, 155, 777—779).—Chenevix's method for the reduction of cupric oxide to cuprous oxide by heating it with excess of copper (compare *Ann. Chim. Phys.*, 1803, [i], 45, 61) finds general application in the preparation of metallic oxides. The author has prepared titanium sesquioxide and titanous oxide from dry titanium dioxide by heating it with excess of titanium in a closed porcelain crucible, sealed to prevent access of air. On heating the mixture at 700° for thirty minutes the sesquioxide is produced, whilst if the temperature is raised to 1500°, the lower oxide is obtained. The excess of titanium is removed by the action of strong potassium hydroxide solution at 130° for four hours, followed by treatment with hydrochloric acid.

Analogous reductions have been successfully carried out with tungsten and molybdenum trioxides, ferric oxide, and manganese dioxide.

W. G.

**Solid Solutions among Haloids of the Same Element. I.** G. B. BERNARDIS (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 438—444).—The paper deals with the thermal analysis of the systems  $\text{SbCl}_3$ — $\text{SbBr}_3$ ,  $\text{SbBr}_3$ — $\text{SbI}_3$ , and  $\text{SbCl}_3$ — $\text{SbI}_3$ . Antimony bromide forms mixed crystals in all proportions with the iodide and with the chloride. The chloride forms mixed crystals with the iodide (limited as regards the iodide) up to a concentration of about 45% of antimony trichloride. The eutectic corresponds with 41.5° and about 82% of antimony trichloride.

R. V. S.

**The Spontaneous Crystallising Power of Bismuth and Antimony.** E. BEKIER (*Zeitsch. anorg. Chem.*, 1912, 78, 178—182).—The ratio spontaneous crystallising power : linear velocity of crystallisation increases with the velocity of cooling in the case of bismuth and antimony. The metal, melted in a Jena-glass tube, is poured into a bath of molten paraffin or into an iron mould, maintained at a definite temperature. The number of crystallites in a given area of the cast surface is measured, and proves to increase with the degree of undercooling, the experiments ranging from 260° to -70° for bismuth, and from 600° to -70° for antimony.

In the case of antimony, the size of the crystallites increases again at a low temperature. The spontaneous crystallising power thus diminishes, and it is possible that with sufficient undercooling the antimony might be obtained in an amorphous condition, as in the black antimony obtained by Stock and Siebert by condensing its vapour or by oxidising hydrogen antimonide at -40° (Abstr., 1906, ii, 34).

C. H. D.

**Atomic Weight of Palladium.** OWEN LOUIS SHINN (*J. Amer. Chem. Soc.*, 1912, 34, 1448—1451).—Determinations of the atomic weight of palladium have been made by reducing palladioammonium chloride,  $\text{Pd}(\text{NH}_3\text{Cl})_2$ , with ammonium formate, collecting the preci-

pitated metal, heating it to  $120^{\circ}$ , and weighing it. Four determinations were made with one specimen of palladioammonium chloride and five with another. The mean value found for the atomic weight was  $106.709 \pm 0.016$  ( $N=14.01$ ,  $H=1.008$ ,  $Cl=35.46$ ). The results showed considerable variation, the extreme discrepancy amounting to 0.188. The author is convinced that this was not due to errors of manipulation, and suggests that possibly the palladium salt may not have been absolutely uniform, or that some of it may have resisted decomposition.

E. G.

**Cathodic Pulverisation and Absorption of Hydrogen by Iridium.** FRANZ ROTHER (*Ber. K. Sachs. Ges. Wiss. Math.-Phys. Kl.*, 1912, **64**, 5—12).—Iridium foil (0.03 mm. thick) when subjected to long-continued cathodic pulverisation in a vacuum becomes capable of absorbing at the ordinary temperature about 800 times its volume of hydrogen. The structure of the plate is apparently much altered; and it appears dull grey and brittle, and the vacuum is increased by the absorption of hydrogen into the iridium cathode surface.

The absorption of hydrogen can readily produce an explosion, but the introduction of nitrogen moderates the pulverisation.

A special arrangement is described by which a constant pressure of hydrogen can be maintained during the pulverisation.

Iridium plates, which have been employed during a long period for cathodic pulverisation, form (unlike fresh iridium) an amalgam with mercury which is completely soluble in aqua regia, and from which iridium-black can be readily obtained; such an iridium cathode plate has the further property of being able to explode electrolytic gas; by long contact with nitrogen its catalytic properties are weakened.

F. M. G. M.

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### Mineralogical Chemistry.

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**Poisonous Gases from Oilfields.** HERBERT S. SHREWSBURY (*Analyst*, 1912, 37, 486—487).—Death having been caused by breathing a gas from an oil-well at La Brea, Trinidad, an analysis of the gas taken from the top of the well was made. After calculating the oxygen (8·7%) to air and allowing for this, the composition of the gas as it issued from the ground was found to be: hydrogen sulphide, 0·2; carbon monoxide, 1·9; unsaturated hydrocarbons, 4·4; saturated hydrocarbons, 7·8; carbon dioxide, 20·9; hydrogen, 31·4, and nitrogen, 33·4%. Its poisonous character (even when diluted with 43% of air) is evident. L. DE K.

**Vanadium and Chromium in Rutile.** THOMAS L. WATSON (*J. Washington Acad. Sci.*, 1912, 2, 431—434. Compare Abstr., 1898, ii, 30).—The following partial analyses, by W. M. Thornton, jun., are

given: I, red rutile from felspathic facies of syenite, Roseland, Nelson Co., Virginia. II, very dark rutile from nelsonite, near Rose's Mill, Nelson Co., Virginia (W. M. Thornton, Abstr., 1911, ii, 406). III, nearly black rutile from Kragerö, Norway. IV, black ilmenite from same locality as II:

	V <sub>2</sub> O <sub>5</sub>	Cr <sub>2</sub> O <sub>3</sub>	FeO.
I.	0.15	0.02	2.35
II.	0.20	0.07	1.68
III.	0.55	0.39	0.81
IV.	0.24	0.07	—

Beside confirming the wide distribution of vanadium and chromium in small amounts, these analyses suggest that the colour of rutile is to be attributed to vanadium rather than to iron oxide. L. J. S.

The Chemical Composition of Red Salt Clay. WILHELM BILTZ and E. MARCUS (*Zeitsch. anorg. Chem.*, 1912, 77, 119—123. Compare Abstr., 1910, ii, 968).—The "red" Stassfurt salt clay also contains bluish-green layers of similar composition. In the following analyses, arranged in order of depth, I is a blue clay from Schönebeck, II and III red clays from the same place, IV red sandstone clay, and V a red clay from Spereberg:

*Soluble in Water.*

	NaCl.	KCl.	MgCl <sub>2</sub> .	K <sub>2</sub> SO <sub>4</sub> .	Na <sub>2</sub> SO <sub>4</sub> .	CaSO <sub>4</sub> .	MgSO <sub>4</sub> .
I.	1.65	0.46	1.21	—	—	20.48	0.06
II.	2.34	0.50	1.10	—	—	16.27	0.40
III.	8.74	0.48	1.25	—	—	3.50	0.36
IV.	5.89	—	—	0.13	0.43	6.25	0.35
V.	14.69	0.21	3.83	—	—	4.52	0.15

*Insoluble.*

	CaSO <sub>4</sub> .	CaO.	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.
I.	4.52	0.41	8.75	2.24	0.68	9.14	1.17	0.88
II.	2.96	0.48	5.92	2.11	0.44	10.73	2.71	0.89
III.	0.27	0.18	5.98	2.53	0.01	13.26	2.16	0.93
IV.	0.02	0.69	11.20	2.49	0.91	14.63	3.59	1.43
V.	0.27	0.0	7.37	1.78	0.03	11.09	2.15	0.63

	Mn <sub>2</sub> O <sub>3</sub> .	ZnO.	SiO <sub>2</sub> .	TiO <sub>2</sub> .	P <sub>2</sub> O <sub>5</sub> .	H <sub>2</sub> O.	C.	CO <sub>2</sub> .	V <sub>2</sub> O <sub>5</sub> .	Total. (corrected).
I.	0.17	35.45	0.43	0.15	0.15	6.15	0.09	6.30	0.02	100.43
II.	0.05	45.24	0.53	0.11	0.11	7.36	0.03	0.19	0.01	100.37
III.	0.09	52.24	0.52	0.12	0.12	7.56	0.08	0.02	0.01	100.28
IV.	0.10	42.93	0.76	0.10	0.10	7.97	0.06	0.07	0.03	100.02
V.	0.08	40.17	0.51	0.05	0.05	11.85	0.18	0.03	0.01	100.07

All contain traces of lithium, nickel, chromium, boron, and bromine. C. H. D.

Difference in Chemical Composition of Aragonite and Calcite. WILHELM VAUBEL (*J. pr. Chem.*, 1912, [ii], 86, 366—381).—The author reviews the differences in the chemical behaviour of aragonite and calcite, and suggests that these may be explained on the

assumption that aragonite contains a small amount of the basic carbonate,  $\text{CO}_2(\text{O} \cdot \text{Ca} \cdot \text{OH})_2$ . F. B.

**Lüneburgite.** WILHELM BILTZ and E. MARCUS (*Zeitsch. anorg. Chem.*, 1912, 77, 124—130).—Lüneburgite has been described by Noellner (*Münch. Akad. Ber.*, 1870, 291) as having the composition  $3\text{MgO}, \text{P}_2\text{O}_5, \text{B}_2\text{O}_3, 8\text{H}_2\text{O}$ . A new analysis shows  $\text{H}_2\text{O}$  32·16%,  $\text{B}_2\text{O}_3$  12·9,  $\text{P}_2\text{O}_5$  29·61,  $\text{MgO}$  25·13,  $\text{CaO}$  0·15, corresponding with the formula  $\text{Mg}_3(\text{PO}_4)_2 \cdot 1\cdot77\text{H}_3\text{BO}_3 \cdot 6\text{H}_2\text{O}$ . Details of the method of analysis are given. Dehydration curves show that  $6\text{H}_2\text{O}$  are lost sharply at  $200^\circ$ , the remainder passing away slowly up to  $600^\circ$ .

Boric acid is not present in the free condition, but the microscopical examination does not determine whether the magnesium phosphate and boric acid are in solid solution. C. H. D.

**Adamite from Reichenbach, Lahr, Baden.** V. DÜRRFELD (*Zeitsch. Kryst. Min.*, 1912, 51, 279).—Adamite has been found in barytes at this locality as small, bluish-green spheres with radially fibrous structure. Analysis by Meigen corresponds with the usual formula:  $\text{Zn}_3(\text{AsO}_4)_2 \cdot \text{Zn}(\text{OH})_2$ .

$\text{As}_2\text{O}_5$	$\text{ZnO}$	$\text{}^2\text{O}$ (at $120^\circ$ ).	$\text{H}_2\text{O}$ (Ign.)	Insol.	Total.
33·44	48·45	0·15	4·42	11·04	97·50.

L. J. S.

**Composition of Thorianite.** MATSUSUKE KOBAYASHI (*Sci. Rep. Tôhoku Imp. Univ.*, 1912, i, 201—206).—According to analyses of the different crystalline and, apparently, homogeneous constituents of thorianite there appear to be two distinct varieties of this mineral. One of these contains about 78% of thorium oxide and 15% of uranium oxide ( $\text{U}_3\text{O}_8$ ), whilst the corresponding numbers for the second variety are 60 and 33. The molecular ratio of  $\text{ThO}_2$  to  $\text{UO}_2$  is almost exactly 6:1 in the one case and 2:1 in the other. The existence of these simple ratios does not support the view that thorianite is to be regarded as an isomorphous mixture of the two oxides.

The divergent analytical results obtained by others may be explained on the assumption that the analyses refer to mixtures containing the two varieties of thorianite in different proportions. H. M. D.

**A New Chlorite from Northern Wyoming.** JOHN E. WOLFF (*Amer. J. Sci.*, 1912, [iv], 34, 475—476).—This talc-like mineral was found in Sheridan County, Wyoming. It consists of a pale silvery-green, foliated mass of small scales, which are colourless and transparent. Refractive indices,  $\alpha = 1\cdot580$ ,  $\beta = 1\cdot580$ — $1\cdot581$ ,  $\gamma = 1\cdot589$ ;  $2E = 26$ — $50^\circ$ ; optically positive. The mineral is slowly decomposed by boiling sulphuric acid, and with difficulty by hydrochloric acid. Before the blowpipe it is fusible with difficulty to a white enamel. Very little water is expelled at  $350^\circ$ .

Analysis agrees with the formula  $H_6Mg_3Al_2Si_2O_{13}$ .

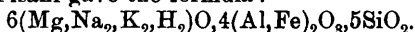
SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	Na <sub>2</sub> O.	K <sub>2</sub> O.	H <sub>2</sub> O. 110°.	H <sub>2</sub> O. >110°.	Total.	Sp. gr.
28·81	26·43	0·24	0·40	31·21	0·35	0·14	0·09	12·62	100·29	2·702

The mineral differs from other chlorites in the large percentage of alumina and the small amount of iron, approximating most nearly to leuchtenbergite. It is named sheridanite. L. J. S.

**Some Minerals from Madagascar, Several of which can be Used as Gems.** ALFRED LACROIX (*Compt. rend.*, 1911, 155, 672—677).—A preliminary description of the constituent minerals of the felspathic rock, pegmatite, found in various bearings in Madagascar. Specimens of quartz, chalcedony, orthoclase, diopside, and apatite as obtained were transparent and sufficiently limpid to be used as gems. The orthoclase is perfectly limpid, generally yellow to orange in colour, and occurs only in its common forms. Its density varies with the specimen from 2·558 to 2·596. The diopside is often bottle-green in colour. Its density is 3·23.

In a second bearing other minerals were obtained. A species of kornerupine constitutes a gem of intense brilliancy. It is optically negative, and is only decomposed on prolonged boiling with hydrofluoric acid, but it melts to a white enamel in the blow-pipe.

Analysis by Pisani gave the formula :



Its optical characters are given :

SiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	MgO.	K <sub>2</sub> O.	Na <sub>2</sub> O.	H <sub>2</sub> O.
31·35	41·20	2·27	23·80	0·24	0·60	0·64

A second mineral, saphirine, seems much rarer. The fragments of crystals obtained were deep blue, and exhibited a marked pleochroism. The optical characters are given. Analysis gave the formula :  $4·5(Mg, Fe)O, 5Al_2O_3, 2SiO_2$ , as compared with  $5MgO, 6Al_2O_3, 2SiO_2$  for saphirine from Greenland.

Fragments of zircon were also found, brown, black, or olive-green in colour, their density varying from 3·98 to 4·08. They behave in the same way towards heat in respect to birefracton and density as do the zircons of Ceylon. Another mineral, malgache, occurring in these bearings is black in colour, and is related to tschewkinite. Analyses of two specimens from different bearings gave the following results :

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	ThO <sub>2</sub> .	Ce <sub>2</sub> O <sub>3</sub> .	(La, Di) <sub>2</sub> O <sub>3</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MgO.	CaO.
I.	18·60	19·30	0·83	22·67	21·83	3·35	1·21	8·20	0·60	3·30
II.	22·60	16·10	0·57	33·13	5·51	7·00	2·08	4·40	1·10	7·20

The second specimen shows a remarkably high cerium content.

W. G.

**Pyroxenes of the Province of Rome.** NICOLA PARRAVANO (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 469—471).—Of the two minerals analysed, I. was a green pyroxene from Castelnuovo di Porto,

II. a crystal of back augite from Tavalato. The minerals had the following compositions :

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	FeO.	MnO.	CaO.
I.	53·81	0·44	10·82	2·13	1·27	—	22·46
II.	44·53	0·69	10·29	2·95	9·14	0·04	25·22

	MgO.	Na <sub>2</sub> O.	H <sub>2</sub> O below 110°.	H <sub>2</sub> O above 110°.	Total.
I.	7·54	0·86	0·07	0·34	99·78
II.	5·78	—	—	0·02	99·77

R. V. S.

Epidote from Notodden, Telemark, Norway. OLAF ANDERSEN (*Jahrb. Min.*, 1912, ii, Ref. 35—36; from *Archiv Math. og Naturv.*, 1911, 31, No. 15, 48 pp.).—Green, brown, and red epidote is of abundant occurrence as a primary constituent in the pegmatite-veins intersecting granulite at this locality. New crystal-forms are noted and the optical constants determined. Analyses are given of: I the green, and II the red epidote.

	SiO <sub>2</sub> .	TiO <sub>2</sub> .	Al <sub>2</sub> O <sub>3</sub> .	Fe <sub>2</sub> O <sub>3</sub> .	Mn <sub>2</sub> O <sub>3</sub> .	FeO.	CaO.	Ign.	Total.	Sp. gr.
I.	37·61	—	25·46	12·03	trace	0·09	22·39	2·22	99·80	3·386
II.	38·02	trace	25·78	11·24	0·58	trace	22·44	2·25	100·31	3·402

The red colour is due to the presence of tervalent manganese in the piemontite molecule. The connexion between the optical constants and the chemical composition is discussed: a variation of 0·3% in the ferric iron of epidote is accompanied by a change in the double-refraction of 0·001. The associated crystallised minerals in the pegmatite are titanite, hæmatite, apatite, microcline, oligoclase, etc.

L. J. S.

A Meteorite of the Hedjaz (Arabia). J. COUYAT (*Compt. rend.*, 1912, 155, 916—918).—A description of a meteorite reported to have fallen in Arabia in the spring of 1910. Mineralogical examination shows that the meteorite consists essentially of olivine, enstatite, and clinoenstatite, with a small quantity of felspar and troilite, and nickel iron. A chemical analysis by Pisani, detailed results of which are given, confirms this. Its density is 3·53.

W. G.

Shower of Meteoric Stones near Holbrook, Arizona. WARREN M. FOOTE (*Amer. J. Sci.*, 1912, [iv], 34, 437—456).—At 6.30 p.m. on July 19, 1912, a fall of meteoric stones was witnessed at Aztec, near Holbrook in Navajo County, Arizona. Over fourteen thousand stones with a total weight of more than 218 kilos. were collected; they range in weight from 6665 to less than 0·1 gram. The material, D 3·22, consists of enstatite (50—60%), olivine, diallage, and glass, together with small amounts of nickel-iron, pyrrhotite, magnetite, and chromite. In one section was seen ruby-red spinel embedded in quartz. Well-marked chondrules of enstatite are present. The magnetic portion (3·67%) contains Fe 80·86, Ni 15·79%.

L. J. S.

Presence of Notable Quantities of Boric Acid in the Mineral Waters of Salsomaggiore. RAFFAELE NASINI and C. PORLEZZA (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 379—383).—The authors have repeated with improved methods the estimation of boric acid in this water, and find the amount to be greater than that stated by Nasini and Anderlini (Abstr., 1900, ii, 489). The amount now found (in grams per litre) is:  $\text{H}_3\text{BO}_3$  2.22793,  $(\text{NH}_4)_2\text{O} \cdot 6\text{B}_2\text{O}_3$  0.23605.  
R. V. S.

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## Physiological Chemistry

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**Animal Calorimetry- I. A Small Respiration Calorimeter.** HORATIO B. WILLIAMS (*J. Biol. Chem.*, 1912, 12, 317—348).—The apparatus, which is a constant-temperature, water-cooled one, is described with full details and illustrations. W. D. H.

**The Electrometric Method for Estimation of the Alkalinity of the Blood.** LEONOR MICHAELIS and W. DAVIDOFF (*Biochem. Zeitsch.*, 1912, 46, 131—150).—A description is given of the adaptation of Michaelis' form of electrode for small quantities of substance to the principle of the shaking electrode described by Hasselbalch. For the purpose of estimating the alkalinity by this process, 1—1.5 c.c. of serum suffices. The mean value for normal human venous blood was found to be  $p=7.35$  at  $37.5^{\circ}$ . The value at  $18^{\circ}$  is 0.21 greater. The mean value, therefore, for human venous blood is  $[H^+]=0.45 \times 10^{-7}$ . There are deviations from this value in certain pathological conditions. S. B. S.

**The Amino-acid Nitrogen of the Blood. Preliminary Experiments on Protein Assimilation.** DONALD D. VAN SLYKE and GUSTAVE M. MEYER (*J. Biol. Chem.*, 1912, 12, 399—410).—The determination of amino-acid nitrogen in blood is best accomplished by a gasometric method after the proteins have been precipitated by alcohol. The amount in fasting animals is 0.003—0.005 gram per 100 c.c. of blood. Absorption of 10 grams of alanine from the intestine increases this figure to 0.004—0.0063. During normal digestion of meat, the amount is doubled or more than doubled. Twelve grams of alanine injected into the blood disappear rapidly; five minutes later only 1.5 grams were left in the blood, and 1.5 grams passed into the urine; the remainder must have been taken up by the tissues. The theory that amino-acids are synthesised into blood-protein while passing through the intestinal wall becomes superfluous. The amino-acids pass directly into the blood-stream. The liver appears to have no special part in picking up these acids, but doubtless the other tissues all help themselves; this conclusion is based on the observation that the blood of the femoral artery during digestion contains nearly as much amino-acid as that in the mesenteric veins. W. D. H.

**Glycolysis in Blood.** G. SPENCER MELVIN (*Bio-Chem. J.*, 1912, 6, 422—428).—Blood outside the body at room or body temperature when aseptic suffers no loss of sugar. There is also no loss when dextrose is added to the blood. Extracts of fibrin have no glycolytic power. Alcohol-coagulated blood protein gave similar negative results. A stream of air or carbon dioxide makes no difference

W. D. H.

**Animal Calorimetry. IV. The Absorption of Dextrose and the Effect it has on the Composition of the Blood.** GERTRUDE FISHER and MARY B. WISHART (*J. Biol. Chem.*, 1912, 13, 49—62).—After ingesting 50 grams of dextrose, the sugar in the blood rises above the normal during the first hour, and the hæmoglobin content is but little altered, owing to the absorption of water being slight. An hour later, from two-thirds to three-quarters of the sugar has been absorbed, and relatively little retained as glycogen; the sugar percentage in the blood returns to normal, and, owing to the absorption of water, the blood is more dilute, as seen by a fall in hæmoglobin content. Metabolism is 20% higher; this lasts through the third hour. In the fourth hour, sugar absorption is completed and urine is secreted abundantly, and the blood-volume returns to normal. With 20 grams of sugar these reactions are less marked, and with 75 grams the high metabolism lasts an hour longer. W. D. H.

**The Rotatory Power of Blood Plasma and Serum of Different Animals of Varying Age and Sex.** EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1912, 81, 233—238).—The lævorotatory action of the plasma and serum in the animals examined show but little difference. In the guinea-pig the rotation is less. A high rotation was found in cases of pernicious anæmia and tuberculosis.

W. D. H.

**Effect of Carbon Dioxide and Oxygen on Muscular Tone in the Blood Vessels and Alimentary Canal.** DONALD R. HOOKER (*Amer. J. Physiol.*, 1912, 31, 47—58).—Carbon dioxide is not directly beneficial to the muscular tissue, except in the case of intestinal muscle when arrhythmic. It always relaxes vascular muscles. Oxygen is essential to rhythmical action and tone of vascular muscle. Intestinal muscle if rhythmic responds in the same way, but if arrhythmic responds by contraction to carbon dioxide and by relaxation to oxygen.

W. D. H.

**Normal and Pathological Conditions of Digestion in Dogs.** EFIM S. LONDON (*Zeitsch. physiol. Chem.*, 1912, 81, 369—438).—1. *Methods.*—Details of operative procedures by producing fistulæ, occlusion of parts of the alimentary canal and so forth.

2. *Normal Gastric Digestion.*—F. J. RIWOSCH.—If meat is mixed with very varying quantities of water, two and a-half hours later the stomach contains the same amount of chyme, and the same acidity. Very large amounts of water favour the acidity and increase the amount of coagulable protein in the chyme. The amount of digestion varies with the kind of protein administered.

3. *Digestion of different kinds of nutriment.*—L. J. MEPISSOFF.—Different foods leave the stomach at varying speeds, but this depends largely on the order in which they are taken, for instance, flesh leaves the stomach sooner than bread if the former is given first, but later if given last. If a mixture of flesh and milk is given, the undigested meat residues leave the stomach more rapidly than when the meat is given first.

4. *The digestion of mixed nutriment.*—B. D. STASSOFF.—This also relates to the speed with which substances leave the stomach, and is of subsidiary chemical interest.

5. *The emptying of the stomach after feeding on starch.*—L. J. MAZIJEWSKI.—For the first three hours after starch is taken the stomach empties itself according to the laws of unimolecular reactions; this is followed by a period of three or four hours, in which little or none passes into the intestine, and finally the stomach rapidly empties itself.

6. *The influence of the intestine on the emptying of the stomach.*—W. F. DAGAEFF.—There is a mechanical action; opening of the intestinal fistula leads to a rapid emptying of the stomach, especially if the opening is near the stomach. Acid in the intestine delays the emptying of the stomach, and in pyloric antrum hastens it.

7. *Digestion and absorption in experimental defects of the stomach.*—L. F. MAZIJEWSKI.—Removal of the pyloric ring accelerates the time at which the stomach begins to empty. The regulatory action of the pylorus is most marked in early stages of the digestive process. Removal of the pyloric ring and antrum delays matters, but after a year or so the animal has returned to normal. Stricture of the stomach's outlet delays its emptying.

8. *The rôle of the fundus and antrum in the evacuation of fluid contents.*—O. E. GABRILOWITSCH.—The separation of fluid from solid constituents is mainly related to the pyloric portion of the stomach. Details are also given of the peristalsis in different regions of the stomach.

9. *Action of pancreatic juice on gastric digestion.*—R. S. KRYM.—In-activated pancreatic juice has no effect; the active juice only slightly accelerates gastric digestion. Previous action of pancreatic juice on meat accelerates its digestion in the stomach.

10. *Digestion and absorption when pancreatic juice is excluded.*—O. J. HOLMBERG.—In a dog with a stomach fistula, occlusion of the pancreatic mechanism accelerates gastric digestion for a certain period. Entrance of pancreatic juice into the stomach hastens the digestion of fat. In the intestine loss of pancreatic juice is followed by some compensatory action of other juices, but protein cleavage does not go so far.

11. *Compensatory action in resection of the intestine.*—B. D. STASSOFF.—Resection of the small intestine delays emptying of the stomach; of the duodenum delays digestion and absorption generally. Under ordinary conditions the large intestine seems chiefly to form faeces, but in pathological conditions of other parts of the canal it has a compensatory action; when the large intestine is removed this compensatory action cannot be obtained.

12. *Interference with digestion in injuries of the bile ducts.*—H. K.

WIEDEMANN.—The principal result is delay in the digestion and absorption of fat.

13. *Digestive disturbances on removal of portions of the mesentery.*—M. R. GILLELS.—This severe injury leads to many pathological changes in the canal and to pain.

14. *Nutrition in defective digestion.*—S. K. SOLOWÉEFF.—Various abnormalities in metabolism follow different severe injuries.

15. *Feeding experiments after jejunostomy.*—R. S. KRYM.—The results given are preliminary only, and further work is promised. W. D. H.

Free and Combined Hydrochloric Acid in Stomach Contents. I. Estimation of Free Hydrochloric Acid in Gastric Juice. JOHANNE CHRISTIANSEN (*Biochem. Zeitsch.*, 1912, 46, 24—49).—The hydrogen ion concentration of gastric juice was measured by concentration cells, and the neutralisation point to various indicators was determined. Congo paper gives a sharp turning point to the juice (after an Ewald test-meal) at  $p=4.6$ . Günzberg's reaction, carried out in the ordinary way, depends on the character of the acids present, and not on the hydrogen ion concentration. Nevertheless, for clinical purposes it gives a sufficiently good measurement of the amount of free hydrochloric acid present, and also of the hydrogen ion concentration, as the errors due to other acids are not great. S. B. S.

Free and Combined Hydrochloric Acid in Stomach Contents. II. Titrations of the Products of Peptic Digestion. JOHANNE CHRISTIANSEN (*Biochem. Zeitsch.*, 1912, 46, 50—70).—When titrated with alkali, the difference between the end-points of artificial digests in the presence of Günzberg's reagent and Congo paper is the same as that between Congo paper and phenolphthalein. The same relationships hold in human gastric juice. During the course of a digest, the amount of free hydrochloric acid as measured by Günzberg's reagent diminishes, owing to its combination with the simpler digestion products, produced by the setting free of amino-groups. This fact is demonstrated by the increase of the titration number after addition of formaldehyde. S. B. S.

Free and Combined Hydrochloric Acid in Stomach Contents. III. The Titrations of Pancreatin-erepsin Digests and of Amino-acids and Polypeptides. JOHANNE CHRISTIANSEN (*Biochem. Zeitsch.*, 1912, 46, 71—81).—Günzberg's reagent can be employed for ascertaining the amount of hydrolysis in solutions of the hydrochlorides of amino-acids, etc. The hydrochlorides of natural proteins and their products of peptic digestion are only slightly hydrolysed and act as polypeptides, whereas the hydrochlorides of a pancreatin-erepsin digest show considerable amount of hydrolysis, and act in this respect like the pure amino-acids. S. B. S.

Free and Combined Hydrochloric Acid in Stomach Contents. IV. The Estimation of Total Hydrochloric Acid in Stomach Contents. JOHANNE CHRISTIANSEN (*Biochem. Zeitsch.*, 1912, 46, 82—93).—The total acidity is due almost entirely to hydro-

chloric acid, as lactic acid is generally only present in negligible quantity, and the amount of acid phosphates is also small. Litmus or alizarin give the best results in the titration of a test-meal, those given by phenolphthalein being too high. For estimation of acidity, an unfiltered, well shaken juice is best employed. S. B. S.

**The Influence of Gases, Specially Oxygen, on Tryptic and Peptic Digestion.** ERNST LAQUEUR and KURT BRÜNECKE (*Zeitsch. physiol. Chem.*, 1912, 81, 239—259).—At atmospheric pressure oxygen has no influence; at 9—13 atmos. it inhibits the digestive process, except that the peptolytic action is unaffected. Nitrogen at 12 atmos. has no effect. Carbon dioxide at atmospheric pressure and at 10 atmos. has little or no action. W. D. H.

**Plastein Formation.** II. VALDEMAR HENRIQUES and J. K. GJALDBÆK (*Zeitsch. physiol. Chem.*, 1911, 81, 439—457).—By the action of pepsin-hydrochloric acid on the products of gastric digestion, typical plastein formation takes place, but with gelatinisation; there is good ground for assuming that synthesis occurs. The same results were obtained by the action of trypsin, tyrosine being split off at the same time.

No plastein formation occurred when the products of tryptic digestion were subjected to the further action of either pepsin-hydrochloric acid or trypsin.

The products of acid hydrolysis behaved like those of gastric digestion. The products of alkali hydrolysis gave plastein when subjected to gastric, but not when subjected to tryptic, digestion. W. D. H.

**Pancreas Diastase.** WALTHER LÖB (*Biochem. Zeitsch.*, 1912, 46, 125—130).—Description is given of attempts to prepare a pure diastase preparation from pigs' pancreas, which contains a powerful ferment, the action of which was estimated by Wohlgemuth's method. It was found that a neutral mixture of the sodium phosphates greatly accelerates diastatic action when not present in too large a quantity. If a large excess is added, the action is inhibitory. Phosphates also accelerate the hydrolytic action of hydrogen peroxide on starch. This action, whether in presence or absence of phosphates, is, however, inhibited by the action of diastase. S. B. S.

**The Influence of Certain Inorganic Salts on the Action of Pancreatic Lipase.** CORNELIS A. PEKELHARING (*Zeitsch. physiol. Chem.*, 1912, 81, 355—368; *Proc. K. Akad. Wetensch. Amsterdam*, 1912, 15, 336—347).—It has long been known that bile salts favourably influence the activity of pancreatic lipase. The recent work of Rosenheim on the separation of this enzyme into an active and inactive component is confirmed. It is further shown that various inorganic salts (of calcium, barium, magnesium, and sodium) are also favourable. Their action is not very great, and is explained by the circumstances that they form soaps and so remove the liberated fatty acids, and thus allow the enzyme to act on more of the substrate. W. D. H.

**Protein Metabolism from the Standpoint of Blood and Tissue Analysis.** EFIM S. LONDON (*Zeitsch. physiol. Chem.*, 1912, 81, 283—284).—Folin and Lyman's results (this vol., ii, 853) are not considered conclusive. It cannot be stated positively that absorption is occurring from the stomach, unless the rest of the alimentary canal is excluded; absorption might be occurring there from the auto-digestion of the juices. W. D. H.

**Animal Calorimetry. II Metabolism of the Dog following the Ingestion of Meat in Large Quantities.** HORATIO B. WILLIAMS, J. A. RICKE, and GRAHAM LUSK (*J. Biol. Chem.*, 1912, 12, 349—376. Compare this vol., ii, 270).—A dog, the heat production of which was 22—23 cal. per hour, received 1200 grams of meat at noon. In the second hour, the heat production rose to 40, and 42 in the third hour; it remained at 40 until the tenth hour, and then fell, reaching 25 in the 21st hour. Ingestion of 700 grams of meat caused a smaller but proportionate rise. The increase of metabolism was proportional to the nitrogen elimination, except in the second and third hours. The high heat production then is attributed to the incoming amino-acids stimulating protoplasm to higher oxidation. The rectal temperature does not always give a true record, for often the skin temperature rises more than the rectal after the ingestion of food. The carbon of the protein is retained as dextrose; this in relation to nitrogen eliminated was 1·2 : 1.

Intestinal work is believed to have little or nothing to do with the high metabolism. W. D. H.

**Animal Calorimetry. III. Metabolism after the Ingestion of Dextrose and Fat, Including the Behaviour of Water, Urea, and Sodium Chloride Solutions.** GRAHAM LUSK (*J. Biol. Chem.*, 1912, 13, 27—48).—After giving 50 grams of dextrose to a dog, the percentage of blood sugar rises within an hour, and then slowly returns after several hours to normal. Water is retained by the organism during the period of high metabolism, and is then suddenly eliminated during the fourth hour after the taking of the sugar. The high metabolism is attributed to osmotic changes between the blood and the tissues, and is due to the presence of a greater amount of free diffusible carbohydrate than is present when none is being absorbed from the intestine. Details of experiments are given in which the dose of sugar varied from 10 to 100 grams. W. D. H.

**Feeding Experiments with Gelatin, Ammonium Salts, Completely Hydrolysed Flesh, and a Mixture of Amino-acids on Young Dogs.** EMIL ABDERHALDEN and PAUL HIRSCH (*Zeitsch. physiol. Chem.*, 1912, 81, 323—328).—A mixture of amino-acids kept young dogs healthy, but they grew but little. The other mixtures, ereptone and ammonium acetate, promoted growth also. W. D. H.

**The Fate of Individual Amino-acids, Mixtures of Amino-acids, Peptones, and Proteins in the Alimentary Canal.** EMIL ABDERHALDEN and ARNO ED. LAMPÉ (*Zeitsch. physiol. Chem.*, 1912, 81, 473—507).—The work of Folin and his colleagues is criticised,

the main point being that, although their method proves the increase of non-protein nitrogen in the blood after feeding on amino-acids, etc., there is no direct proof of the exact nature of the compounds in which the nitrogen is combined. A new method is suggested, namely, treating the dialysate of blood-serum with triketohydrindene hydrate; this reacts with amino-compounds which contains a carboxyl group in the  $\alpha$ -position. After feeding on meat and peptone, the blood of the dog contains excess of amino-acids, which pass into it directly from the intestine.

W. D. H.

**The Rôle of Gliadin in Nutrition.** THOMAS B. OSBORNE, LAFAYETTE B. MENDEL, and EDNA L. FERRY (*J. Biol. Chem.*, 1912, 12, 473—510).—The experiments deal with the question of the differences between foods in maintaining adult metabolism and those necessary for growth in young animals. A gliadin food-mixture given to a young growing animal in place of its mother's milk led to typical failure in growth, although the mother dog thrived on the same diet, and had actually produced young and secreted milk in sufficient quantity and quality to induce normal growth in her offspring. No stronger proof could be adduced of a power to synthesise "Bausteine" in the body which are absent from the food.

W. D. H.

**Isolation of Glycyl-*l*-phenylalanine from the Chyme of Small Intestine.** Biological Studies with the Help of Different Protein Cleavage Products and Synthetically prepared Polypeptides. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1912, 81, 315—322).—Various amino-acids are separated from the intestinal chyme, but special interest attaches to the separation of glycyl-*l*-phenylalanine, as it is the first depeptide so far identified in this material. Anaphylaxis was induced by the injection of a 14-peptide (*l*-leucyltriglycyl-*l*-leucyl-octaglycyl-glycine), but some doubt is expressed as to the trustworthiness of the experiment and it is to be repeated.

W. D. H.

**Synthetic Powers of Animal Cells. The Value of Nitrogen from Different Sources in the Dog's Organism.** EMIL ABDERHALDEN and PAUL HIRSCH (*Zeitsch. physiol. Chem.*, 1912, 82, 1—20).—The general conclusion is drawn that ammonium salts, and especially the acetate, influence the nitrogenous balance and lead to retention of nitrogen. The assumption that animal cells can build up protein from ammonia and non-nitrogenous compounds (carbohydrate, etc.) is not, however, proved by the experiments given.

W. D. H.

**Synthetic Powers of Animal Cells. The Value of Nitrogen from Different Sources in the Dog's Organism.** EMIL ABDERHALDEN and ARNO ED. LAMPÉ (*Zeitsch. physiol. Chem.*, 1912, 82, 21—95).—Addition of ammonium salts to a nitrogen-free diet in many cases depresses nitrogenous katabolism. Added to gelatin they do not prevent loss of nitrogen. There is as yet no proof that cells can build up protein from ammonia and substances

free from nitrogen. Retention of nitrogen when it occurs does not prove the point; the ammonia may be held back as such or in compounds other than protein. The contrary conclusions drawn by Grafe are criticised. W. D. H.

**Comparative Investigations on the Amount of Amino-acids in Various Constituents of the Nervous System. I. The Amino-acids of Peripheral Nerves, and the White Matter of the Spinal Cord.** EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1912, 81, 207—225).—The results of analyses on the question mentioned in the sub-title are given in detail. W. D. H.

**The Effect of Carbon Dioxide on the Isolated Heart.** C. S. KETCHAM, J. T. KING, jun., and DONALD R. HOOKER (*Amer. J. Physiol.*, 1912, 31, 64—74).—Carbon dioxide, 2.5 to 3%, in an excess of oxygen when dissolved in the perfusion fluid depresses the heart of the terrapin and cat, and increases the rate of outflow. W. D. H.

**The Reduction of Ferric Chloride by Surviving Organs.** DAVID FRASER HARRIS and HENRY JERMAIN M. CREIGHTON (*Bio-Chem. J.*, 1912, 6, 429—432).—Surviving liver and kidney reduce ferric chloride to a ferrous condition, owing to the reductase in these organs being still active. The bile and urine respectively are more reduced than the venous blood, since these fluids come into actual contact with the cells which contain the reducing enzyme. The degree of reduction is greater in the liver than in the kidney. W. D. H.

**The Osmotic Properties of the Kidneys.** RICHARD SIEBECK (*Pflüger's Archiv*, 1912, 148, 443—521).—In Ringer's solution and other isotonic fluids, frogs' kidneys do not alter, but when the solutions are hypotonic the kidneys gain weight. In isotonic solutions, alteration of the reaction makes no difference, provided the cells are intact. In cases where swelling occurs, the amount of swelling is less than would be expected from the lowering of osmotic pressure. In isotonic solutions of potassium chloride, however, the kidneys increase in weight, and this is reversible. This action is inhibited by dextrose and sodium chloride, and still more by chlorides of bivalent cations; it is increased by alkalinity. Ammonium chloride acts more strongly than potassium chloride, and various potassium salts vary in their action. Observations on the oxidation processes in the kidney cells confirm those of Warburg on blood-corpuscles. W. D. H.

**The Phosphatides of the Kidney.** HUGH MACLEAN (*Bio-Chem. J.*, 1912, 6, 333—354).—From the study of extracts of horses' kidneys made with ether, alcohol, and acetone, it was found that the phosphatides present are lecithin, cuorin (Erlandsen), and carnaubon (Dunham and Jacobson). Details for their separation are given in full. A contamination with another nitrogenous substance explains some divergent results. Carnaubon is not a triamino-phosphatide, but a diamino-phosphatide. W. D. H.

**Purification of Phosphatides.** HUGH MACLEAN (*Bio-Chem. J.*, 1912, 6, 355—361).—The phosphatide of kidney and muscle which is soluble in alcohol is lecithin (N:P=1:1). The method of purification consists of emulsification and precipitation with acetone. No substance was found in the alcohol extract having a higher percentage of nitrogen than lecithin. From an aqueous extract of the nitrogenous impurity of lecithin, a basic substance crystallises out; after this is separated out, the mother liquor is very effective in curing polyneuritis (beri-beri). This explains the anomalous results of other observers in their attempts to cure polyneuritis in birds with lecithin.

W. D. H.

**The Iodine Content of the Thyroid of Sheep, Ox, and Pig.** THOMAS B. ALDRICH (*Amer. J. Physiol.*, 1912, 31, 125—130).—In general, the largest thyroids contain most iodine, and in the mixed glands, the proportions in sheep, ox, and pig have the ratio 5:7:9. For therapeutic purposes, those richest in iodine should be selected.

W. D. H.

**The Nuclein of the Thymus, and Anaphylaxis Studies with Nuclear Materials (Nucleo-proteins, Nucleins, and Nucleic Acids).** EMIL ABDERHALDEN and T. KASHIWADO (*Zeitsch. physiol. Chem.*, 1912, 81, 285—293).—Part of the phosphorus in nuclear material is easily split off, for instance, by simply boiling with water, or by the action of artificial gastric juice. Various amino-acids (glycine, alanine, valine, leucine, proline, aspartic acid, glutamic acid, phenylalanine, tyrosine, tryptophan, and cystine) can also be separated by the ester method. Anaphylaxis cannot be induced by nucleic acid; when produced by nucleo-proteins, it is due to the protein constituent.

W. D. H.

**The Feeding of White Rats on the Pituitary Body.** THOMAS B. ALDRICH (*Amer. J. Physiol.*, 1912, 31, 94—101).—The daily ingestion of pituitary body (anterior or posterior lobes) did not accelerate growth in rats.

W. D. H.

**Chemical and Physico-chemical Properties of Liquids Expressed from Striated and Plain Muscle.** FILIPPO BOTTAZZI (*Atti R. Accad. Lincei*, 1912, [v], 21, ii, 493—500).—The liquids were obtained from muscles of mammals and fishes by trituration with sand and subsequent expression. They contained only ultramicroscopic granules which appear to consist of protein (myosin). There is also dissolved protein (myoprotein). The granular material is precipitated slowly but spontaneously; the precipitation is hastened by dilution, by dialysis, or by warming. The dissolved protein is precipitated at a higher temperature (50—80°). The yield of liquid varies from 40—63%. The dry residue is about 6% in the case of plain muscle, 7—12% for striated muscle. The total amount of protein is 3—4%. The specific gravity is similar to that of blood-serum; the osmotic pressure is always greater than that of blood. The reaction (measured by *E.M.F.* methods) is acid. The electrical conductivity, the viscosity and the surface tension were also measured.

R. V. S.

**Occurrence of Manganese in Animal Organs.** P. CABLES (*Ann. Chim. anal.*, 1912, 17, 411—412).—Manganese may be detected in many animal organs by the use of potassium persulphate as an oxidising agent for the conversion of the manganese compounds into permanganates. Human blood contains a trace of manganese, but the metal is not present in the blood of oxen, rabbits, fowls, or ducks. Somewhat larger quantities are present in the liver and kidneys, and still more is present in the hair and nails. W. P. S.

**The Chemical Composition of Young Eels under Various Conditions.** HANS REUSS and ERNST WEINLAND (*Zeitsch. Biol.*, 1912, 59, 283—296).—The interest of the eel (*Anguilla vulgaris*) arises from the fact that its early life is spent in fresh-water before it migrates to the sea. The present analyses of water, ash, fat, glycogen, nitrogen, and calcium are compared with the condition in the adult, and various factors (feeding, temperature, etc.) are considered in influencing the results. The analyses are given in tabular form. W. D. H.

**Work and Gaseous Metabolism in the Frog's Heart.** VIKTOR WEIZSÄCKER (*Pflüger's Archiv*, 1912, 148, 535—563).—The resting metabolism of the frog's ventricle at 20° is 0.064 c.c. of oxygen per gram per hour; this is increased two- or three-fold by raising the temperature 10°. With medium activity (30 beats per minute) the metabolism rises 4—12%; this is more marked when the beats are increased in rate, but beyond a certain limit this falls off. Elevation of temperature increases the heart's rate, but for constant amounts of work, the temperature-coefficient is 1.6. W. D. H.

**The Action of Drugs and the Function of the Anterior Lymph Hearts in Cardiectomised Frogs.** JOHN J. ABEL (*J. Pharmacol. and expt. Ther.*, 1912, 3, 581—608).—In frogs, minus a heart, diffusion of drugs occurs viâ the lymphatic system; the main propulsive force resides in the still intact anterior lymph hearts. If these are not beating, no convulsions occur after injections of acid-magenta, or unless enough of the drug is absorbed by the brain and spinal cord to give a pink colour when hydrochloric acid is added to the crushed tissue. In the normal frog, the efficiency of the circulation leads to greater diffusion of the drug, and it does not accumulate in the central nervous system to such a high degree. It is not necessary to assume, as Meltzer does, that the absence of a special antitoxic substance in cardiectomised frogs will explain the phenomena. The same holds true for other drugs, such as strychnine and morphine. W. D. H.

**Two Crystalline Pharmacological Agents Obtained from the Tropical Toad (Bufo Agua).** JOHN J. ABEL and DAVID I. MACHT (*J. Pharmacol. and expt. Ther.*, 1912, 3, 319—377).—Two distinct active principles were separated from the toad's parotoid glands; one of these is adrenaline, of which the crude venom contains 6.7%. The other, named *bufagin*,  $C_{18}H_{24}O_4$ , is dextrorotatory (+11°), sparingly soluble in water, and melts at 217—218°. It does not contain

the unsaturated carbon linking of cholesterol. Physiologically it is an efficient member of the digitalis series. The toad is not immune to adrenaline, but is relatively so to bufagin. W. D. H.

**The Fatty Acids of Butter.** IDA SMEDLEY (*Bio-Chem. J.*, 1912, 6, 451—460).—No acetic acid was found. The hexoic acid possesses the normal structure. Stearic acid occurs in a percentage of 10—15. Evidence was obtained of the presence of lower members of the oleic series; possibly one of these is a decenoic acid. Two samples out of five gave the reactions for acetoacetic acid and acetone, which possibly originated from bacterial action. W. D. H.

**The Secretion of Urine in Birds.** N. C. SHARPE (*Amer. J. Physiol.*, 1912, 31, 75—84).—The urine of hens collected from the ureter may contain a deposit of urates, but is usually clear. Its water must be largely re-absorbed from the bowel. Ordinary diuretics act as in other animals. W. D. H.

**The Occurrence of Methylguanidine in the Urine of Parathyroidectomised Animals.** W. F. KOCH (*J. Biol. Chem.*, 1912, 12, 313—316).—In a dog from which the thyroid and parathyroid glands had been removed, methylguanidine was separated as a gold salt in considerable amount (1.9 gram of gold salt per litre). In normal urine of man and dog the amount is 0.07 gram per litre. How far this substance is responsible for the symptoms exhibited and death is to be the subject of further work. W. D. H.

**The Distribution of Phosphoric Acid between Urine and Fæces.** AD. WÜRTZ (*Biochem. Zeitsch.*, 1912, 46, 103—111).—The effect on the distribution of administering to rabbits, on the one hand, hydrochloric acid and, on the other, calcium carbonate was studied. It was found in the latter case that there was a relative increase in the phosphorus in the fæces. The author discusses the influence of the following factors on phosphorus secretion: (1) The resorbability of calcium and phosphates in the small intestine; (2) the reaction of the urine; (3) the excretion of calcium salts in the intestine.

S. B. S.

**The Relation of Potassium Salts and Other Substances to Local Anæsthesia of Nerves.** M. L. MENTEN (*Amer. J. Physiol.*, 1912, 31, 85—93).—On injury, heating, and in anæsthesia produced by lipid solvents, the amount of potassium which is revealed by Macallum's reagent increases in medullated nerve. Solutions of various potassium salts (except the tartrate, oxalate, citrate, and acetate) isotonic with plasma suspend conductivity when injected into nerve fibres. W. D. H.

**Anaphylaxis.** EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1912, 82, 109—112).—The injection of a foreign protein into the blood stream calls forth the production there of proteolytic enzymes. This is considered to be a necessary factor in the production of anaphylaxis;

and in cases where anaphylactic shock occurred, the serum was found to contain "peptone." W. D. H.

**A Case of Hæmatoporphyrinuria in Typhoid Fever.** VINZENZ ARNOLD (*Zeitsch. physiol. Chem.*, 1912, 82, 172—174).—Mainly clinical details. The spectroscopic appearances of the urine are fully described. W. D. H.

**Protein Metabolism in Experimental Diabetes.** A. I. RINGER (*J. Biol. Chem.*, 1912, 12, 431—446).—In phloridzin glycosuria, protein metabolism rises in part because of the hypoglycæmia present. The giving of small quantities of dextrose to such animals spares the protein, although all the sugar given appears in the urine. This supports Landergren's hypothesis that in starvation a fraction of the protein is metabolised for the formation of sugar, and that this can be spared by carbohydrates, but not by fat. The protein metabolism does not rise so high in pancreatic as in phloridzin diabetes, and the giving of dextrose to a depancreatized dog does not spare any protein; in pancreatic diabetes the hyperglycæmia prevents the katabolism of the so-called "dextrose-protein." W. D. H.

**Mechanism of Phloridzin Diabetes.** FRANK P. UNDERHILL (*J. Biol. Chem.*, 1912, 13, 15—26).—The curious feature about phloridzin diabetes is the diminution of sugar in the blood. This has received several explanations, but the most feasible is that the kidney is rendered so permeable for sugar that it all passes rapidly into the urine, and leaves the blood with even less than the normal amount in it. This view is supported by the present experiments, which show that if the secretion of urine is rendered impossible by ligaturing the renal structures, or by giving animals sodium tartrate, which stops the activity of the kidney, then a significant hyperglycæmia occurs. The experiments were performed on dogs and rabbits. W. D. H.

**The Treatment of Peritonitic Fall of Blood-pressure.** ERNST HOLZBACH (*Arch. exp. Path. Pharm.*, 1912, 70, 183—232).—In peritonitis, low blood-pressure is a characteristic symptom. This is believed to be due to a peripheral cause (poisoning of the capillaries), and suggestions for treatment are made. The experimental part of the paper deals, however, with poisons which produce a similar fall of blood-pressure. Arsenic is one of these, and experiments on frogs and mammals show that its effect on the peripheral vessels and heart can be counteracted by adrenaline. The action of the latter drug is evanescent, and its effect can only be kept up by repeated doses. Veronal also causes the pressure to sink, and this is not complicated with any cardiac effects. The action is abolished by adrenaline, and in a more lasting manner by injection of barium salts. W. D. H.

**Experiments in Radio-activity; the Production of the Thorium Emanation and its Use in Therapeutics.** DAWSON TURNER (*Proc. Roy. Soc. Edin.*, 1912, 393—395).—Active thorium

compounds for therapeutic use may be given by inhalation, by ingestion, by baths, by wet packs, or by the injection of radioactive water into the tumour mass, or into the veins. Too large doses may be dangerous to life; nausea, giddiness, and other symptoms often occur in animals. The scanty details given of the effect on malignant tumours in animals and man (one case only) do not appear to be conclusive. W. D. H.

**The Narcotic Action of Substances of the Alcohol Group with the Simultaneous Administration of Fat. on the Ground of their Partition Coefficients in Fat and Water. A New Antidiabetic "Barzarin."** MAX SALZMANN (*Arch. expt. Path. Pharm.*, 1912, 70, 233—254). **Barzarin.** HEINRICH WALBAUM and MAX SALZMANN (*ibid.*, 255—257).—"Barzarin" is an antidiabetic preparation prepared from the bark of a South American tree. It is harmful to cats, in part because of its high percentage of tannic acid. It is not recommended. Its high percentage of alcohol led to an investigation of substances of the alcohol group in relation to the Meyer-Overton theory of narcosis. This action is increased when fat is given also. If, however, amylene hydrate and paraldehyde are given mixed with fat, the partition coefficient of fat for these substances is such that little or none of the drug is absorbed, and very little narcotic action occurs. W. D. H.

**Comparative Investigations on the Pharmacology of the Terpene Series.** HERMANN SCHWALB (*Arch. expt. Path. Pharm.*, 1912, 70, 71—108).—Small doses of terpenes act stimulatingly on unicellular organisms, and on the frog's heart. The compounds which contain oxygen are the more powerful. On *Paramoecia* the degree of activity runs parallel with the power to lower surface tension in aqueous solutions. W. D. H.

**Gluco-Neogenesis. I. The Quantitative Conversion of Propionic Acid into Dextrose.** A. I. RINGER (*J. Biol. Chem.*, 1912, 12, 511—515).—The experiments were performed on phloridzinised dogs, which received 10 grams of propionic acid either subcutaneously or by the mouth. The results justify the conclusion that the acid is completely converted into dextrose. W. D. H.

**The Behaviour of  $\alpha$ -Pyrrolidonecarboxylic Acid in the Animal Organism.** EMIL ABDERHALDEN and RUDOLF HANSLIAN (*Zeitsch. physiol. Chem.*, 1912, 81, 228—232).—This acid in the form of its sodium salt lowers the temperature; when the *dl*-acid is employed, almost pure *d*-acid is excreted. W. D. H.

**The Effects of Alkaloids on the Development of Fish (*Fundulus*) Eggs.** J. F. M'CLENDON (*Amer. J. Physiol.*, 1912, 31, 131—140).—Alkaloids of both the aliphatic and cyclic series have the same morphological effect on *Fundulus* embryos. Distension of the pericardium and effects on the circulatory system are frequent, but cyclopia was rare. W. D. H.

**The Comparative Sensitiveness of Blood-pressure and Intestinal Peristalsis to Adrenaline.** R. G. HOSKINS and C. W. M'CLURE (*Amer. J. Physiol.*, 1912, 31, 59—63).—Intestinal depression

is caused by injections of adrenaline decidedly smaller than those requisite to raise blood-pressure. W. D. H.

**The Rôle of Caffeine in the Diuretic Action of Coffee.** MARC TIFFENEAU and H. BUSQUET (*Compt. rend.*, 1912, 155, 857—859).—The variations in the renal secretions of a dog were noticed after injection of infusions of coffee, of coffee deprived of its caffeine, and of such extracted coffee to which its normal percentage of pure caffeine had been restored. Coffee deprived of caffeine loses the major part of its diuretic effect on the renal secretion, caffeine being the principal, if not the exclusive, agent in the diuresis produced by coffee. W. G.

**Action of the Opium Alkaloids with Special Reference to Pantopon.** OTTO BARTH (*Arch. expt. Path. Pharm.*, 1912, 70, 258—291).—Experiments on frogs show that pantopon (a mixture of all the opium alkaloids) is in comparison with morphine, narcotine, and meconic acid rather more than twice as powerful. W. D. H.

**The Action of the Opium Alkaloids.** F. W. WATKYN-THOMAS (*Bio-Chem. J.*, 1912, 6, 433—443).—A series of experiments on anaesthetised animals (mainly rabbits), in which the effects on the circulation, respiration, etc., of some of the individual alkaloids in opium are compared with those produced by omnopon (or pantopon, a solution of all the alkaloids). No general conclusions are drawn.

W. D. H.

**The Behaviour of Fat-soluble Dyes and Stained Fat in the Animal Organism.** LAFAYETTE B. MENDEL and AMY L. DANIELS (*J. Biol. Chem.*, 1912, 13, 71—96).—Fat-soluble dyes introduced into the body are deposited in adipose tissue and bone-marrow. Renal, nervous, and muscular tissues are free from stain, as is also the liver, because the dyes dissolve readily in bile. They enter the body from the alimentary tract through the lymphatics in solution in fat, or by the portal blood dissolved in re-absorbed bile. They do not pass beyond the liver unless fat is present to transport them. Then they may be found in the blood; they return to the intestine by the bile, whence they may be once more absorbed. Stained fat, like unstained, is available to the organism. In cases conducive to fat transport (starvation, phosphorus or phloridzin poisoning), stained fat migrates from the stained depôts to blood and liver cells. It does not traverse the placenta. Sudan III and Biebrich-scarlet given with food-fat are found in the milk in cats, rats, guinea-pigs, and goats. In the cow this has not yet been demonstrated. W. D. H.

**The Action of Organic Mercury Compounds in Infections by Spirochaetæ.** CL. SCHILLING, M. VON KROGH, WALTHER SCHRAUTH, and WALTER SCHOELLER (*Zeitsch. Chemotherapie u. verwandte Gebiete*, 1912, 1, 21—43).—The study of the action of these compounds in recurrent infections in mice is complicated by the fact that both the infection and the medicament attack the small intestine. In combatting the infection, only the mercury derivatives of the phenols,

amongst the compounds investigated, appear to have any action. This action appears to be one of stimulation of formation of anti-substances in the organism, in contrast to the action of such substances as salvarsan, which is directly toxic to the spirochaete. S. B. S.

**The Chemical Mechanism of the Toxic and Curative Actions of Organic Mercury Compounds.** WALTER SCHOELLER and WALTHER SCHRAUTH (*Medizinische Klinik*, 1912, No. 29).—The organic mercury derivatives can be divided into four classes, namely: (1) those in which the mercury is readily removed by alkali hydroxides and hydrogen sulphide; (2) those in which the mercury is removed readily by hydrogen sulphide, but not by alkali hydroxides (pseudo-complexes); (3) those in which the mercury is directly united to one carbon atom (half-complexes); (4) those in which it is united to two carbon atoms (full-complexes). In the last class the mercury is removed with the greatest difficulty, and the direct corrosive action on tissues is least. These are the most interesting from a therapeutical point of view, and their toxicity is directly proportional to the chemical stability and inversely proportional to the rate at which they are excreted by the organism. The authors discuss the various problems connected with their therapeutic investigation, calling attention more especially to the difficulties of applying directly the results obtained from protozoal infections of animals to treatment of infections in man. S. B. S.

**The Respiratory Quotient in Acid Poisoning.** OTTO PORGES (*Biochem. Zeitsch.*, 1912, 46, 1—6).—It has been shown by the author, that by excluding the liver from the circulation, the respiratory quotient rises to 0.9—1.0. The explanation offered is, that when the liver is excluded, the proteins and fats are not metabolised, and that the rise of the quotient is due to the fact that only ready-formed carbohydrates are burnt. Rolly has, however, urged that the rise of respiratory quotient is due to acid poisoning. The author now shows that acid poisoning in the case of rabbits does not lead to an appreciable rise, and Rolly's explanation cannot therefore hold good. S. B. S.

**The Action of Sodium Carbonate on Certain Alkaloid Salts and Dyes.** HELENE TSCHERNORUTZKY (*Biochem. Zeitsch.*, 1912, 46, 112—120).—The experiments were carried out with the object of testing Traube's theory, according to which, the more the addition of alkali to an alkaloid salt or dye lowers the surface tension of the solution, the more rapidly will such an addition increase its toxicity. The toxicities were measured by the effects on tadpoles and the surface tensions by a stalagmometer. The experiments did not in all cases confirm Traube's theory. Explanations for the exceptions are offered. S. B. S.

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## Chemistry of Vegetable Physiology and Agriculture.

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**Bacterial Metabolism.** V, VI, VII. ARTHUR I. KENDALL and CHESTER J. FARMER (*J. Biol. Chem.*, 1912, 12, 465—468, 469—472; 13, 71—96).—The authors confirm on other strains of micro-organisms their contention that “fermentation takes precedence over putrefaction,” by which they mean that these organisms act on carbohydrates before they act on proteins. W. D. H.

**Fermentation of Sugar by *Bacillus subtilis*.** Production of Butylene  $\beta$ -Glycol. LEMOIGNE (*Compt. rend.*, 1912, 155, 792—795).—The author confirms the results of Desmots (*Abstr.*, 1904, ii, 276) and Harden and Norris (this vol., ii, 474), that acetylmethylcarbinol is one of the products of the action of *Bacillus subtilis* on a sugar solution, and, in addition, has obtained some butylene  $\beta$ -glycol. The combustion of sugar in aerobic conditions by *B. subtilis* therefore consists of three stages. The first product is butylene  $\beta$ -glycol, which is then oxidised to acetylmethylcarbinol, which in its turn is destroyed by the microbe. W. G.

**The Relations of Phenol and *m*-Cresol to Proteins.** The Mechanism of Disinfection. EVELYN A. COOPER (*Bio-Chem. J.*, 1912, 6, 362—387).—The absorption of the phenols by bacteria is merely the initial stage in disinfection. The germicidal action which follows is not the result of a chemical union between the phenols and the bacterial proteins (as is the case with formaldehyde), but is associated with the de-emulsification of the colloidal suspension as evidenced by the precipitation of proteins when a certain phenol concentration is reached. The action thus appears to be similar to heat coagulation. This may explain the fact that below a certain percentage (0.5%), the bactericidal action is very feeble, there being a disproportionate falling off in germicidal power when the concentration is reduced to this point. W. D. H.

**Quantitative Reduction of Methylene-blue by Bacteria Found in Milk, and the Use of this Stain in Estimating the Keeping Quality of Milk.** EDWIN BROUN FRED (*Centr. Bakt. Par.*, 1912, ii, 35, 391—428).—Methylene-blue is the most suitable stain for measuring reduction by microbes. Out of twenty-two species of milk micro-organisms, twenty-one were found to reduce. Temperature and stain reduction are inversely proportional up to 37°. The quantitative reduction of methylene-blue varies with different types; each species, however, seems to have a definite reducing coefficient. The growth and reduction curves for all species have the same general form.

Peroxydase is initially present in milk, and is not formed to any great extent by the growth of bacteria; catalase is produced to a great extent by the development of microbes in the milk. Reductases do not occur in milk when first drawn, but are formed by the growth of micro-organisms.

Although the reduction test shows wide variations, it is useful in

ascertaining the approximate bacterial content of milk. Milk which reduces methylene-blue in from one to one and a-quarter hour contains 15—50 million bacteria per c.c., whilst a sample that requires seven hours or more contains less than 1 million. If colourless in three hours, or less, the milk must be considered of poor quality; if seven hours, or more, is required, the milk will be of good quality.

N. H. J. M.

#### Toxic Effects of "Alkali Salts" in Soils on Soil Bacteria.

III. Nitrogen Fixation. CHARLES B. LIPMAN and L. T. SHARP (*Centr. Bakt. Par.*, 1912, ii, 35, 647—655).—Sodium chloride in concentrations of 0.5—0.6% of dry soil is toxic to nitrogen-fixing organisms, whilst sodium sulphate is only toxic when 1.25% is present. Sodium carbonate is the most toxic of the "alkali salts," inhibiting nitrogen fixation in concentrations of only 0.4—0.5%.

Whilst the "alkali salts" are relatively only slightly toxic to nitrogen-fixing organisms as compared with other soil organisms, the toxic point, when reached, manifests itself much more sharply.

It would seem possible that, sufficient organic matter being present, nitrogen fixation could go on in soils containing relatively large amounts of "alkali salts."

Sodium chloride, and especially sodium sulphate, are less toxic for nitrogen-fixing organisms than for ammonifying and nitrifying organisms. Sodium carbonate is much more toxic for nitrogen-fixing than for ammonifying organisms, but much less than for nitrifying organisms.

No stimulating effect was observed with any concentrations of the salts.

Nitrogen-fixing organisms seem physiologically to resemble alkali-resisting plants much more than other soil organisms. N. H. J. M.

The Physiology of Denitrifying Sulphur Bacteria. RUDOLF LIESKE (*Ber. Deut. bot. Ges.*, 1912, 30, 12—22).—An anaerobic organism, probably identical with *Thiobacillus denitrificans*, was isolated from pond mud, and its behaviour in culture solutions observed. Under suitable conditions it is able to obtain all the carbon necessary for growth from ammonium, sodium, calcium, or magnesium carbonates, but not from carbon dioxide. Energy is derived from the oxidation of hydrogen sulphide, sulphur, and sodium thiosulphate or tetrathionate. The amount of carbon assimilated by the organism is, in fact, about 1% of the weight of sodium thiosulphate oxidised. Where sulphur was supplied to a culture, experiment showed that intermediate compounds are formed in the early stages of growth, and that sulphates occur chiefly when the fermentation is nearing completion. Under anaerobic conditions and in the presence of nitrates and thiosulphates, the organism produces a mixture of gases consisting of about 80% of nitrogen and 20% of carbon dioxide with traces of sulphur dioxide.

H. B. H.

The Antiseptic Rôle of Sea-salt and of Sugar. LÉON LINDET (*Compt. rend.*, 1912, 155, 790—792\*).—Brewer's yeast when left in

\* and *Bull. Soc. chim.*, 1912, [iv], 11, 952—953.

contact with strong solutions of sea-salt or of sugar becomes weakened and no longer has the same capacity for reproduction. This, the author suggests, is due to the yeast losing a portion of its constituent elements to the salt or sugar solution. Estimations of nitrogen, phosphoric acid, and potassium were made in the filtered liquids after twenty hours contact, and the results are given showing the amounts extracted. Yeast, after contact, when grown in bouillon produces a far smaller number of colonies than fresh yeast. W. G.

**The Action of Metallic Salts on Yeasts and Other Fungi.** THOMAS BOKORNY (*Centr. Bakt. Par.*, 1912, ii, 35, 118—197).—The action of the salts of a large number of metals was tested on yeasts, bacteria, algae, infusoria, and, in some cases, seedlings of higher plants. Many of the salts show only an inhibitory action, and even in very concentrated solutions fail to cause death. Compounds of this class are potassium sulphate (4% solution), monopotassium phosphate (4%), calcium chloride (10%), and magnesium chloride (70%). The fact that solutions of potassium oxalate (10%) are without effect is assumed to indicate the absence of calcium compounds in organic combination in the yeast cell.

Solutions of caesium and rubidium sulphate (0.05%) exert a stimulating action on yeasts, whilst growth is retarded by potassium iodide and bromide (0.1%), lithium sulphate (0.05%), cadmium sulphate (0.025%) and ferrous sulphate (0.2%).

Copper sulphate, silver nitrate, and osmic acid prevent growth if present in greater quantities than 0.001%.

The mode of action of such salts on the cell plasma is held to be similar to that of aniline dyes. Even in extremely dilute solutions there occurs a gradual withdrawal of the compound from solution until the lethal dose is reached. H. B. H.

**Chemical Composition and Formation of Enzymes. VII. Development of Yeasts in Various Nutrient Solutions.** HANS VON EULER and BJÖRN PALM (*Zeitsch. physiol. Chem.*, 1912, 81, 59—70).—The rate of growth of a normal yeast in nutrient solutions containing dextrose or sucrose follows the logarithmic law. In the case of beer-yeast, or of *Saccharomyces apiculatus* or *S. marxianus*, the growth curve is of the same character whether the solution contains dextrose or a disaccharide which is not fermented by the yeast. It is considered improbable that such disaccharides are assimilated without being hydrolysed, and it is suggested that the yeasts contain enzymes able to hydrolyse these sugars, although no alcoholic fermentation takes place. E. F. A.

**Determination of Respiratory Quotients.** LÉON MAQUENNE and EM. DEMOUSSY (*Compt. rend.*, 1912, 155, 881—886).—A mathematical discussion of the relationship between the true and apparent respiratory coefficients when determined in an enclosed volume of air. Two methods are given for determining the apparent respiratory coefficient, and the results from them show close agreement. From the data obtained, the authors calculate the coefficient of absorption

of carbon dioxide by the leaves of the species examined, and find that, in round numbers, it is 2. W. G.

**Action of Fermentation Products and Phosphates on the Respiration of Plants.** S. KOSTYTSCHIEFF and SCHELOUMOFF (*Bied. Zentr.*, 1912, 41, 716; from *Jahrb. wiss. Bot.*, 50, 157).—Experiments with wheat seedlings showed that the action of secondary phosphates on the production of carbon dioxide is chiefly due to the alkaline reaction. Phosphates have very little effect in neutral solutions, and then only when the solutions are dilute. The same effect can be obtained in absence of phosphates by dilute solutions of sodium hydroxide or carbonate, or by zymin extracts or solution of dextrose fermented by zymin. N. H. J. M.

**The Effects of Purine Derivatives and Other Organic Compounds on Growth and Cell-division in Plants.** N. G. S. COPPIN (*Bio-Chem. J.*, 1912, 6, 416—421).—The growth of bulbs is stimulated by dilute solutions of sodium humate, malate, urate, and oxalate, and to a less extent by bovril. This is more marked in the rootlets than in the leaves. Cell-division is also stimulated by dilute solutions of sodium humate, oxalate, oleate, and linoleate, and to a less extent by caffeine and sodium malate. Both growth and cell-division are inhibited by stronger solutions of all the above compounds, and by all solutions of allantoin, guanine hydrochloride, xanthine, hypoxanthine hydrochloride, and sodium nucleate. W. D. H.

**Nitrate and Nitrite Assimilation.** IV. OSKAR BAUDISCH (*Ber.*, 1912, 45, 2879—2883).—In reply to Loew's criticisms (this vol., ii, 797) of his work (*Abstr.*, 1911, ii, 523), the author contends that, with regard to the reduction of nitrates by aldehydes in the presence of light, a true comparison is not possible between Loew's experiments with platinum-black at 100° and his own experiments in light at the ordinary temperature. C. S.

**Presence of Nitrous Acid in the Sap of the Higher Plants.** PIERRE MAZÉ (*Compt. rend.*, 1912, 155, 781—783. Compare *Abstr.*, 1911, ii, 643, 918).—Nitrous acid exists normally in plant sap, being produced by the living cells and not derived from nitrates by reduction, since its presence can be detected in the sap from maize plants grown in a mineral solution, containing no nitrate, but ammonium chloride or sulphate as the source of nitrogen. The concentration of nitrous acid in the sap is in inverse ratio to the plant activity. The sap exuded on a dull rainy day is richer in nitrous acid than that exuded at the close of a bright sunny day. W. G.

**Formaldehyde in the Cambial Sap of Conifers.** M. KLEINSTRÜCK (*Ber.*, 1912, 45, 2902—2904).—Formaldehyde is probably present in the cambial sap of conifers, since the latter, when distilled in steam in the presence of dilute sulphuric acid, yields a distillate which immediately reduces an alkaline silver solution in the cold, gives a precipitate with aniline and with alkaline potassium mercury iodide,

and a characteristic orange coloration with hydrochloric acid, ferric chloride, and sulphuric acids. Further evidence has been obtained during attempts to colour living wood. The chlorides of aniline and of *p*-aminophenol have been found to impart a very dark hue to the cambial layer, whilst the wood itself acquires a yellow tint. By means of minute quantities of formaldehyde, it has been found possible to darken the latter tint.

H. W.

Carbamide [in Plants]. ROBERT FOSSE (*Compt. rend.*, 1912, 155, 851—852).—The presence of carbamide in minute quantities has been proved by isolation as its xanthhydrol derivative in the juice from the washed leaves of a number of plants. Whether it is a physiological product of the plant-cells or comes from the soil is not yet known.

W. G.

Existence of Cyanogenetic Principles in a New *Centaurea* (*Centaurea Crocodylium*) and in a Commelinaceae (*Tinantia fugax*). MARCEL MIRANDE (*Compt. rend.*, 1912, 155, 925—926).—*Centaurea Crocodylium* contains in its green organs a glucoside of the amygdalin group, which is split by the enzyme present, giving benzaldehyde and hydrogen cyanide, the yield of the latter being 0.0238 gram per 100 grams of leaf, and 0.0131 gram per 100 grams of stem.

*Tinantia fugax* contains a cyanogenetic principle in its leaves, but no benzaldehyde can be detected in the distillate. The quantity of hydrogen cyanide present diminishes during the course of the annual vegetation of the plant. This is the first member of the Commelinaceae found to yield hydrogen cyanide.

W. G.

A New Natural Group of Plants Producing Hydrogen Cyanide, the Calycanthaceae. MARCEL MIRANDE (*Compt. rend.*, 1912, 155, 783—784).—The two classes, *Calycanthus* and *Chimonanthus*, of this group contain hydrogen cyanide in a combined state, and an enzyme by which it is set free on macerating the fresh leaves. Analyses of four species of *Calycanthus* are given showing amounts of hydrogen cyanide varying from 0.004 gram to 0.019 gram per 100 grams of fresh leaves.

W. G.

The General Occurrence of Choline. ERNST SCHULZE and GEORG TRIER (*Zeitsch. physiol. Chem.*, 1912, 81, 53—58).—The occurrence of betaines in plants is sporadic; on the other hand, the quaternary base choline appears to be widely distributed. The base has now been isolated as such from ten species, representing different families. It is considered that choline is not liberated from lecithin during the manipulation of the extracts.

E. F. A.

Production of Proteins by Higher Plants in Darkness. J. SCHULOFF (*Bied. Zentr.*, 1912, 41, 717—718; from *J. exper. Landw.*, 1912, 209).—The results of experiments with sterile maize plants, supplied with sucrose and kept in darkness, showed that non-nitrogenous material was assimilated, and that ammonium sulphate

hindered growth, whilst with ammonium nitrate there was a considerable increase in the proteins.

N. H. J. M.

**The Nitrogenous Constituents of Higher Fungi.** ERNST WINTERSTEIN and C. REUTER (*Centr. Bakt. Par.*, 1912, ii, 34, 566—572).—The alcoholic extract of dry *Boletus edulis* was found to contain lecithin, trimethylhistidine, adenine, guanine, hypoxanthine, choline, leucine, alanine, and phenylalanine, but not proline. The aqueous extract contained, in addition to the above, tetramethylenediamine, whilst ammonia and trimethylamine were the chief volatile bases. The aqueous extract of 2500 grams of the fungus yielded 132 grams of "viscosin" containing 4.25% nitrogen and composed to a large extent of glycogen. Autolysis of the fresh fungus for six weeks at 37° gave large quantities of ammonia and isoamylamine, and also hypoxanthine, guanine, trimethylhistidine, and putrescine. Passage of sterilised air through the mash during autolysis leads to the production of brownish-black, humus-like substances, and the authors indicate the possibility of the production of nitrogenous humin substances in soils by autolysis. The approximate composition of the air-dry fungus is given as being: water 10%; ether extract 4%, consisting of fat 3.2%, cholesterol 0.5%, and lecithin; alcohol extract 12%, containing trehalose 3%, sugar, lecithin, bases, amino-acids, purine substances, etc. 9%; aqueous extract 28%, of which glycogen 5%, sugar, purine substances, bases, amino-acids, ash, etc. 23%; and residue 46%, consisting of protein 30%, amorphous carbohydrates 10%, and chitin 6%.

H. B. H.

**Plant Micro-chemistry.** OTTO TUNMANN (*Pharm. Zentr.-h.*, 1912, 53, 1175—1179).—It is shown that *Inula Helenium* roots are characterised by the presence of crystals of alantic anhydride in the "resin" glands, and that sections of madder root when heated yield sublimes containing crystals of ruberythric acid. The appearance and micro-chemical reactions of these two substances are described.

T. A. H.

**Occurrence of Lactic Acid in Sisal.** WILLIAM McGEORGE (*J. Amer. Chem. Soc.*, 1912, 34, 1625—1627).—The normal acidity of the leaves of the Sisal hemp plant (*Agave sisalana*) is due almost entirely to lactic acid. Although lactic acid is said to exist in many seeds, it is believed that this is the first case in which a plant has been found to develop it as its normal vegetable acid.

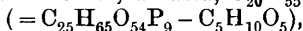
E. G.

**Pollen Toxin.** O. KAMMANN (*Biochem. Zeitsch.*, 1912, 46, 151—169).—A very active preparation was obtained in the following way. An aqueous extract of ground rye-pollen was submitted to diastatic digestion to destroy the starch, the proteins from the filtrate were precipitated by alcohol, this precipitate was dried at low temperature, and an aqueous extract of the product thus obtained was made. This was kept for at least eight days in a refrigerator, during which time the proteoclastic enzyme contained in the preparation acted, and the toxic action became much more powerful. In rye-

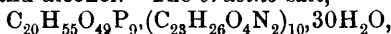
pollen the following enzymes were found : protease, diastase, and lipase. It also contains a hæmotoxic amboceptor, which is activated by lecithin and serum lipoids.

S. B. S.

**Organic Phosphoric Acid Compound of Wheat Bran.** R. J. ANDERSON (*J. Biol. Chem.*, 1912, 12, 447—464).—When wheat bran is extracted with 0·2% hydrochloric acid and the extract precipitated with alcohol, a white, amorphous substance is obtained, which when redissolved and precipitated several times has a relatively constant composition. On heating the substance with barium hydroxide solution, it yields a sparingly soluble *barium* salt,  $C_{25}H_{55}O_{54}P_9Ba_5$ , which could not be crystallised. Attempts to obtain the free acid,  $C_{25}H_{65}O_{54}P_9$ , were unsuccessful; an *acid*,  $C_{20}H_{55}O_{49}P_9$



was, however, obtained, which forms a viscid, sticky mass readily soluble in water and alcohol. The *brucine* salt,



forms long, white, silky needles very soluble in water, readily soluble in alcohol, and insoluble in ether and chloroform; m. p. 196—198°. No crystalline metallic salts of the acid could be obtained.

As no compound corresponding in composition with phytic acid could be obtained from wheat bran, the conclusion is drawn that wheat does not contain phytin, and that the compound  $C_{20}H_{55}O_{49}P_9$  is the only organic phosphoric acid in bran. Patten and Hart's anhydroxy-methylenediphosphoric acid is a mixture of the above compound and free phosphoric acid.

N. H. J. M.

**Volatile Fatty Acids and Alcohols in Corn Silage.** EDWIN B. HART and J. J. WILLAMAN (*J. Amer. Chem. Soc.*, 1912, 34, 1619—1625).—A study of samples of maize silage has been made with the following results: Volatile acids were present to the extent of 0·84% (calculated as acetic acid), and non-volatile acids to the extent of 0·13% (calculated as lactic acid). The volatile acids consisted of formic acid (17%), acetic acid (75%), propionic acid (8%), and butyric acid (0·6%). The silage was free from esters, but contained a trace of aldehyde. The volatile alcohols amounted to 0·31% (calculated as ethyl alcohol), and consisted of methyl alcohol (21%), ethyl alcohol (72%), and propyl alcohol (7%).

E. G.

**Production of Sucrose in Sugar Beet.** FRIEDRICH STROHMER, HERMANN BRIEM, and OTTOKAR FALLADA (*Bied. Zentr.*, 1912, 41, 690—692; from *Oesterr.-Ung. Zeits. Ind. Landw.*, 1911, 857).—The results of analyses of seed sugar-beet, in the second year, at the flowering and ripening periods (June 9th and August 2nd) showed that when ripe the roots and main stem contained considerably more sucrose than at the earlier period, whilst the leaves and side stems lost the whole of their sucrose.

As regards invert sugar it was found that all the above-ground parts of the plants contained considerably more in June than in August.

N. H. J. M.

**Behaviour of Nitrates in Field Soils.** J. VOGEL (*Centr. Bakt. Par.*, 1912, ii, 34, 540—561).—Considerable losses of nitric nitrogen (upwards of 70% of the amount originally present) were found to occur when field soils were kept thoroughly aerated in the presence of 15—20% of water. The process appeared to be increased by the addition of calcium carbonate to the soil, and is independent of the supply of soluble organic matter. The author is inclined to attribute the change to some purely chemical action. H. B. H.

**Increasing the Ammonia-fixing Power of Soils under the Influence of Calcium Carbonate.** OTTO LEMMERMANN and L. FRESSENIUS (*Bied. Zentr.*, 1912, 41, 666—671; from *Fühling's Landw. Zeit.*, 1912, 240 and 274).—Addition of calcium carbonate (0.1%) to soil containing 199 mg. of nitrogen as ammonium carbonate was found to diminish the loss of ammonia. Similar results, indicating increased absorptive power, were obtained when air containing ammonium carbonate was passed over soils both with or without sodium carbonate. When, however, the amount of calcium carbonate in relation to the ammonium carbonate is considerably increased, the absorptive power of the soil is diminished.

The absorptive power of soil for ammonia is hardly appreciably altered by digesting the soil with alcohol; addition of calcium carbonate has the same effect as it had before treatment with alcohol. Ignition reduced the absorptive power of soil without destroying it altogether; addition of calcium carbonate to ignited soil, or to sand, diminishes the absorptive power. Other calcium compounds, as well as magnesium, sodium, and potassium salts, had practically no effect, although calcium and magnesium chloride and calcium sulphate caused a slight increase, due, probably, to reactions with the ammonium carbonate.

Different soils showed great variations in their power of absorbing ammonia, and the effect of calcium carbonate varies with different soils.

Potassium salts are generally more unfavourable than sodium salts, and the latter more than magnesium salts. N. H. J. M.

**Non-fixation of Phosphoric Acid by an Acid Forest Soil.** AUGUSTE PETIT (*Compt. rend.*, 1912, 155, 921—923. Compare Abstr., 1911, ii, 649).—Acid forest soil not only does not fix phosphoric acid, applied in the form of a solution of monocalcium phosphate, but, on the contrary, loses a certain amount of its own phosphoric acid to the solution. The amount so lost is practically constant, and independent of the strength of the phosphate solution, provided that the same volume of liquid is employed in each case. The phosphoric acid content of the soil was 0.09%. W. G.

**Change in the Reaction of Soils by Growth of Plants and Manuring.** J. G. MASCHHAUPT (*Bied. Zentr.*, 1912, 41, 655—657; from *Verslag. Landbouwkund. Onderzoek. Rijkslandbouwproefstat*, 1911, No. 10).—Various plants were grown in garden soil in pots resting on beakers containing the nutritive solution, or on sand saturated with

the nutritive solution. Alkalinity was produced when sodium nitrate was employed, and acidity with ammonium salts, whilst ammonium nitrate became acid, but less acid than ammonium sulphate. On two occasions, the whole of the roots being immersed in the solution, a slight alkalinity was observed with ammonium nitrate. Solutions of potassium, sodium, calcium, and magnesium chlorides and sulphates always produced slight alkalinity.

N. H. J. M.

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## Analytical Chemistry.

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**Weighing in Analytical Operations.** RICHARD KEMPF (*Chem. Zeit.*, 1912, **36**, 1349—1350).—Precautions to be taken to ensure correct weighings, mostly taken from the literature on the subject.

L. DE K.

**Method of Classifying Indicators According to their Sensitiveness to Acids and Alkalis.** M. WAGENAAR (*Pharm. Weekblad*, 1912, **49**, 949—953).—A description of a method for comparing the sensitiveness of methyl-orange, phenolphthalein, and litmus, depending on the slow diffusion of glacial acetic acid or acetic anhydride into *N*/10-sodium hydroxide. The indicators diminish in sensitiveness in the order in which they are named.

A. J. W.

**Crystallochemical Analysis.** THOMAS V. BARKER (*Chem. News*, 1912, **106**, 199—201).—A description of Federoff's method of identifying chemical compounds by means of their crystallographic character is given. Some of the angles of the crystal are measured, and from the results the standard position in which the crystal must be set in order to measure its characteristic angles is deduced. The crystal is then set up, and the five (or fewer) characteristic angles measured. Reference is then made to an index compiled by Federoff, in which the data for all crystals hitherto examined are classified, and if the substance has been previously examined its identity can at once be established (except for crystals of the cubic system, to which the method does not apply). The method does not, of course, distinguish between isomorphous substances. As an example of its applicability it is stated that of fifty substances, crystals of which were sent from this country to Federoff, forty-eight were identified.

G. S.

**The Applicability of the Methods of Estimating Water in Silicate Minerals and Rocks.** MAX DITTRICH (*Zeitsch. anorg. Chem.*, 1912, **78**, 191—200. Compare this vol., ii, 804).—A comparison has been made between the results obtained from a number of minerals and rocks by estimating water by several different methods, that of Ludwig and Sipőcz (fusion with a dry mixture of sodium

and potassium carbonates in a platinum boat in a porcelain tube) being taken as the standard.

Heating with a blowpipe flame in a silica tube gives in most cases the same result as the standard method, but epidote and muscovite only lose their water completely at the full temperature of the blowpipe flame. Some hornblende requires heating at  $1250^{\circ}$  in an electric furnace. Penfield's method gives good results with serpentine and prehnite, but many minerals give numbers which are too low, unless the temperature is raised by wrapping the tube in platinum foil. The determination of the loss by ignition in a crucible is successful with prehnite, but fails if carbonates or iron compounds are present, whilst mica may give a result which is double that obtained by the correct method.

Rocks give low figures by Penfield's method, even when the platinum wrapping is used, whilst direct heating in a silica tube gives good results, even those rocks which lose water with difficulty being dehydrated at  $1250^{\circ}$ , whilst this method has the further advantage of allowing the simultaneous estimation of carbon dioxide. C. H. D.

**A New, Very Sensitive and Characteristic Reaction of Free Bromine.** GEORGES DENIGÈS (*Compt. rend.*, 1912, 155, 721—723).—An aqueous solution of bromine acts on a solution of rosaniline decolorised by sodium hydrogen sulphite giving a violet or purple coloration, followed by a violet precipitate, which is readily soluble in chloroform to a violet solution, the absorption spectrum of which shows two characteristic bands, one in the blue and the other, sharply defined, in the orange-yellow.

For small quantities of bromine, the test is best conducted in the presence of a little hydrogen peroxide (2—10 vols. strength), and the characteristic colour is exhibited by the chloroform layer with only 0.01 mg. of bromine present. In testing for bromine vapour the reagent should be absorbed on blotting paper, and this inserted into the gas under examination. Traces of bromides can be detected in chlorides or iodides by oxidation with potassium chromate and sulphuric acid, and allowing the issuing gas to impinge on the test paper. W. G.

**Relative Stability of Cadmium Potassium Iodide and its Application in the Estimation of Ozone.** CHARLES BASKERVILLE and W. J. CROZIER (*J. Amer. Chem. Soc.*, 1912, 34, 1332—1337).—Ladenburg and Quasig (*Abstr.*, 1901, ii, 420) have found that in estimating ozone by means of potassium iodide, accurate results can be obtained by the use of neutral solutions, but that with acid solutions the results are too high. This observation has now been confirmed.

Baskerville and Hamor (*J. Ind. Eng. Chem.*, 1911, 3, No. 6) have shown that cadmium potassium iodide,  $\text{CdKI}_3 \cdot \text{H}_2\text{O}$ , is preferable to potassium iodide for the detection of peroxidised compounds in ether, since solutions of corresponding strength are much more stable in light. The reagent has now been applied to the estimation of ozone.

It has been found that the results obtained with either neutral or

acid 0.1*N*-cadmium potassium iodide solutions are lower than those obtained with neutral potassium iodide solutions on account of the greater stability of the former salt towards light and certain common impurities of ozonised air. When the method of absorbing the ozone in turpentine is used, a solution of cadmium potassium iodide acidified with hydrochloric acid must be employed, and it is considered that this is a more trustworthy reagent than a neutral solution of potassium iodide. If Schönbein's method, as used by Ladenburg and Quasig (*loc. cit.*), is adopted, either neutral or acid solutions of cadmium potassium iodide may be used; by this means sharp end-points are obtained, and the results are not too high. E. G.

**Titrimetric Estimation of Sulphur.** J. D. RUYLS (*Chem. Weekblad*, 1912, 9, 892—894. Compare Holliger, *Abstr.*, 1909, ii, 343; Bruhns, *Zeitsch. anal. Chem.*, 1910, 49, 84).—Holliger's titrimetric method has been applied to the estimation of sulphur in coal, slag, ashes, and soot, and also to the estimation of the amount of sulphate present in water. A. J. W.

**Assay of Fuming Sulphuric Acid.** JOSEF KNORR (*Chem. Zeit.*, 1912, 36, 1262).—Titration with standard alkali cannot be recommended, but a gravimetric analysis should be carried out as follows: About 1 gram of the sample is weighed, as in Lunge's process, in a thin glass bulb drawn out to a capillary tube. In an Erlenmeyer flask is placed distilled water, acidified with hydrochloric acid, which is then heated to boiling. After adding excess of barium chloride, the bulb containing the acid is introduced, the flask closed with rubber stopper, and well shaken so as to break the bulb. The stopper is removed, and the liquid boiled again for 10 minutes. The barium sulphate plus the glass fragments are collected, well washed, heated to dull redness, and weighed. Allowance is then made for the weight of the glass.

Sulphur dioxide is estimated iodometrically in a separate portion of the acid. L. DE K.

**The Titration of Phosphoric and Boric Acids.** WILHELM BILTZ and E. MARCUS (*Zeitsch. anorg. Chem.*, 1912 77, 131—136).—In the titration of phosphoric acid with sodium hydroxide, methyl-orange being used for the first equivalent and phenolphthalein for the second, the quantity of alkali used for the first stage is always slightly greater than for the second. In presence of boric acid, the titration is carried out as above, mannitol is then added, and the solution is further titrated with phenolphthalein as indicator. The presence of even a large excess of calcium and magnesium chlorides is without influence on the titration of boric acid. The titration of phosphoric acid is not affected by the presence of magnesium salts, whilst calcium salts are without influence on the first stage (titration in presence of methyl-orange), but the phenolphthalein titration corresponds with the tribasic character of the acid if sufficient calcium is present to form the salt. The accuracy of the titration on this assumption is satisfactory. C. H. D.

**A Rearrangement of Procedure for the Removal of Phosphate Ions from the Iron and Alkaline Earth Groups.** CARLETON BELL NICKERSON (*Trans. Nova Scotia Inst. Sci.*, 1912, 13, 95—98).—The precipitate, obtained by the addition of ammonium chloride and a slight excess of ammonia, is dissolved in dilute hydrochloric acid, the phosphate precipitated by ferric chloride, and then ammonium chloride and ammonia are added to the solution. The filtrate from this is added to the filtrate resulting from the initial precipitation, and examined for the metals of the last three groups. The precipitate, consisting of ferric phosphate and the hydroxides of iron, aluminium, and chromium, is dissolved in dilute hydrochloric acid and the solution treated with sodium hydroxide and hydrogen peroxide, etc. H. M. D.

**New Method for the Detection of Traces of Arsenic and Antimony.** DONALD R. STADDON (*Chem. News*, 1912, 106, 199).—0.5 to 2 Grams of the substance suspected to contain arsenic or antimony are dissolved in 5 c.c. of water, 0.5 to 2 grams of sodium hyposulphite (commercially known as blankit) added, and, on warming, finely divided arsenic or antimony is rapidly precipitated. The arsenic is soluble, the antimony insoluble, in a solution of sodium hypochlorite. Acids and acid salts must be neutralised before applying the method. One part of sodium arsenite in 50,000 parts of water can be detected by this test. G. S.

**Apparatus for the Estimation of Carbon.** GEORG PREUSS (*Zeitsch. angew. Chem.*, 1912, 25, 2159).—The author describes a slight modification in the construction of the Corleis flask for the estimation of carbon by the wet method, whereby the air entering the flask is freed from carbon dioxide and the apparatus made more compact. F. B.

**A Simple Potash Bulb.** W. R. FORBES (*Chem. News*, 1912, 106, 225).—A modification of the potash bulb described by Waters (*Abstr.*, 1911, ii, 153). It may be described as a calcium chloride drying tube, the narrow tube of which is bent so that the whole is U-shaped, the end of the narrow tube being again bent at right angles. The wide tube is fitted with a ground glass stopper carrying the exit tube.

At the bottom of the wide tube are fused internal glass projections on which a perforated plate rests; above the plate is packed, first fairly loosely and then very loosely, glass wool. The tube is filled with potassium hydroxide up to the level of the top of the first layer of glass wool, the second layer being to retard evaporation. T. S. P.

**Estimation of Small Quantities of Carbon Dioxide Dissolved in Water.** OTTO WARBURG (*Zeitsch. physiol. Chem.*, 1912, 81, 202).—Carbon dioxide dissolved in water is completely removed in an hour by making the water acid with phosphoric acid, and passing a stream of purified air through it. A Walter's gas washing-bottle is used to

absorb the carbon dioxide which is retained in  $N/100$ -barium hydroxide, and titrated with  $N/100$ -hydrochloric acid. E. F. A.

**Estimation of Free Carbon Dioxide in Water by Titration with Alkalis in the Presence of Phenolphthalein** J. TILLMANS and O. HEUBLEIN (*Zeitsch. Nahr. Genussm.*, 1912, 24, 429—449. Compare Abstr., 1911, ii, 70, 658; 1912, ii, 685).—Chiefly a reply to Noll (*loc. cit.*). The authors maintain that free carbon dioxide in water may be accurately estimated by titration with alkali solution (sodium hydroxide, sodium carbonate, or calcium hydroxide), using phenolphthalein as indicator, provided that the amount of carbon dioxide does not exceed 100 mg. per litre of water, and that the temporary hardness of the latter is not more than  $10^\circ$  (German). Excess of phenolphthalein must be avoided, and it is recommended that 1 c.c. of a 0.035% solution of the indicator be used per 200 c.c. of water. W. P. S.

**Estimation of Potassium in Potassium Silicate.** ERNST WILKE-DÖRFURT (*Zeitsch. anal. Chem.*, 1912, 51, 755—760).—For the estimation of potassium in commercial potassium silicate ("phonolith") the original Lawrence Smith method (ignition with calcium carbonate and ammonium chloride, boiling the mass with water, etc.) is recommended. Verwey's modification of this process, which dispenses with the removal of the calcium before proceeding to the separation with platinum, gives results largely in excess of the truth. L. DE K.

**Method for the Systematic Qualitative Detection of Barium and Strontium.** LOUIS J. CURTMAN and EDWARD M. FRANKEL (*J. Amer. Chem. Soc.*, 1912, 34, 1493—1497).—It has been shown in an earlier paper (Abstr., 1911, ii, 659) that the ordinary method of detecting barium in systematic qualitative analysis is not trustworthy. The following plan has therefore been devised.

The alkaline-earth metals are precipitated as sulphates, together with part of the lead, by the addition of sulphuric acid and alcohol to a solution of definite acidity. The lead sulphate is extracted with ammonium acetate, and the sulphates of the alkaline earth metals are converted into the carbonates by boiling them with sodium carbonate solution. The carbonates are then dissolved in acetic acid, and the resulting solution is analysed in the usual way. E. G.

**Gravimetric Estimation of Glucinum.** BENNO BLEYER and K. BOSHAUT (*Zeitsch. anal. Chem.*, 1912, 51, 748—754).—Experiments showing that the precipitation of glucinum by ammonia in the cold is complete in the presence of ammonium chloride. Ammonium sulphide also effects a complete precipitation if sufficient time is allowed.

The precipitate should be washed with hot water containing a little ammonia and ammonium nitrate. Glassmann's process (warming with a mixture of potassium iodide and iodate) also precipitates the glucinum completely; it is recommended that any iodine liberated should be removed with thiosulphate. L. DE K.

**Gravimetric Estimation of Magnesium.** L. KARAOGLANOFF (*Chem. Zentr.*, 1912, ii, 547—548; from *Jahrbuch Univ. Sofia*, 1910—1911, Reprint 55 pp.).—In order to bleach blackish magnesium pyrophosphate without loss in weight, it should be dissolved in pure hydrochloric acid, evaporated, and re-ignited.

The triple phosphate obtained from solutions containing ammonium chloride or nitrate should be washed with dilute ammonia containing ammonium chloride; when only ammonium sulphate is present, 2½% ammonia solution should be used.

Pellet's process, heating with sulphuric acid and finally weighing as magnesium sulphopyrophosphate, is not accurate, as the composition of the residue is not constant.

L. DE K.

**Gravimetric Estimation of Zinc.** H. SCHILLING (*Chem. Zeit.*, 1912, 36, 1352).—The zinc solution containing about 0.25 gram of the ore and freed as usual from other metals is mixed with an excess of potassium hydroxide and then with an excess of benzenesulphonic acid. This solution is treated, first at boiling heat, with hydrogen sulphide, which causes a quantitative separation of the zinc as sulphide. Unlike zinc precipitated from an acetic acid solution, this precipitate is readily washed, and gives no turbid filtrate.

L. DE K.

**Influence of Non-Volatile Organic Matter and Certain Acids on the Precipitation of the Ammonium Sulphide Group of Metals.** LOUIS J. CURTMAN and HARRY DUBIN (*J. Amer. Chem. Soc.*, 1912, 34, 1485—1493).—It is well known that the precipitation of metals of the ammonium sulphide group is interfered with by (1) non-volatile organic matter, which prevents or hinders the precipitation of iron, chromium, and aluminium by ammonia; and (2) phosphoric, hydrofluoric, silicic, oxalic, and boric acids, which yield insoluble salts with the alkaline earth metals, and so cause their precipitation in the third group. The present work was undertaken with the object of determining the extent to which these substances interfere under the ordinary conditions of qualitative analysis.

The precipitation of aluminium, chromium, and iron by ammonia is hindered by the following substances in the order named: citric acid, tartaric acid, dextrin, sucrose, dextrose, lactose. Citric acid causes the greatest interference, whilst the sugars interfere but slightly. Tables are given indicating the effect of each of these substances under ordinary conditions.

It has been found that 2 grams of ammonium chloride, formed in the course of the analysis, are sufficient to prevent any interference by boric acid or borates, but that this is not the case with fluorides even in presence of larger quantities of ammonium chloride. The effect of varying quantities of oxalates and phosphates on the precipitation of barium, strontium, calcium, or magnesium, in the third group, has also been investigated.

E. G.

**Estimation and Separation of Copper by means of Hydroxylamine Hydrochloride.** ALEXANDER BAYER (*Zeitsch. anal. Chem.*, 1912, 51, 729—735).—Fifty c.c. of copper sulphate solution

(containing about 1.2 gram of the salt) are mixed with 50 c.c. of Rochelle salt (170 grams per half litre) and 25 c.c. of aqueous sodium hydroxide (80 grams per half litre) and heated to boiling. The copper is then precipitated as cuprous oxide by adding 2 c.c. of 5% solution of hydroxylamine hydrochloride and boiling for another minute. As in the analysis of sugars, the precipitate is collected in an asbestos-tube and ignited to oxide in a current of air.

The following metals do not interfere: antimony, zinc, bismuth, lead, ferric iron, stannic tin, sodium arsenate, and even ammonium. Silver may be precipitated by adding hydrogen dioxide to the alkaline solution, but it is perhaps better to remove it previously by hydrochloric acid. When mercuric mercury is present, this is not readily removed, and contaminates the cuprous oxide, but when this is ignited to oxide, the mercury is completely driven off.

L. DE K.

**The Rapid Electro-analytical Separation of Copper from Nickel or Zinc.** ROBERT KREMAN (Monatsh., 1912, 33, 1077—1079).—The electrolyte used consists of 125 c.c. of a solution of the sulphates of the metals containing 0.25 gram of each sulphate; after the addition of 0.25 c.c. of concentrated nitric acid and 3 grams of ammonium nitrate, it is heated to boiling and electrolysed with a current density of 4 amperes per sq. dcm. at 5 volts. The electrodes are concentric cylinders of platinum gauze, the electrolyte being stirred by a glass stirrer rotating with 1000 revolutions per minute.

After all the copper has been deposited, the electrolyte is siphoned off and continuously replaced by pure water whilst the current is still on, and it is found that during this washing appreciable quantities of nickel or zinc are deposited on the cathode, owing to the diminution in the concentration of the hydrions. The error thus caused can be obviated by first washing with a solution of 0.2 c.c. of concentrated nitric acid in 100 c.c. of water until practically all the nickel or zinc is found in the washings, and then using pure water.

T. S. P.

**New Reagent for Testing Bordeaux Mixture.** ED. CROUZEL (*Ann. Chim. anal.*, 1912, 17, 409—411).—The insecticide used in viticulture and known under the name of Bordeaux mixture should be prepared by adding just sufficient calcium hydroxide to a copper sulphate solution to precipitate all the copper; if such a mixture is treated with a small quantity of fluorescein and then allowed to settle, the supernatant liquid will exhibit a green colour and fluorescence, a green zone also appearing at the surface. When an insufficient quantity of calcium hydroxide is present, the liquid will be yellow and non-fluorescent.

W. P. S.

**Occurrence of Mercury in the Hair of Persons who have Received Subcutaneous Doses of Mercury Compounds. Micro-chemical Detection of very Small Quantities of Mercury.** CASIMIR STRYZOWSKI (*Chem. Zeit.*, 1912, 36, 1237—1239).—By means of the following method the author has detected very minute quantities of mercury in the hair of persons who had received

mercury compounds subcutaneously. From 2 to 10 grams of the hair are washed with alcohol, ether, and water, and then heated for several hours with hydrochloric acid and potassium chlorate until dissolved. The solution is filtered, heated to expel chlorine, and then treated with hydrogen sulphide. After forty-eight hours, the precipitate (consisting of sulphur and traces of mercury sulphide) is collected on a filter, dissolved in a small quantity of hydrochloric acid with the addition of potassium chlorate, and the solution is evaporated at a temperature of about  $60^{\circ}$  to a volume of 1.5 c.c. A few small pieces of copper foil are now added to the solution, and, after boiling, the copper foil is removed, dried, and transferred to a tube, the upper end of which is then drawn out to a capillary. The tube is heated to  $130^{\circ}$ , and the air is exhausted from it, the capillary being then sealed. The lower end of the tube is now heated over a flame in order to volatilise the mercury from the copper into the capillary, and the metallic globules may be detected in the latter by means of the microscope. The globules may also be rinsed from the capillary with alcohol, collected on a microscope slide, and treated with iodine.

W. P. S.

**Estimation of Manganese as Sulphate and by the Sodium Bismuthate Method.** WILLIAM BLUM (*J. Amer. Chem. Soc.*, 1912, 34, 1379—1398).—This investigation was carried out with the object of finding a method for the accurate estimation of manganese, yielding results which do not depend on the exact conditions of working.

It has been found that trustworthy results can be obtained by the bismuthate method if carried out in the following manner: To 50—150 c.c. of the manganese solution in 20—40% nitric acid, free from nitrous acid, a slight excess of sodium bismuthate (usually 0.5—1.0 gram) is added, and the mixture is shaken well for about half a minute. The sides of the flask are washed down with 3% nitric acid, the liquid is filtered through asbestos, ferrous sulphate is added in slight excess, and immediately titrated with potassium permanganate. The results obtained in this way are accurate over a wide range of conditions for amounts of manganese up to 0.05 gram. For the estimation of manganese in rich ores, the use of 0.1*N*-permanganate is recommended, whilst for iron and steel, Blair's method (*Abstr.*, 1904, ii, 683) is quite satisfactory.

Experiments have shown that pure anhydrous manganous sulphate can only be obtained by heating the salt for a long time at  $450$ — $500^{\circ}$ ; at  $550$ — $600^{\circ}$  the salt slowly decomposes. In view of the difficulties attending the use of manganous sulphate, the standardisation of the permanganate is best effected by means of sodium oxalate. The strength of filtered permanganate solutions is not affected by diffused light if the solution is protected from dust and reducing substances; in presence of the latter, alkaline solutions decompose less rapidly than neutral solutions.

E. G.

**Volumetric Estimation of Manganese.** L. KARAOGLANOFF (*Chem. Zentr.*, 1912, ii, 548—549; from *Jahrbuch Univ. Sofia*, 1910—1911, Reprint 33 pp.).—When using Volhard's permanganate

process some of its disadvantages may be avoided by titrating the nitrate instead of the sulphate; the presence of ferric iron or alumina does not interfere; in fact, the presence of ferric nitrate or silver nitrate improves the titration. Rössler's process based on the preparation of silver manganite by Rose's method, is untrustworthy.

L. DE K.

**Volumetric Estimation of Iron in Alloys with Potassium Permanganate in Phosphoric Acid Solution.** MAX WUNDER and A. STOICOFF (*Ann. Chim. anal.*, 1912, 17, 361—363).—The method of dissolving the sample by heating with phosphoric acid is recommended. When dealing with almost pure iron (containing but little carbon) it is advisable to add a drop of sulphuric acid, which retards the oxidation by atmospheric oxygen.

Satisfactory results were obtained with magnetite, ferro-silicon, and ferro-chrome; on account of the green colour, the solution of the latter must be very weak, otherwise the change into the permanganate colour will be indistinct.

L. DE K.

**Assay of Ferro-silicon.** S. CAMILLA and C. PERTUSI (*Chem. Zentr.*, 1912, ii, 549; from *Giorn. Farm. Chim.*, 1912, 61, 247—250).—Two commercial varieties exist, one with about 10%, the other with nearly 50% of silicon. The first kind is conveniently decomposed with hydrochloric acid; for the other, the authors recommend the following method: 0.4—0.5 gram of the finely powdered sample is heated in a platinum dish with 20—30 c.c. of hydrofluoric acid and a few drops of nitric acid, and the resulting solution is evaporated to dryness with a few c.c. of dilute sulphuric acid. The residue is then ignited to ferric oxide and weighed.

L. DE K.

**Estimation of Tungstic Acid and Silicic Acid.** HUGO HERMANN (*Zeitsch. anal. Chem.*, 1912, 51, 736—748).—A critical study. The author arrives at the following conclusions:

In the presence of a moderate excess of tungstic acid dissolved silicic acid can be converted quantitatively into the compound  $\text{SiO}_2 \cdot 12\text{WO}_3$ . Mineral acids in any quantity interfere with the reaction; acetic or formic acids do not. The compound, however, when once formed is decomposed by nitric acid with great difficulty.

Glass and porcelain vessels are attacked by solutions of paratungstic acid and should not be used. The mercurous salts of the complicated silico-tungstic acids are sensibly soluble in hot acidified water, hence the results of a tungsten determination based on the use of mercurous nitrate are below the truth.

On prolonged warming of a solution of sodium tungstate acidified with acetic acid, any silicic acid present will be converted quantitatively into complex tungstates, and can be calculated from the loss in tungsten trioxide by dividing by the factor 46.2; or the acids may be precipitated by the usual processes, and the silicic acid found by dividing the joint weight by the factor 47.2.

L. DE K.

**Acidity and Alkalinity of Natural Waters.** JAMES WALKER and SIDNEY A. KAY (*J. Soc. Chem. Ind.*, 1912, 31, 1013—1016).—The

authors propose that the acidity or alkalinity of a solution be stated in terms of the acidity or alkalinity of ideally pure water at the same temperature. They take the acidity of pure water as being equal to 1, and the alkalinity of the same as 1 at all temperatures; thus a water which has a hydron concentration of  $1.36 \times 10^{-7}$ , and a hydroxidion concentration of  $0.34 \times 10^{-7}$  at  $18^\circ$ , would be stated to have a relative acidity of 2 and a relative alkalinity of 0.5. Two solutions are required in the estimation, one containing 23.88 grams of crystallised disodium phosphate per litre, and the other 9.08 grams of potassium dihydrogen phosphate per litre. A table is given showing the proportions by volume in which these solutions must be mixed in order to give the different degrees of relative acidity or alkalinity. A measured quantity of the water under examination is tinted with a quantity of azolitmin and compared with the neutral standard; if the water is acid, 25 c.c. of the acid phosphate solution are tinted with azolitmin, and then titrated with the alkaline phosphate solution until the colour matches that of the water. It is recommended that 1 c.c. of a 0.1% solution of the indicator should be used for each mixture. A method of applying the process to coloured waters is described.

W. P. S.

**Reactions of Hydrocærulignone.** EDUARD SCHÄR (*Schweiz. Woch. Chem. Pharm.*, 1912, Reprint).—The author finds that the reaction described by Moir (*Proc.*, 1910, 26, 115), in which hydrocærulignone (tetramethoxydiphenol) in presence of minute quantities of copper acetate in acetic acid is used as a test for hydrocyanic acid, is analogous to the guaiacum and aloin reactions formerly described by him (*Ber.*, 1869, 2, 730; 1870, 3, 21; *Abstr.*, 1902, i, 168), and like these, is given more or less rapidly by soluble cyanides and inorganic and organic cyanogen compounds.

Hydrocærulignone is not oxidised to cærulignone by hydrogen peroxide alone, but the action takes place rapidly in presence of any "activating" agent, such as colloidal solution of platinum or gold, or the various oxydases and peroxydases. Solutions of hydrocærulignone in water also undergo oxidation in presence of alkalis or alkaloids by (1) atmospheric air (compare *Abstr.*, 1905, i, 434), and (2) certain metallic salts (compare *Abstr.*, 1902, ii, 140); the action of these salts is also intensified by hydrogen peroxide (compare *Abstr.*, 1902, ii, 603). In view of these facts the author suggests that hydrocærulignone may be used as a test for hydrocyanic acid and cyanogen compounds, blood and free alkaloids, and may be employed to demonstrate the "activation" of spontaneous oxidation by alkalis and other reagents.

T. A. H.

**Detection of Sucrose.** S. ROTHENFUSSER (*Zeitsch. Nahr. Genussm.*, 1912, 24, 558—570).—Experiments with a large number of substances, including alcohols, aldehydes, organic acids, certain sugars, esters, yeast constituents, proteins, and preservatives, were carried out and yielded results which show that none of these substances interfere with the test described previously by the author (*Abstr.*, 1910, ii, 463; 1911, ii, 665; this vol., ii, 1003) for the detection of sucrose. All

sweet wines, however, contain a substance which yields a positive reaction with the test, even when sucrose is not present; in most cases the reaction is very feeble. The nature of this substance has not yet been ascertained. In testing beer, a preliminary treatment with acetone is necessary in order to precipitate dextrins, and the same applies to honey and biscuits; milk may also be treated previously with acetone.

W. P. S.

**Polarimetric Estimation of Starch in Bananas.** GEORG BAUMERT (*Zeitsch. Nahr. Genussm.*, 1912, 24, 449—452).—The substance is treated, successively with cold water, alcohol, and ether, and the starch in it is then estimated by either Lintner's or Ewers' polarimetric methods (compare Abstr., 1911, ii, 1037). The author finds that, under the conditions of Lintner's method, banana starch has a rotatory power of  $+209.8^\circ$ , whilst with Ewers' method it has a rotatory power of  $+196.4^\circ$ .

W. P. S.

**Estimation of Oxalic Acid in Vegetable Substances.** ACH. GRÉGOIRE and EM. CARPIAUX (*Bull. Soc. chim. Belg.*, 1912, 26, 431—434).—The following process may be used for the estimation of oxalic acid in such substances as sesame-seed cakes and other materials containing considerable quantities of phosphates and proteins. Five grams of the powdered substances are heated on a water-bath for one hour with 20 c.c. of 4% hydrochloric acid, sodium sulphate and 100 c.c. of alcohol are then added, and the mixture is filtered, the insoluble portion being washed with alcohol. The filtrate is rendered ammoniacal, the alcohol is removed by evaporation, and the solution is filtered after the addition of hydrochloric acid. The oxalic acid in the filtrate is precipitated by the addition of calcium acetate, the precipitate is collected on a filter, washed, and re-dissolved in hydrochloric acid. This solution is evaporated nearly to dryness, a few drops of 25% sulphuric acid are added, and then a quantity of anhydrous sodium sulphate sufficient to make the whole into a dry mass. The latter is extracted with ether, the ethereal solution is evaporated, and the oxalic acid in the residue is precipitated as calcium oxalate by the addition of calcium acetate. Sesame-seed cakes examined by the authors contained a quantity of oxalic acid corresponding with 2.9% of crystallised calcium oxalate.

W. P. S.

**Detection of Glycuronic Acid in Diabetic Urine.** ADOLF JOLLES (*Zeitsch. physiol. Chem.*, 1912, 81, 203—204).—Lead acetate is added to 200—400 c.c. of urine until no further precipitate is formed, the precipitate is allowed to settle, the liquid filtered, and the precipitate washed three or four times by decantation with 400 c.c. of water each time. Basic lead acetate is added to the first filtrate as long as a precipitate forms; this is washed by decantation in a similar manner. The precipitates are united, stirred with water, warmed to  $70^\circ$ , and the lead precipitated as sulphide. After filtering, the filtrate is evaporated to 20 c.c., and 5 c.c. are taken for the Tollens naphtharesorcinol reaction.

E. F. A.

**Preservation of Milk Samples.** XAVIER ROCQUES (*Ann. Chim. anal.*, 1912, 17, 413—418).—It is the practice of French officials to add a quantity of potassium dichromate, in the proportion of 1 gram per litre, to samples of milk taken for analysis, with the object of preserving the samples should the analyses not be made immediately. The addition of the dichromate effects this purpose when the milk is quite fresh at the time of treatment, but in the case of milk in which fermentation has commenced, the dichromate is reduced within a comparatively short period of time, and the milk decomposes. The author finds that the reduction of the dichromate is caused by the lactic acid, particularly in the presence of lactose, although the latter itself is not acted on by the dichromate.  
W. P. S.

**The Total Solids of Milk.** A. SPLITTGERBER (*Zeitsch. Nahr. Genussm.*, 1912, 24, 493—507).—When milk solids are dried until constant in weight, the weight found is less than that of the sum of the various constituents; the two agree more nearly when the solids have only been heated for one hour. This is due to the action of lactic acid on certain milk constituents, especially on casein and lactose, during prolonged heating. Although lactic acid by itself is volatile at 100°, such is not the case in the presence of other milk constituents; it combines with these, and a very small proportion of the acid is volatilised during the first hour of drying. The acid, however, gradually disappears when the drying process is continued for several hours. This loss in weight is considerable when sour milk is evaporated, and the solids are dried for many hours.  
W. P. S.

**Interference of Hydrogen Peroxide with the Milk Tests for Formaldehyde.** HARRY D. GIBBS (*Philippine J. Sci.*, 1912, 7, 77—78).—The Hehner and Leach tests for the presence of formaldehyde in milk are unsatisfactory in the presence of hydrogen peroxide, although the Rimini reaction may still be employed. After removal of hydrogen peroxide by means of reducing agents, positive tests may, however, be obtained.  
H. W.

**Estimation of Casein and Lactose in Milk.** R. MALENFANT (*J. Pharm. Chim.*, 1912, [vii], 6, 390—397).—Ten c.c. of the milk are added to a mixture consisting of 25 c.c. of 65% alcohol and 3 drops of glacial acetic acid, and, after shaking for about thirty seconds, the precipitated casein is collected on a weighed filter and washed with 65% alcohol. The filtrate and washings are collected in a 100 c.c. flask, diluted with water to the mark, and the lactose is estimated in a portion of this solution by titration with Fehling's solution. The casein is then washed with boiling 95% alcohol, boiling acetone, and ether, dried for seven hours at 100°, and weighed. The weight found is multiplied by 0.925 to obtain the quantity of casein present.  
W. P. S.

**Composition of Butter.** MORITZ SIEGFELD (*Zeitsch. Nahr. Genussm.*, 1912, 24, 453—463).—Analyses of nineteen samples of dairy butter are recorded, and the following are the minimum and

maximum results obtained: Reichert-Meissl number, 23·80 to 32·15; Polenske number, 1·65 to 3·35; saponification number, 225·1 to 238·7; iodine number, 29·0 to 41·5; total fatty acids, 94·61 to 94·99%; volatile soluble acids, 5·71 to 7·68%; volatile insoluble acids, 0·95 to 3·28%. The mean molecular weight of the volatile soluble acids varied from 93·2 to 105·2, and that of the volatile insoluble acids from 189·4 to 207·1, showing that these portions contain very varying proportions of the different acids. The non-volatile fatty acids were found to consist of oleic, myristic, and palmitic acids; stearic acid was not present in the butter fats. Myristic acid appears to be present in considerable quantity.

W. P. S.

**New Colour Reactions of Diphenylamine.** J. J. LUTSCHINSKY (*Chem. Zeit.*, 1912, 36, 1239).—A sulphuric acid solution of diphenylamine yields a blue coloration with chlorine water, and a similar coloration is produced on the addition of hydrochloric acid, together with a small quantity of either potassium hypochlorite, potassium permanganate, potassium chlorate, or manganese dioxide; permanganate in the absence of hydrochloric acid gives a yellow coloration with the reagent. A 0·01% solution of hydrogen peroxide also causes the development of the blue colour. Pure sulphuric acid, which has been electrolysed at  $-10^{\circ}$  with platinum electrodes and then diluted with water, yields a blue coloration with diphenylamine, but not if it has been warmed after electrolysis.

W. P. S.

**Estimation of Quinine in Urine and in Blood.** ALESSANDRO BALDONI (*Chem. Zentr.*, 1912, ii, 554; from *Arch. Farm. speriment.*, 13, 324—326).—Kleine's process (*ibid.*, 1902, 1, 140) and Nishi's method (*Abstr.*, 1909, ii, 710) gave unsatisfactory results. The processes devised by Gordin (*Abstr.*, 1900, ii, 119) and Gaglio gave concordant results. Quinine is absorbed more rapidly in the blood after oral administration than after subcutaneous injection. Contrary to De Luca's statement, no quinine could ever be detected in the blood after twenty-four hours.

L. DE K.

**Rapid Testing of Dyes and Pigments.** GEORGE E. GRANT and ARTHUR S. ELSENBAST (*J. Physical Chem.*, 1912, 16, 546—555).—The action of an intense artificial light, as from a mercury vapour lamp, on a dye, is often quite different from the action of sunlight. Since most colours are bleached by oxidation, it should be possible to prepare solutions of oxidising agents, the action of which would be reasonably similar to that of prolonged exposure to sunlight.

The following dyes are arranged in order of increasing sensitiveness to hydrogen peroxide: methylene-blue, azo-red, methyl-violet, and eosin, Victoria-green, and magenta. The order of sensitiveness to sunlight is somewhat different.

Potassium persulphate acts more rapidly on these dyes and a number of others than hydrogen peroxide of equivalent strength. A number of lakes which were tested bled rather badly, but were more resistant to hydrogen peroxide and to sunlight than the corresponding dyes.

R. J. C.

**The Volumetric Estimation of Azo-dyes by means of Hypo-sulphite.** EUGÈNE GRANDMOUGIN and EM. HAVAS (*Chem. Zeit.*, 1912, 36, 1167—1169. Compare Abstr., 1906, i, 716, 967; Franzen and Stieldorf, Abstr., 1908, i, 113).—The standard solution is prepared by adding 5 c.c. of 30% sodium hydroxide solution and 3 grams of solid sodium hyposulphite to a litre of boiled and cooled water. After one or two hours the solution is fit for use. The titration is carried out in an atmosphere of coal gas. Fifty c.c. of the dye solution are diluted to 100—150 c.c., acidified with 5 c.c. of 1:10-hydrochloric acid, and boiled to expel air. After cooling rapidly by means of ice, the titration is performed rapidly. The end-point is sharp. Specimen analyses are given. The method has only been employed for acid monoazo-dyes, which yield colourless reduction products, but it may be extended to other dyes. C. H. D.

**The Bardach Test for Proteins.** CHARLES WEISMAN (*Biochem. Bull.*, 1912, 1, 538—539).—Bardach's test is based on the fact that acetone and iodo-potassium iodide in the presence of alkali yield with protein, yellow needles of an unidentified nitro- [iodo-]-material instead of iodoform. The test, however, is not specific, but is given by a number of protein hydrolytic products. W. D. H.

**A Colorimetric Method for the Estimation of Tryptophan, and the Tryptophan Content of Horny Substances and other Proteins.** HUGO FASAL (*Biochem. Zeitsch.*, 1912, 44, 392—401).—The basis of the method is the Hopkins-Cole colour reaction with glyoxylic acid and sulphuric acid. Comparisons are made with standard solutions of tryptophan (1:1000 to 1:50,000), of which 1 c.c. is treated with 2 c.c. of glyoxylic acid reagent and 6 c.c. of sulphuric acid. The colour most nearly corresponding to that produced by a weighed quantity of the substance under investigation is then compared with it in a Duboseq colorimeter, and in this way the amount of tryptophan can be accurately gauged. Horny substances are first digested with pepsin or trypsin, and then extracted with alcohol and ether. Keratinised human skin treated in this way contained 0.30% of tryptophan, which was practically absent from the normal cutis treated in the same way. Horn shavings contained 0.17%. It was practically absent from hair and wool. By this method, caseinogen was found to contain 0.65%, lactalbumin 3.07%, and edestin 0.38%.

S. B. S.

**The Estimation of Colloid Material in Soils.** PAUL ROHLAND (*Landw. Jahrb.*, 1912, 42, 329—330). A method based on the work of Ashley (*U.S. Geol. Survey Bull.* 388, 1909), by which the colloids in the soil are estimated by the amount of a standard solution of malachite-green which is adsorbed. F. M. G. M.